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Relative Importance of Dissociative Loss of Carbon Monoxide and Formation of Benzyl Radicals from Photoexcitation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and Evidence for Reaction of Carbon Monoxide with 17-Electron Radicals

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Abstract: Near-UV irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ (R = H, Me) yields both loss of CO and $CH_2C_6H_5$ radicals as primary photoprocesses, though the loss of CO dominates the excited-state chemistry. At 77 K in a rigid alkane matrix the only detectable photoreaction is loss of CO to form $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$. In fluid alkane solution at 298 K the dominant metal-containing photoproduct is $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$, unless the solution is actively purged with a stream of an inert gas such as Ar or N_2. When the solution is purged with Ar there are two main products: $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ (90–95%) and $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ (5–10%). The 366-nm quantum efficiency for CO loss is ~0.5, and that for $CH_2C_6H_5$ loss is ~0.05. When $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is irradiated under 2 atm of CO in alkane solution at 298 K $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$ is formed in good chemical yield (>50%). X-ray crystallography establishes $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$ to have the $CH_2C_6H_5$ group in an exo position. The formation of $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$ occurs via light-induced loss of a $CH_2C_6H_5$ radical from $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ followed by reaction of $(\eta^5\text{-}C_5R_5)Fe(CO)_2$ with CO to form $(C_5R_5)Fe(CO)_3$ that then couples with a $CH_2C_6H_5$ radical to give the exo isomer of $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$.

In this paper we wish to report on the relative importance of two chemical results from photoexcitation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ (R = H, Me) in alkane solvents: loss of CO, eq 1, and loss of a $CH_2C_6H_5$ radical, eq 2. Our investigation was stimulated by reports[1,2] that clean photochemical conversion occurs according to eq 3, apparently via light-induced loss of $CH_2C_6H_5$, whereas research in this laboratory[3] has established that dissociative loss of CO from photoexcited $(\eta^5\text{-}C_5H_5)Fe(CO)_2R'$ (R' = Me, Et) dominates all other chemical results, though radical formation has been invoked as well.[4] It has been reported[5] that

$$(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5) \xrightarrow{h\nu} (\eta^5\text{-}C_5R_5)Fe(CO)(\eta^1\text{-}CH_2C_6H_5) + CO \quad (1)$$

$$(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5) \xrightarrow{h\nu} (C_5R_5)Fe(CO)_2 + CH_2C_6H_5 \quad (2)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5) \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4 + \text{bibenzyl} \quad (3)$$

the irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in the presence of PPh_3 yields $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$ consistent with eq 1 as the primary photoreaction. The related $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-allyl})$ complex undergoes conversion to $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-allyl})$ upon photoexcitation,[6] again consistent with loss of CO as the principal result of photoexcitation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ complexes. Our new results with $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ are consistent with a photoexcited species that reacts relatively inefficiently to give a $CH_2C_6H_5$ radical, eq 2, and more efficiently to give dissociative loss of CO, eq 1. However, the reversibility of CO loss allows chemical yields of products according to eq 3 to be high, unless the 16-valence-electron species from loss of CO is trapped.

A new finding relates to the chemistry of the 17-valence-electron $(C_5R_5)Fe(CO)_2$ species formed from loss of a $CH_2C_6H_5$ radical. Apparently, this species can react with 2 e⁻ donor ligands, L, to give $(C_5R_5)Fe(CO)_2L$ that can couple with other radicals R' to give $(\eta^4\text{-}C_5R_5R')Fe(CO)_2L$. This provides a rationale for the formation of $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_2(PPh_3)$ that has been found[7] as a product, in unspecified yield, from the irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in the presence of PPh_3. Also, it appears that $(\eta^4\text{-}C_5H_5Me)Fe(CO)_3$, not $(\eta^3\text{-}C_5H_5)Fe(CO)_3Me$, is the product that results from photoexcitation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ in a CO matrix.[8]

Experimental Section

Instruments and Equipment. UV–vis spectra were recorded with a Cary 17 spectrophotometer; IR spectra were recorded with a Perkin-Elmer 180 dispersion spectrometer or a Nicolet 7199 Fourier transform spectrophotometer; ^1H NMR spectra were recorded with a JEOL FX90Q Fourier transform or a Bruker 250 or 270-MHz Fourier transform spectrometer.

Low-temperature UV–vis and IR spectra were recorded with deoxygenated alkane (3-methylpentane or methylcyclohexane) solution samples held in a Specac Model P/N 21.000 variable-temperature cell with CaF_2 windows, with either liquid N_2 or dry ice/acetone as coolant.

Chemicals. All solvents were reagent grade and freshly distilled before use. Hexane and toluene were distilled from CaH_2 under N_2. Methylcyclohexane (MCH) and tetrahydrofuran (THF) were distilled from Na under N_2. PPh_3 (Aldrich) was recrystallized three times from absolute EtOH. $C_6H_5CH_2Br$ (Aldrich), CH_3I (Aldrich), and $C_6H_5CH_2Cl$ (Aldrich) were passed through an alumina (Woelm Alumina, AKt. I; ICN Nutritional Biochemicals) column and deoxygenated before use. The CO was obtained from Matheson as CP grade. Alumina used for chromatography was activated alumina from MCB and used as received. All reactions and manipulations of the organometallic reagents were carried out by using standard Schlenk techniques under an Ar atmosphere or in a Vacuum Atmospheres drybox under N_2.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ was prepared according to literature procedure.[9] Spectroscopic (IR and ^1H NMR) data for this and other complexes are found in Tables I and II.

$(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ was prepared via a modification of the literature preparation for $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$.[9] A solution of 4.9 g (10.0 mmol) of $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ (available from previous synthesis)[10] in 200 mL of THF was stirred with 50.0 g of 1%

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Table I. Spectroscopic Data for Relevant Compounds[a]

compound	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)
$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}Bz)$	298	2009 (5600), 1958 (5000)	320 (10 000), 270 (sh)
	196	2009 ($\sim$1), 1956 ($\sim$0.8)	
	77	2006 ($\sim$1), 1952 ($\sim$0.6)	
$(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}Bz)$	298	1943	
	196	1941	
	77	1938	
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^1\text{-}Bz)^b$	298	1909	
$(\eta^4\text{-}C_5H_5Bz)Fe(CO)_3$	298	2049 ($\sim$0.8), 1982 ($\sim$1), 1974 ($\sim$0.9)	345 (sh), 275 (7800)
	196	2045 ($\sim$0.8), 1981 ($\sim$1), 1972 ($\sim$0.9)	
	77	2043 ($\sim$0.8), 1976 ($\sim$1), 1965 ($\sim$0.9)	
$(\eta^4\text{-}C_5H_5Bz)Fe(CO)_2PPh_3$	298	1977 (1.0), 1924 (0.7)	
$(\eta^4\text{-}C_5H_6)Fe(CO)_3$	298	2047 (4600), 1980 (6000), 1972 (5400)	280 (4100), 360 (sh)
	77	2045 ($\sim$0.8), 1976 ($\sim$1.0), 1967 ($\sim$0.9)	
$(\eta^5\text{-}C_5H_4Bz)Fe(CO)_2H$	196	2016 ($\sim$1), 1957 ($\sim$1)	
	77	2013 ($\sim$1), 1953 ($\sim$1)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2H$	298	2024 ($\sim$1), 1967 ($\sim$1)	
	77	2018 ($\sim$1), 1959 ($\sim$1)	
$(\eta^5\text{-}C_5H_4Bz)Fe(CO)_2Cl^c$	298	2051 ($\sim$1), 2007 ($\sim$1)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl^c$	298	2056 (3700), 2004 (3400)	
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}Bz)$	298	1993 (4600), 1941 (5700)	355 (800), 280 (sh)
	196	1992 (0.8), 1939 (1.0)	
	77	1990 (0.8), 1937 (1.0)	
$(\eta^5\text{-}C_5Me_5)Fe(CO)(\eta^3\text{-}Bz)$	298	1921	
	196	1920	
	77	1919	
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)(\eta^1\text{-}Bz)$	298	1889	
$(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_3$	298	2027 (7700), 1956 (9600)	355 (sh), 275 (7850)
	77	2025 (1.0), 1954 (0.7)	
$(\eta^5\text{-}C_5Me_4Bz)Fe(CO)_2Me$	298	1994 (0.9), 1939 (1.0)	
$(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_2PPh_3$	298	1964 (1.0), 1899 (0.8)	
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$	298	1992 (0.95), 1938 (1.0)	358 (850), 280 (sh)
$(\eta^4\text{-}C_5Me_6)Fe(CO)_3$	298	2029 (0.8), 1958 (1.0)	
$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$	298	2004 (3000), 1960 (6400), 1792 (6200)	520 (800), 409 (2100), 348 (8300)
$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Bz)Fe_2(CO)_4$	298	2004 (0.6), 1959 (1.0), 1787 (0.5)	
$(\eta^5\text{-}C_5H_4Bz)_2Fe_2(CO)_4{}^d$	298	1999 (0.6), 1955 (1.0), 1781 (0.8)	510 (0.2), 400 (0.5), 356 (1.0)
$(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$	298	1929 (13000), 1760 (7400)	533 (1500), 420 (3000), 362 (10000)
$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4$	298	2004 (0.6), 1944 (1.0), 1776 (0.8)	
$(\eta^5\text{-}C_5Me_4Bz)_2Fe_2(CO)_4$	298	1931 (1.0), 1762 (0.6)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_5$	298	2080 (4800), 2013 (2800), 1990 (14400), 1974 (7160)	475 (1090), 386 (7760)
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2Mn(CO)_5$	298	2070 (0.1), 2045 (0.6), 2010 (1.0), 1980 (0.2)	536 (0.2), 410 (0.4) 364 (1.0)
$Mn_2(CO)_{10}$	298	2046 (14000), 2015 (40000), 1982 (7900)	390 (sh), 324 (21000)

[a] In deoxygenated methylcyclohexane, unless otherwise noted; Bz ≡ $CH_2C_6H_5$. [b] In isooctane. [c] In hexane/CCl_4. [d] In 66% MCH and 34% 3-methylpentane.

Na (by mass) in Hg amalgam (22 mmol of Na). After the mixture was stirred for 1 h, the excess amalgam was drained from the reaction flask. To the resulting $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^-$ solution was added 3.4 g of $C_6H_5CH_2Br$ (20 mmol) by syringe. After the mixture was stirred for 15 min, the solvent was removed in vacuo and the reaction mixture was extracted with hexanes. The hexane extract was concentrated down to about 10 mL and was then chromatographed on an alumina column. Elution with hexanes gave a yellow fraction which upon removal of the solvent yielded 3.5 g ($\sim$10 mmol, 50% yield) of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ as dark yellow minicrystals. A red band left on the column was eluted with THF and found to be $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$. The $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ was characterized by mass spectrum ($M^+ = 338$) and elemental analysis (Schwarzkopf): calcd (found) C, 67.5 (67.0%); H, 6.51 (6.65%).

$\mathbf{(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me}$ was prepared in an analogous manner with 2.8 g (20 mmol) of CH_3I instead of $C_6H_5CH_2Br$. This yielded 2.9 g of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ (70%) as bright yellow crystals.

The $\mathbf{(\eta^5\text{-}C_5R_5)Fe(CO)_2Mn(CO)_5}$ (R = H, Me) were prepared by "cross coupling" of $Mn_2(CO)_{10}$ and $(\eta^5\text{-}C_5R_5)Fe_2(CO)_4$ in an alkane solvent as previously described[11] and purified by chromatography on alumina.

The $\mathbf{(\eta^5\text{-}C_5R_4(CH_2C_6H_5))_2Fe_2(CO)_4}$ (R = H, Me) dimers were prepared via a modification of the literature preparation for $(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4$.[10] Typically, 0.5 mmol of $Fe_2(CO)_9$ was refluxed with 0.6 mol of the appropriate $C_5R_4H(CH_2C_6H_5)$ ligand (vide infra) (R = H, Me) in decane for 4–6 h during which time a purple-black powder precipitated. This was filtered off and chromatographed on alumina. Elution with THF and subsequent solvent removal resulted in the appropriate $(\eta^5\text{-}C_5R_4(CH_2C_6H_5))_2Fe_2(CO)_4$ dimers.

$\mathbf{C_5H_5(CH_2C_6H_5)}$ was prepared by the reaction of $C_6H_5CH_2Cl$ with $Li[C_5H_5]$. The $Li[C_5H_5]$ was synthesized according to the following procedure: 33 g (0.5 mol) of freshly cracked C_5H_6 (Aldrich) dissolved in 300 mL of anhydrous Et_2O was charged into a 2-L, 3-necked flask equipped with a reflux condenser and additional funnel. To this was added dropwise, under N_2, 330 mL (0.5 mol) of 1.6 M *n*-BuLi in hexane (Aldrich). The $Li[C_5H_5]$ precipitated instantly as a white solid. With constant stirring, 65 g (0.5 mol) of $C_6H_5CH_2Cl$ (Aldrich) was added to the suspended $Li[C_5H_5]$ and the reaction mixture was then refluxed for $\sim$6 h. Upon cooling, the Li salts were filtered off and washed with two 100-mL portions of Et_2O. The ether fractions were combined and concentrated to about 50 mL. Fractional distillation yielded 30 g of a mixture of isomers of $C_5H_5CH_2C_6H_5$ (50% yield (28–30 °C (0.1 torr)). This was characterized by ^1H NMR in $CDCl_3$: δ 7.9 (m) (phenyl); 7.09 (dd), 7.00 (t), 6.77 (t) (unsaturated CH); 5.5 (s) (benzylmethylene); 3.82 (d) (saturated CH); 3.37 (t) (saturated CH); 3.67 (s) (benzylmethylene). The mixture of isomers of $C_5H_5(CH_2C_6H_5)$ was used without further purification in reactions with $Fe_2(CO)_9$.

The starting $C_5Me_4(CH_2C_6H_5)H$ ligand was prepared via a modification of the literature preparation for C_5Me_5H.[12] Li shot, 9.7 g (1.5 mol, −4 + 16 mesh dry, Aldrich), was loaded under Ar into a 2-L, 3-necked flask equipped with a pressure equalizing addition funnel, reflux condenser, and efficient stir bar. Anhydrous Et_2O (500 mL) was added to the flask. The addition funnel was charged with 22 g (0.16 mol) of 2-bromo-2-butene (mixture of cis and trans isomers, Columbia Or-

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Table II. ^{1}H NMR Data for Relevant Compounds[a]

compound	chemical shift, δ vs. $Si(CH_3)_4$
$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}Bz)$[b]	7.10 m (5 H); 4.46 s (5 H); 2.62 s (2 H)
$(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}Bz)$[b,c]	~7.0 m (5 H); 4.41 s (5 H); 3.59 br s (2 H)
$(\eta^4\text{-}C_5H_4Bz)Fe(CO)_3$[d]	7.1 m (5 H); 4.89 t (2 H); 2.78 t (1 H_{endo}); 2.68 dd (2 H); 1.79 d (2 H)
$(\eta^5\text{-}C_5H_4Bz)Fe(CO)_2H$[c,d]	~7 m (5 H); 4.06 d (2 H); 3.98 d (2 H); 3.09 d (2 H); ~11.6 s (1 H)
$(\eta^4\text{-}C_5H_6)Fe(CO)_3$[e]	5.06 d (2 H); 2.49 m (2 H); 2.4 dd (H_{exo}); 1.98 dd (1 H_{endo})
$(\eta^5\text{-}C_5H_4Bz)Fe(CO)_2Cl$[d]	~7 m (5 H); 4.15 d (2 H); 3.40 d (2 H); 3.25 (2 H)
$(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^1\text{-}Bz)(PPh_3)$[d]	7.5 m, 7.2 m, 7.0 m (20 H); 4.05 s (5 H); 2.71 q (1 H); 2.21 dd (1 H); 1.85 d (2 H)
$(\eta^4\text{-}C_5H_5Bz)Fe(CO)_2(PPh_3)$[d]	7.5 m, 7.4 m, 6.9 m (20 H); 4.93 q (2 H); 3.00 dd (1 H_{endo}); 2.47 q (2 H); 1.85 d (2 H)
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}Bz)$[f]	7.1 m (5 H); 2.70 s (2 H); 1.38 s (15 H)
$(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_3$[d]	7.3 (1 H); 6.95 d (2 H); 6.43 (2 H); 2.01 s (2 H); 1.39 s (6 H); 1.38 s (3 H); 1.06 (6 H)
$(\eta^5\text{-}C_5Me_4Bz)Fe(CO)_2Me$[f]	~7 m (5 H); 3.35 s (2 H); 1.47 s (6 H); 1.37 s (6 H); 0.19 s (3 H)
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$[f]	1.38 s (15 H); 0.14 s (3 H)
$(\eta^4\text{-}C_5Me_6)Fe(CO)_3$[e]	1.69 s (6 H); 1.66 s (3 H); 1.63 s (3 H); 1.60 s (6 H)
$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$[d]	4.22 s
$(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$[d]	1.61 s
$(\eta^5\text{-}C_5H_4Bz)Fe_2(CO)_4$[d]	~7.0 m (5 H); 4.1 s (2 H); 3.64 d (2 H); 3.25 d (2 H)
$(\eta^5\text{-}C_5Me_4Bz)_2Fe_2(CO)_4$[f]	~7.03 m (5 H); 3.80 s (2 H); 1.72 s (6 H); 1.60 s (6 H)

[a] All spectra are for 298 K solutions unless noted otherwise; Bz ≡ $CH_2C_6H_5$. [b] In methylcyclohexane-d_{14} solvent. [c] At 196 K. [d] In toluene-d_8 solvent. [e] In cyclohexane-d_{12} solvent. [f] In benzene-d_6 solvent.

ganics) which was added to the Li/Et_2O mixture with stirring. This was added dropwise at a rate to maintain reflux of the Et_2O. After the addition of the 2-bromo-2-butene was complete, a solution of 51 g (0.3 mol) of ethyl phenylacetate (Aldrich, previously dried over 4 Å molecular sieves) and 79 g (0.5 mol) of 2-bromo-2-butene was added dropwise over a period of 2 h, maintaining reflux. After the addition was completed, the reaction flask was stirred for 15 min. About 5 g of ethyl phenylacetate was added to the mixture until all refluxing of the soluton ceased. The reaction mixture was cooled, and 200 mL of a saturated NH_4Cl aqueous solution was added dropwise to hydrolyze the remaining Li. The Et_2O layer was isolated, and the aqueous layer was extracted three times with 100-mL portions of Et_2O. The other fractions were combined and concentrated to about 150 mL.

The resulting Et_2O concentrate was added dropwise to a slurry of 6 g of *p*-toluenesulfonic acid monohydrate (Aldrich) in 100 mL of Et_2O in a 3-necked flask equipped with a condenser. After the mixture was stirred for 5 min, the reaction mixture was poured into 600 mL of a saturated NH_4Cl aqueous solution containing 5 g of $Na_2(CO_3)$. The yellow aqueous phase was removed and extracted with three 50-mL portions of Et_2O. The ether solutions were combined and concentrated to ca. 100 mL and dried over $MgSO_4$ (Aldrich). The crude product was trap-to-trap distilled in vacuo and further vacuum distilled with a fractionating column. The product distilled at 72–76 °C (0.1 torr) as a yellow liquid. About 30 g of $C_5Me_4(CH_2C_6H_5)(H)$ was obtained, a 57% yield. ^{1}H NMR in $CDCl_3$: δ 7.0 (m, 5 H); 3.3 (s, 2 H); 1.35 (br s, 12 H), 1.05 (t, 1 H).

Irradiations. A near-UV lamp consisting of two General Electric blacklight bulbs (355 ± 20 nm, $\sim 2 \times 10^{-6}$ einstein/min) was used for room-temperature irradiations. A Bausch and Lomb SP208 high-pressure Hg lamp (output filtered with Pyrex and ~10 cm of water to remove deep UV and IR light) was used for low-temperature irradiations. Samples of 0.01 M solutions of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ (with or without 0.05 M PPh_3; 3.0 mL) for quantum yields at 366 nm were freeze–pump–thaw degassed ($<10^{-5}$ torr, 3 cycles) in 13 × 100 mm Pyrex test tubes with constrictions and hermetically sealed. Irradiation was carried out in a merry-go-round.[13] The light source was a 550-W medium-pressure mercury lamp (Hanovia) equipped with Corning glass filters to isolate the 366-nm Hg emission. Ferrioxalate actinometry[14] was used to determine the excitation rate which was typically $\sim 10^{-7}$ einstein/min.

Photoreaction of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ under CO. A hexane solution of the complex (~0.05 M) was loaded into a heavy-walled glass reactor tube equipped with a high-pressure gas valve. Photolysis of the sample was carried out under 2 atm of CO, with the reaction monitored by removing aliquots for analysis by IR spectroscopy. Upon completion of the reaction, the solvent was stripped off and the residue chromatographed on activated alumina (Merck). For R = H, elution with hexane yielded a colorless fraction containing bibenzyl and a yellow fraction established to be $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$ by IR and ^{1}H NMR, Tables I and II. Elution with THF yielded a red fraction containing a mixture of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))_2Fe_2(CO)_4$, and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4(CH_2C_6H_5))Fe_2(CO)_4$ as deduced from IR spectra in the CO stretching region (cf. Table I). The identification of $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))_2Fe_2(CO)_4$ was established by comparison with an independently synthesized sample.[10] The $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4(CH_2C_6H_5))Fe_2(CO)_4$ was identified by generating the material by irradiating (355 nm) a deoxygenated alkane solution of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))_2Fe_2(CO)_4$ as has been done for other related M–M bonded complexes.[11]

For R = Me, elution with hexane yielded a colorless fraction containing dibenzyl followed by a yellow fraction containing $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$. Little or no $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ is formed in the reaction. The hexane was removed from the $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$ fraction, and the samples was characterized by IR, ^{1}H NMR (Tables I and II), mass spectrum ($M^+ = 366$), elemental analysis [Schwarzkopf] [calcd (found): C, 65.6 (65.5); H, 6.01 (6.00)]; and X-ray crystallography, vide infra.

Photoreaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in the Presence of PPh_3. A hexane solution of the complex (~0.05 M) saturated with PPh_3 was loaded into a Pyrex reactor tube and irradiated at room temperature. The reaction was monitored by IR spectroscopy. When the reaction was completed, the solvent was stripped off and the residue chromatographed on alumina (Merck). Elution with 7:1 hexane/THF yielded an orange fraction containing a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^1\text{-}CH_2C_6H_5)(PPh_3)$ and PPh_3. Elution with pure THF and removal of solvent yielded orange crystals which were shown to be $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_2(PPh_3)$ by IR and ^{1}H NMR, Tables I and II.

Photochemical Cross-Coupling Reactions under CO. A variety of experiments were carried out to demonstrate that photogenerated radicals from metal–metal bonded precursors ($(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$; $(\eta^5\text{-}C_5R_5)Fe(CO)_2Mn(CO)_5$) can react with photogenerated radicals from $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ (R = H, Me; R' = Me, $CH_2C_6H_5$). Typically, an equimolar (~0.01 M) mixture of a metal–metal bonded complex and an iron alkyl in alkane solvent was loaded into a Pyrex reaction vessel. The solution was purged with CO for a few minutes to remove O_2 and then pressurized to 2 atm with CO. The vessel was then irradiated with near-UV light from a 450-W medium-pressure Hg lamp (Hanovia). Aliquots of the reaction mixture were removed and analyzed by IR to determine product distribution.

X-ray Crystallography. Crystals of $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$ were grown from a concentrated hexane solution. Only small crystals could be grown (0.1 × 0.05 × 0.05 mm). Data were collected on an Enraf-Nonius CAD4F-11 diffractometer with Ni-filtered Cu Kα radiation. The data collection, reduction, and refinement procedures used in the laboratory have been described in detail elsewhere.[15] A total of 1480 reflections ($+h,+h,+l$) were collected in the range $3° < 2\theta < 90°$ with the 880 having $F_o < 4\sigma(F_o)$ being used in the structure refinement with was by full matrix least squares techniques (102 variables) with use of SHELX-76. Final $R_1 = 0.113$ and $R_2 = 0.133$.

Data were corrected for a 5% isotropic decay. The Fe atom was refined anisotropically with all other atoms refined isotropically because of the small number of observed data which is most likely due to the small size of the data crystal. Hydrogen atoms were ignored. A final difference map showed no peak of any chemical significance.

Results and Discussion

(a) Low-Temperature Irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$. Near-UV irradiation of ~5 mM $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in an alkane (methylcyclohexane or 3-

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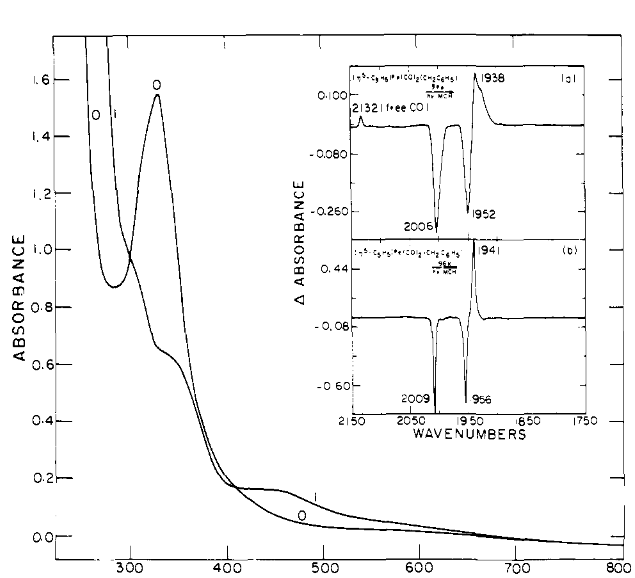

Figure 1. UV-vis and IR spectral changes accompanying near-UV irradiation-induced conversion of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ to $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ in deoxygenated methylcyclohexane. The UV-vis is for the conversion at 196 K; curve 0 is before irradiation and curve 1 is after complete conversion. The IR spectra (inset) are difference spectra at 77 K (top) and 196 K (bottom).

methylpentane) matrix at 77 K results in IR spectral changes consistent with the dissociative loss of CO. Figure 1 shows the spectral changes for the R = H complex, and Tables I and II give relevant spectral data for the complexes studied. The two absorption bands in the CO stretching region for starting material decline with increasing irradiation time, while a band at 2132 cm^{-1}, attributable to free CO, and a strong absorption at 1938 cm^{-1} grow. The amount of free CO generated compared to the amount of starting material consumed is consistent with the loss of only one CO per molecule of starting material, even at >90% conversion.[16] Thus, the single 1938-cm^{-1} absorption is assigned to an Fe species having the formula $(C_5H_5)Fe(CO)(CH_2C_6H_5)$. Interestingly, a monocarbonyl Fe species cannot be observed upon irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ under the same conditions,[3] apparently due to the reversibility of CO loss in the absence of a trap. When $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ is irradiated in a 1-pentene matrix at 77 K, rapid conversion to $(\eta^5\text{-}C_5H_5)Fe(CO)$(1-penten)Me is observed.[3] The 77 K photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2R'$ (R' = Me, $CH_2C_6H_5$) is the same as that for the $(\eta^5\text{-}C_5H_5)$ species: the R' = Me comples is photoinert in an alkane matrix and the R' = $CH_2C_6H_5$ loses one CO per molecule of starting material.

The $(C_5R_5)Fe(CO)(CH_2C_6H_5)$ species from the low-temperature irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$, eq 4, is formulated as an $\eta^3\text{-}CH_2C_6H_5$ complex, analogous to $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-allyl})$.[6] The ability of the η^1-ligand to bind in

$$(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5) \xrightarrow{h\nu} (\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5) + CO \quad (4)$$

an η^3-fashion,[17] saturating the 16-valence-electron intermediate formed immediately after CO loss, accounts for the ability to see a monocarbonyl from the $-CH_2C_6H_5$ species whereas $(\eta^5\text{-}C_5R_5)Fe(CO)_2Me$ does not yield a detectable monocarbonyl in an alkane matrix on the same time scale of irradiation. The 77 K photochemical reaction that occurs according to eq 4 has precedence in that $(\eta^5\text{-}C_5H_5)W(CO)_3(\eta^1\text{-}CH_2C_6H_5)$ yields $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}CH_2C_6H_5)$ at 77 K in an alkane matrix.[18]

There are UV-vis spectral changes that accompany the low-temperature irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$, Figure 1. The lack of a well-defined, significantly lower energy first absorption in the monocarbonyl photoproduct compared to that of the starting complex is consistent with the formulation of the photoproduct as an 18-valence-electron species. Generally, coordinatively unsaturated, 16-valence-electron photofragments have a much lower energy first absorption band than their 18-valence-electron parents, owing to the stabilization of the lowest unoccupied molecular orbital when a 2 e^- donor ligand is extruded from the coordination sphere.[19]

(b) Chemistry of $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$. Warmup to 196 K of a 77 K alkane matrix containing the $\eta^3\text{-}CH_2C_6H_5$ starting complex and the photoejected CO results in essentially no IR spectral changes. In particular, the single absorption at 1938 cm^{-1} for R = H changes only slightly even upon prolonged standing at 196 K, Figure 1. The $\eta^3\text{-}CH_2C_6H_5$ complexes appear to be inert at 196 K. Further, the $\eta^3\text{-}CH_2C_6H_5$ complexes are inert at 196 K in the presence of the $\eta^1\text{-}CH_2C_6H_5$ starting complex as established by warming a 77 K matrix containing both species. Indeed, we find that near-UV irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in alkane solution at 196 K yields $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ with a nearly quantitative chemical yield in a sealed vessel. However, warmup from 196 K to 298 K yields nearly quantitative regeneration of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$, eq 5. This regeneration reaction likely proceeds via

$$(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5) \xrightarrow{CO,\ \Delta} (\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5) \quad (5)$$

the 16-valence-electron $\eta^1\text{-}CH_2C_6H_5$ complex that is in equilibrium with the 18-valence-electron $\eta^3\text{-}CH_2C_6H_5$ species at the higher temperatures, eq 6. At low temperature the rate of interconversion is slower and the equilibrium position likely favors more the 18-valence-electron structure.

$$\underset{(18\ e^-)}{(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)} \rightleftarrows \underset{(16\ e^-)}{(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^1\text{-}CH_2C_6H_5)} \quad (6)$$

The $(\eta^3\text{-}CH_2C_6H_5)$ species are inert at 298 K in alkane solution if CO (and any other 2 e^- donor ligands) is absent. For example, $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ can be generated by irradiating $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 196 K in an alkane while purging the sample with Ar. Warmup to 298 K then yields $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$, and it persists in solution for at least 48 h. Exposure of the $\eta^3\text{-}CH_2C_6H_5$ species in alkane to CO at 298 K immediately regenerates the η^1 species in nearly quantitative yield. Likewise, addition of PPh_3 to an alkane solution of the η^3 species at 298 K yields a PPh_3 complex, eq 7.

$$(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5) \xrightarrow{PPh_3,\ \Delta} (\eta^5\text{-}C_5R_5)Fe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5) \quad (7)$$

In generating the η^3- from the $\eta^1\text{-}CH_2C_6H_5$ species at 196 K in an alkane solution there is negligible formation of $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$, the only Fe-containing product reported at 298 K for R = H.[1,2] Additionally, during the regeneration of the $\eta^1\text{-}CH_2C_6H_5$ species upon warming the $\eta^3\text{-}CH_2C_6H_5$ species in the presence of CO there is no formation of a diiron complex. These results show that thermal reactions of the $\eta^3\text{-}CH_2C_6H_5$ complexes, either with the η^1 species or with itself, do not account for the formation of a diiron complex from the photolysis of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 298 K.

(c) Photoreaction of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 298 K. The results presented so far are consistent with the conclusion that dissociative loss of CO from photoexcited $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 77 or 196 K dominates the chemical results from excited-state decay. This conclusion accords well with results for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ where near-UV photoex-

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[16] The molar absorptivity of CO in the alkane matrix is 400 M^{-1} cm^{-1} ± 20%; Pope, K. R.; Wrighton, M. S., *Inorg. Chem.*, in press.

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citation yields dissociative loss of CO with a quantum yield of ~0.5.[3] Thus, the question is how does $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ form in good chemical yield from the photolysis of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 298 K? The answer appears to be that $Fe\text{-}CH_2C_6H_6$ homolysis, eq 2, has a relatively low quantum efficiency compared to dissociative loss of CO, eq 1. However, loss of CO yields an $\eta^3\text{-}CH_2C_6H_5$ species that can readily back react with CO, eq 5, to regenerate $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$. Reversibility of CO loss coupled with a small, but finite, quantum yield for $Fe\text{-}CH_2C_6H_5$ homolysis thus accounts for the photoproducts from $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 298 K. Consistent with this hypothesis we find that near-UV irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in a vigorously Ar-purged alkane solution at 298 K yields the formation of both $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ and $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ in a ratio of ~10:1. Under the conditions used the products $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ and $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ account for all $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ consumed. Thus, the 10:1 ratio of $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$:$(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ gives a measure of the relative importance of CO loss and $CH_2C_6H_5$ radical formation in fluid solution at 298 K. Clearly, the product from loss of CO dominates the primary photoproducts from $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$, but the appearance of product arising from $CH_2C_6H_5$ radical formation is also significant. The 298 K fluid solution photoproduct ratio is very different from that found at ~77 K in rigid media or even at 196 K in fluid solution. The variation in product ratio can be attributed to differences in the cage escape efficiency of CO and $CH_2C_6H_5$ radicals at the various temperatures and viscosities. In the more viscous media the net loss of CO is relatively more important than net loss of $CH_2C_6H_5$ radicals from $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$, and CO loss can be the exclusive net chemical result from photoexcitation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$.

The reversible, quantum-efficient loss of CO upon photoexcitation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 298 K in alkane solution is also consistent with the photochemistry of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in an alkane solution containing 0.05 M PPh_3. The disappearance quantum yield of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 366 nm is ~0.7, or about the same as that for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$.[3] This high disappearance quantum yield in the presence of 0.05 M PPh_3 contrasts with a modest 366 nm disappearance quantum yield of ~0.10 for $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in the absence of PPh_3 but under otherwise identical conditions. In the presence of PPh_3 the dominant product from irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is $(\eta^5\text{-}C_5R_5)Fe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$. Apparently, PPh_3 captures $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^1\text{-}CH_2C_6H_5)$ to give a simple substitution product with high quantum efficiency, whereas in the absence of PPh_3 back reaction with CO occurs to give little *net* chemical change but yielding $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ in high chemical yield (low quantum yield) via the radical path. The ratio of disappearance quantum yields for $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in the presence and absence of 0.05 M PPh_3 is in agreement with the ratio of $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ to $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ when $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is irradiated at 355 nm at 298 K in a vigorously Ar-purged alkane solution. The quantum yield and product distributions are consistent with a ratio of net quantum yields of ~10:1 for CO loss to $CH_2C_6H_5$ radical formation with an absolute quantum yield of ~0.5 for CO loss.

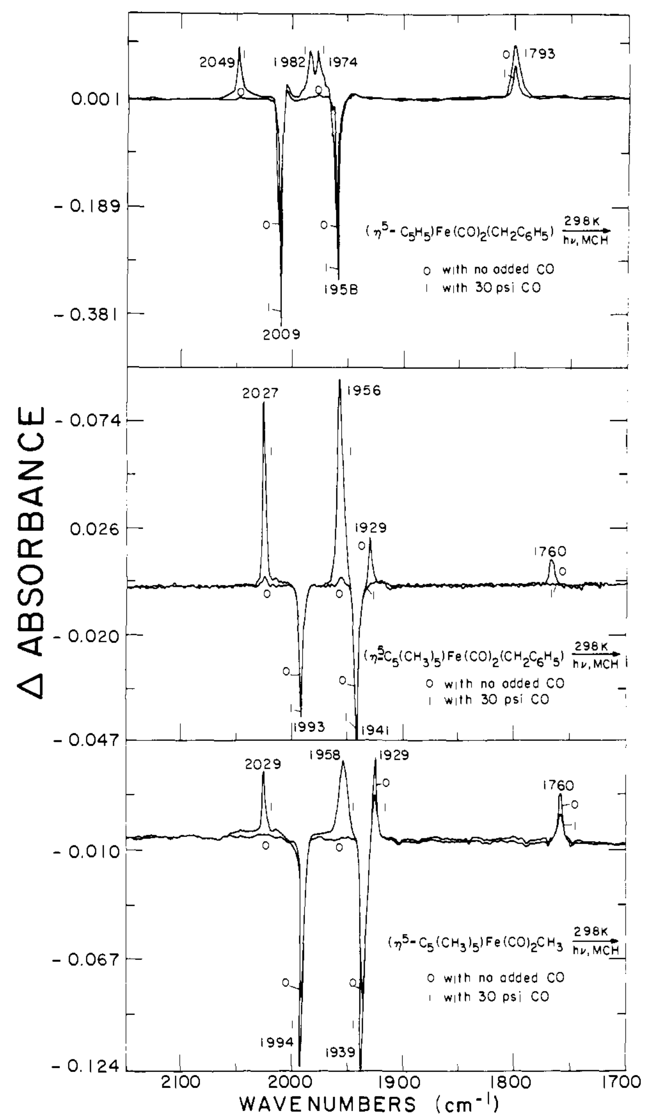

Figure 2. Comparison of the IR difference spectra upon near-UV irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ at 298 k without added CO (0) and with 2 atm of CO (1). All conditions, including irradiation time, are the same except for the difference in CO concentration for the three complexes. Top: Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ with and without CO. The positive peak at 1793 cm^{-1} is due to $(\eta^5\text{-}C_5H_5)_2Fe(CO)_4$ and those at 2049, 1982, and 1974 cm^{-1} are due to $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$. Middle: Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ with and without CO. The positive peaks at 1929 and 1760 cm^{-1} are due to $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ and those at 2027 and 1956 cm^{-1} are due to $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$. Bottom: Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ with and without CO. The positive peaks at 1760 and 1929 cm^{-1} are due to $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ and those at 2029 and 1958 cm^{-1} are due to $(\eta^4\text{-}C_5Me_6)Fe(CO)_3$.

(d) Reactivity of $(C_5R_5)Fe(CO)_2$. From the results described above it would be reasonable to conclude that irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in the presence of CO should suppress net reaction via CO loss and give better chemical yields of products derived from the photochemical formation of $(C_5R_5)Fe(CO)_2$ and $CH_2C_6H_5$ radicals. Interestingly, irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in alkane solution at 298 K under 2 atm of CO yields new chemistry: $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$ is formed in good yield and the yield of $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ is suppressed, Figure 2. For both R = H and Me the 2 atm of CO routinely gives somewhat more net photoreaction of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ than when the irradiation is carried out in the absence of CO. For R = H, the $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$ is characterized by IR bands at 2049, 1982, and 1974 cm^{-1}. These CO stretching features are similar in number, position, and relative intensity to the features for the cornerstone $(\eta^4\text{-}1,3\text{-butadiene})Fe(CO)_3$.[20] The ^1H NMR of $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$ is consistent with its formulation, Table II, but whether the $CH_2C_6H_5$ group is exo or endo cannot be unambiguously determined. However, the photoreaction chemistry of $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$ is consistent with the $CH_2C_6H_5$ group in an exo position. In particular, photolysis of $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$ leads to formation of $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))Fe(CO)_2H$ at 77 K, Figure 3, and the yield is 100 ± 10%, eq 8. The photochemistry of $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ proceeds similarly at 298 K[21] to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, a result that

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[20] (a) Busch, M. A.; Clark, R. J. *Inorg. Chem.* **1975**, *14*, 219. (b) Davidson, G. *Inorg. Chim. Acta* **1969**, *3*, 596.

$$(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3 \xrightarrow[\text{MCH}]{h\nu} (\eta^5\text{-}C_5H_4(CH_2C_6H_5))Fe(CO)_2H + CO \quad (8)$$

we have recently duplicated for irradiation carried out in methylcyclohexane at 77 K as well.[22] Inasmuch as $(\eta^4\text{-}5,5\text{-}Me_2C_5H_4)Fe(CO)_3$ yields $(\eta^4\text{-}C_5H_4Me)Fe(CO)_2Me$ upon irradiation at low temperature,[23] we would expect that $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ would be formed if the $CH_2C_6H_5$ group were in an endo position in the $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$ formed from photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ under CO. The hydride shown as a photoproduct in eq 8 is reactive and thermally reacts with CCl_4 to form $HCCl_3$ upon warmup from 196 to 298 K. The Fe product is $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))Fe(CO)_2Cl$; this chemistry parallels that for $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$. In the absence of CCl_4 the hydride yields some $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))_2Fe_2(CO)_4$. Similarly, $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ gives $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. Small yields of both $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4(CH_2C_6H_5))Fe_2(CO)_4$ are formed upon prolonged irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ under 2 atm of CO. The formation of the mixed dimer results, presumably, from the cross-coupling of radicals from the symmetrical dimers $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))_2Fe_2(CO)_4$.

For the $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ (R = H, Me) species irradiation in the absence of CO actually gives trace yields of the $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$ in addition to $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$. The irradiation under 2 atm of CO for R = Me, however, gives no yield of $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$; rather, $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$ is the only IR-detectable product, Figure 2. To unequivocally establish the position of the $CH_2C_6H_5$ group in $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$ an X-ray crystal structure was determined, Figure 4. The crystallography shows the product to be one with the $CH_2C_6H_5$ group in an exo position as deduced from photoreaction chemistry for $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$. Photolysis of $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$ in methylcyclohexane yields $(\eta^5\text{-}C_5Me_4(CH_2C_6H_5))Fe(CO)_2Me$, Figure 3. The $(\eta^5\text{-}C_5Me_4(CH_2C_6H_5))Fe(CO)_2Me$ was characterized spectroscopically by comparison (IR, ^1H NMR) with an authentic sample prepared from reduction of $(\eta^5\text{-}C_5Me_4(CH_2C_6H_5))_2Fe_2(CO)_4$ followed by reaction with MeI.

We carefully examined the photochemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ in alkane solution in the absence of CO and found no IR evidence for formation of $(\eta^4\text{-}C_5H_5Me)Fe(CO)_3$. Exposure of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ to 2 atm of CO rapidly yields $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)Me$ at 298 K and its photochemistry was not investigated. However, exposure of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ to 2 atm of CO does not lead to rapid CO insertion. Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ under 2 atm of CO does lead to $(\eta^4\text{-}C_5Me_6)Fe(CO)_3$, Figure 3, but in the absence of CO $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ is formed in good yield. Thus, the behavior of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ qualitatively parallels the findings for $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$.

After the discovery of the $(\eta^4\text{-}C_5R_5R')Fe(CO)_3$ photoproducts upon irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ under CO, we examined the nature of the products from the irradiation of alkane solution of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in the presence of 0.05 M PPh_3. For both R = H and Me we find that $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_2(PPh_3)$ is a *primary* photoproduct, albeit one formed in low yield (~10%) compared to $(\eta^5\text{-}C_5R_5)Fe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$. In the presence of 0.05 M PPh_3, the yield of $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ is suppressed, presumably in a manner that is responsible for the suppression of this dinuclear product when irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is carried out under 2 atm of CO.

The photoproducts resulting from photolysis of $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ in the presence of CO or PPh_3 indicate that the $(C_5R_5)Fe(CO)_2$ fragments from homolysis of the Fe–R′ bond react with the 2 e⁻ donors and then couple with the R′ radical. Thus, the $(C_5R_5)Fe(CO)_2$ presumably reacts according to eq 9. The $Fe(CO)_3$ fragment is known as a "diene seeker", and it is reasonable to conclude that the structural formulation of $(C_5R_5)Fe(CO)_2L$ is as shown in eq 9 with considerable radical character in the C_5R_5 system. The nature of the products suggests such a formulation. Coupling the R′ radical with a ring carbon of $(C_5R_5)Fe(CO)_2$ followed by reaction with L is ruled out by the

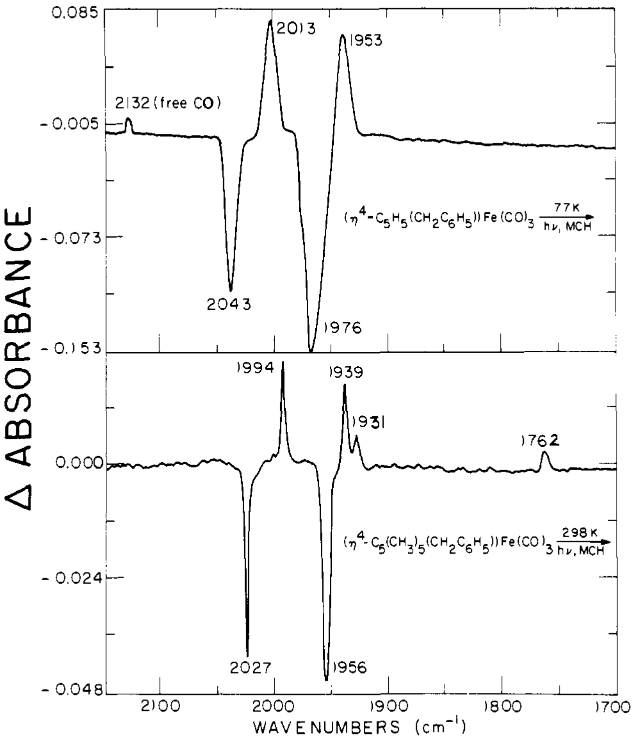

Figure 3. Top: Near-UV irradiation of $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$ in an alkane matrix at 77 K. The positive peaks at 2013 and 1953 cm⁻¹ correspond to $(\eta^5\text{-}C_5H_4CH_2C_6H_5)Fe(CO)_2H$ and the peak at 2132 cm⁻¹ corresponds to free CO. Bottom: Near-UV irradiation of $(\eta^4\text{-}C_5Me_5CH_2C_6H_5)Fe(CO)_3$ in an alkane solution at 298 K. The positive peaks at 1931 and 1762 cm⁻¹ correspond to $(\eta^5\text{-}C_5Me_4(CH_2C_6H_5))_2Fe_2(CO)_4$ and the peaks at 1994 and 1939 cm⁻¹ correspond to $(\eta^5\text{-}C_5Me_4(CH_2C_6H_5))Fe(CO)_2Me$.

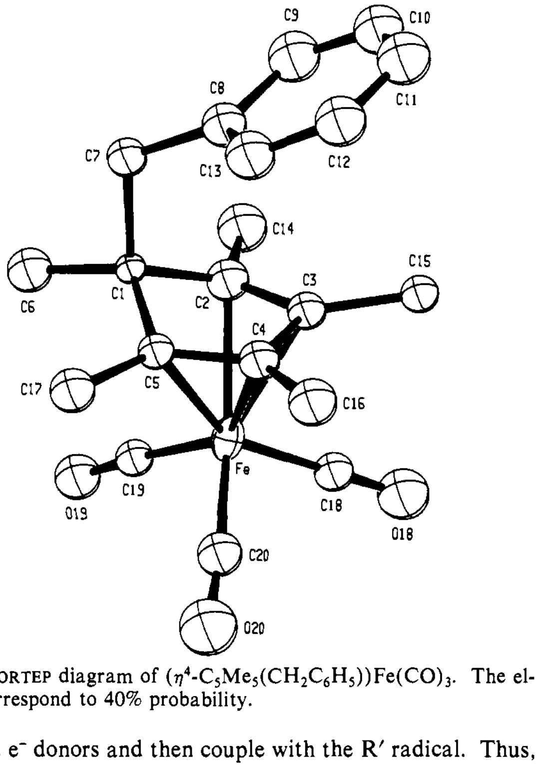

Figure 4. ORTEP diagram of $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$. The ellipsoids correspond to 40% probability.

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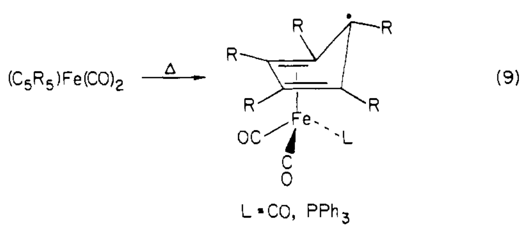
(21) Whitesides, T. H.; Shelley, J. *Organomet. Chem.* **1975**, *92*, 215.

(22) Blaha, J. P.; Wrighton, M. S., unpublished results.

(23) Gerhartz, W.; Ellerhorst, G.; Dahler, P.; Eilbracht, P. *Liebigs Ann. Chem.* **1980**, 1296.



(9)

observation that we do not find $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))_2Fe_2(CO)_4$ or $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4(CH_2C_6H_5))Fe_2(CO)_4$ as products when $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is irradiated in the absence of L. The point is that if the $(C_5H_5)Fe(CO)_2$ reacts with $CH_2C_6H_5$ radicals to form the 16 e^- $(\eta^4\text{-}(C_5H_5(CH_2C_6H_5))Fe(CO)_2$ then the $(\eta^5\text{-}C_5H_4(CH_2C_6H_5))Fe(CO)_2H$ would immediately result and give dinuclear products at 298 K.

The reaction of L = CO or PPh_3 with the 17 e^- $(C_5R_5)Fe(CO)_2$, eq 9, may be reversible. Other 17 e^- radicals, such as $Mn(CO)_5$, are believed to undergo thermal substitution via formation of 19 e^- intermediates.[24] The formulation of $(C_5R_5)Fe(CO)_2L$ as in eq 9 actually gives an 18 e^- Fe center. The special character of the $Fe(CO)_2L$ as a "diene seeker" makes the $(C_5R_5)Fe(CO)_2$ systems different from the $Mn(CO)_5$ species. At this point, there is the possibility that the $(C_5R_5)Fe(CO)_2L$ species should be viewed as an $(\eta^3\text{-}C_5R_5)$, ring-slippage species, with a 17 e^- Fe center, but the chemistry appears best rationalized with an intermediate as represented in eq 9.

There is precedent for transfer of alkyl groups to a complexed $(\eta^5\text{-}C_5H_5)$ ring,[25] as we find in the irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ to give $(\eta^4\text{-}C_5R_5R')Fe(CO)_2L$. Among the previous examples is the formation of $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_2(PPh_3)$, in unspecified yield, from the irradiation of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ in the presence of PPh_3.[7] We do find this compound as a low percentage, but significant, primary photoproduct, vide supra. Also, it has been shown[7] that the $CH_2C_6H_5$ group is in an exo position in the $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_2(PPh_3)$, as we find for $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$, Figure 4. Another relevant finding in the literature concerns the irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ in a CO matrix.[8] The published spectrum for the metal carbonyl product shows bands at 2050, 1982, and 1975; these are nearly identical, in position and relative intensity, to the bands for $(\eta^4\text{-}C_5H_6)Fe(CO)_3$, Table I. The literature[8] assigns the product from the CH_3 complex to $(\eta^3\text{-}C_5H_5)Fe(CO)_3(CH_3)$, though the possibility of $(\eta^4\text{-}C_5H_5CH_3)Fe(CO)_3$ was suggested. We believe that the results that we have obtained with $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ under 2 atm of CO indicate that the tricarbonyl species obtained from irradiating $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ in a CO matrix is in fact $(\eta^4\text{-}C_5H_5Me)Fe(CO)_3$, and not $(\eta^3\text{-}C_5H_5)Fe(CO)_3Me$. Naturally, the product from the irradiation in the marix should be isolated and characterized before this opinion can be accepted.

(e) Crossover Reactions of $(C_5R_5)Fe(CO)_2$ with CO and R′. We noted above that irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ under 2 atm of CO yields somewhat more disappearance than when the irradiation is carried out in the absence of CO. This finding suggests that the R′ radical can back react with $(C_5R_5)Fe(CO)_2$ to regenerate starting material but that the CO can competitively scavenge the $(C_5R_5)Fe(CO)_2$ to suppress back reaction. This fact and the generation of only the isomer of $(\eta^4\text{-}C_5R_5R')Fe(CO)_2L$ with R′ in the exo position suggests that the R′ radicals can completely escape from the vicinity of the Fe center and react with radicals formed from different precursors. Obviously the formation of bibenzyl and $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$, radical coupling products, from irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ establishes that the radicals can undergo cage escape. We have carried out experiments that establish that $(C_5R_5)Fe(CO)_2$ and R′ from different precursors can give $(\eta^4\text{-}C_5R_5R')Fe(CO)_3$.

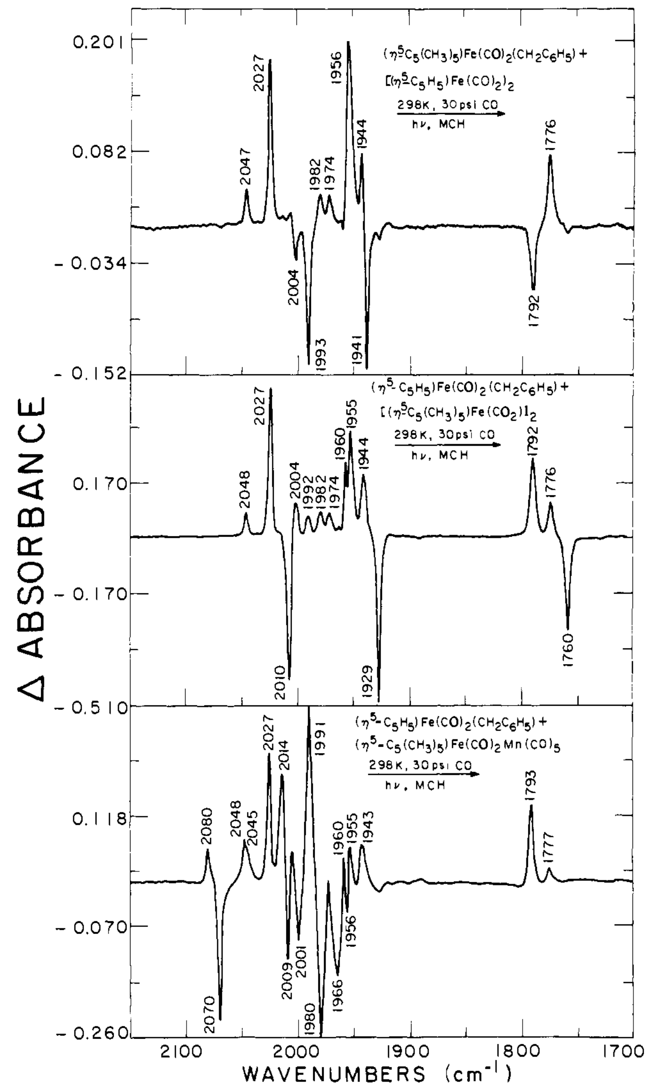


Figure 5. Top: IR difference spectrum upon near-UV irradiation of 0.01 M $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and 0.01 M $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ in methylcyclohexane under 2 atm of CO. The positive peaks at 1944 and 1776 cm^{-1} correspond to the mixed dimer $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4$; those at 2027 and 1956 cm^{-1} correspond to $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$; and those at 2047, 1982, and 1974 correspond to $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$. Middle: IR difference spectrum obtained upon near-UV irradiation of 0.01 M $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ in methylcyclohexane under 2 atm of CO. The product peaks at 2048, 1982, and 1974 cm^{-1} are due to $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$; those at 2027 and 1955 cm^{-1} are due to $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$; and those at 1944 and 1776 cm^{-1} and 2004, 1960, and 1792 cm^{-1} are due to the dimers $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, respectively. Bottom: IR difference spectrum obtained upon near-UV irradiation of 0.01 M $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Mn(CO)_5$ and 0.01 M $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in methylcyclohexane under 2 atm of CO. The positive peaks at 2080, 2014, and 1991 cm^{-1} are due to $(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_5$; the one at 2048 corresponds to $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_3$; the peaks at 2027 and 1955 cm^{-1} are due to $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$; the peaks at 2045 and 2014 cm^{-1} are due to $Mn_2(CO)_{10}$; those at 1943 and 1777 cm^{-1} correspond to $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4$; and those at 2004, 1960, and 1793 cm^{-1} correspond to $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. Note that due to overlap between the starting material peaks and the product peaks peak ratios are not accurate.

Figure 5 shows the IR spectral changes accompanying the irradiation of three different mixtures that establish the expected radical crossover products to be formed in good yield. These data

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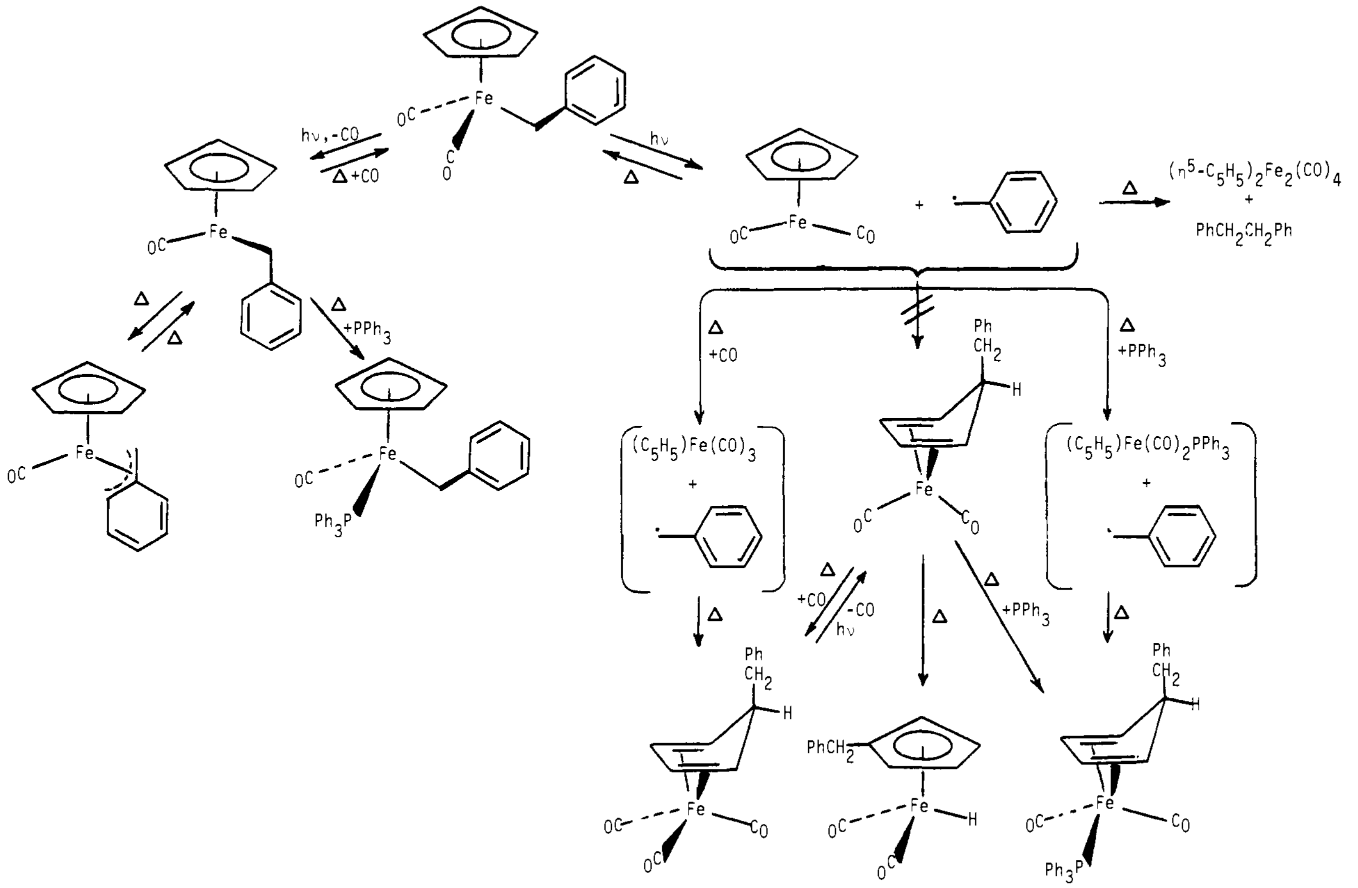
[24] (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (b) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095. (c) Beyers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527. (d) Absi-Halabi, M.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 298, 2. (e) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613. (f) Fox, A.; Malito, J.; Poe, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1052 and references therein. (g) Shi, Q.; Richard, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032.

[25] (a) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* 1976, *203*. (b) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

Scheme I. Summary of the Photochemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-Bz})$



are representative and illustrate clean crossover experiments where good mass balance can be demonstrated. The strategy was to use $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ as a source of $CH_2C_6H_5$ radicals and metal–metal bonded species as independent sources of $(C_5R_5)Fe(CO)_2$. Each of the metal–metal bonded species is believed to undergo metal–metal bond cleavage to give the Fe-centered radical,[11,26] but it is also known to undergo CO loss as a competitive primary process.[27] The presence of 2 atm of CO should rapidly reverse the light-induced loss of CO, however.

Consider first the irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, under 2 atm of CO, Figure 5. *Both* $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$ and $(\eta^4\text{-}C_5H_5\text{-}(CH_2C_6H_5))Fe(CO)_3$ are formed, along with the mixed dinuclear species $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4$. Within an error of 10–20%, the three products account for all of the starting materials consumed. In this experiment the important finding is that there is a significant yield of the crossover product $(\eta^4\text{-}C_5H_5\text{-}(CH_2C_6H_5))Fe(CO)_3$. The second experiment represented in Figure 5 illustrates crossover from irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ under 2 atm of CO. In this case, the key product is $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$, along with the expected dinuclear Fe species. Finally, Figure 5 illustrates the formation of a good yield of $(\eta^4\text{-}C_5Me_5\text{-}(CH_2C_6H_5))Fe(CO)_3$ from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Mn(CO)_5$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ under 2 atm of CO. From all the experiments undertaken, we note the qualitative finding that the $(C_5Me_5)Fe(CO)_2$ radical has a greater tendency than the $(C_5H_5)Fe(CO)_2$ radical to couple with the $CH_2C_6H_5$ radical to form $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$.

Crossover experiments like those represented in Figure 5 have also been carried out under Ar. Under such circumstances low yields of $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$ are found. The extra CO comes from some decomposition. However, the main products are derived from cross-coupling of the various radicals generated. Of particular importance is the observation that $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is generated from irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and $(\eta^5\text{-}C_5H_5)_2Fe(CO)_4$. Likewise, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ can be formed upon irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$. The crossover of the $\eta^1\text{-}CH_2C_6H_5$ fragments is suppressed by the 2 atm of CO as illustrated by data in Figure 5. This is consistent with capture of $(C_5R_5)Fe(CO)_2$ radicals by CO to promote coupling of $CH_2C_6H_5$ radicals with a ring carbon to produce the $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$ at the expense of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ regeneration or of the crossover product.

The coupling of the CH_3 and $CH_2C_6H_5$ radicals to a ring carbon of $(C_5R_5)Fe(CO)_3$ suggests the possibility of coupling a metal-centered radical such as $Mn(CO)_5$ to a ring carbon to produce the species $(\eta^4\text{-}C_5R_5(Mn(CO)_5))Fe(CO)_3$. Curiously, we do not find evidence for this product, Figure 5. It is possible that this product forms with low probability or is unstable, but no evidence for it has been found. Further, when $(\eta^5\text{-}C_5R_5)Fe(CO)_2Mn(CO)_5$ (R = H, Me) alone is photolyzed under 2 atm of CO (without the complication of other metal complexes) we still find no evidence for $(\eta^4\text{-}C_5R_5(Mn(CO)_5))Fe(CO)_3$; rather $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ and $Mn_2(CO)_{10}$ account for the consumed starting material. This result is consistent with the conclusion that CO addition to $C_5R_5Fe(CO)_2$ is reversible or that $Mn(CO)_5$ reacts at the Fe of $(C_5R_5)Fe(CO)_3$ followed by loss of CO. The reactivity of metal-centered radicals with $(C_5R_5)Fe(CO)_3$ will be the object of further study in these laboratories.

Summary and Conclusions

Our work on the photochemistry of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$, summarized by the data in Table III and the mechanism in Scheme I, clarifies several issues and has led to the

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Table III. Summary of Photoproduct Distribution from Irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-Bz})$ under Different Conditions

	product(s), % of mixture					
	$(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-Bz})$		$(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$		$(\eta^4\text{-}C_5R_5Bz)Fe(CO)_3$	
conditions[a]	R = H	R = Me	R = H	R = Me	R = H	R = Me
rigid MCH matrix, 77 K	100	100	0	0	0	0
MCH, 196 K	~100	~100	tr	0	tr	tr
MCH, 298 K (Ar-purged)	90 ± 10	~95	~10 ± 2	~5	0	tr
MCH, 298 K (sealed-vessel)	0	0	~100	~100	tr	tr
MCH, 298 K (2 atm of CO)	0	0	~50 ± 10	0	~50 ± 10	~100

[a] MCH is methylcyclohexane; all media were deoxygenated; Bz ≡ $CH_2C_6H_5$.

discovery of new photochemistry, namely the generation of $(\eta^4\text{-}C_5R_5R')Fe(CO)_3$ when $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ is irradiated under CO. This discovery calls for a change in the interpretation of the photochemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ in a CO matrix. Previously, the formation of a ring slippage product was proposed: $(\eta^3\text{-}C_5H_5)Fe(CO)_3Me$.[8] It now appears the product $(\eta^4\text{-}C_5H_5CH_3)Fe(CO)_3$ should be considered. We can also now rationalize the formation of $(\eta^4\text{-}C_5H_5(CH_2C_6H_5))Fe(CO)_2(PPh_3)$ when $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is irradiated in the presence of PPh_3.[7] The main chemical result of excited-state decay of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is loss of CO, $\Phi_{366m} \approx 0.5$ at 298 K, to give $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ at temperatures as low as 77 K. The $(\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ back reacts rapidly with CO at 298 K. The formation of $(C_5R_5)Fe(CO)_2$ and $CH_2C_6H_5$ radicals from excited-state decay of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ is a much lower probability event compared to the loss of CO. However, the *chemical efficiency* for formation of radical coupling products (or $(\eta^4\text{-}C_5R_5(CH_2C_6H_5))Fe(CO)_3$ under CO) can be high, since back reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ with CO can be completely chemically efficient. The quantum yield for formation of $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ is ~0.05 in the absence of CO, placing a lower limit on the quantum yield for homolysis of the $Fe\text{-}CH_2C_6H_5$ bond. The formation of radicals is ~5–10 times less efficient than loss of CO from photoexcited $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ at 298 K in alkane media.

One of the important aspects of this work is the demonstration that the rigidity of the photoreaction medium has a very profound effect on the observable chemical products. In rigid media, we find negligible importance for products from the homolysis to form $CH_2C_6H_5$ radicals; only CO loss is observed. Such an effect can be regarded as arising from a cage effect. We have previously noted this in connection with the photochemistry of $Mn_2(CO)_{10}$ where CO loss is the only detected photoreaction in rigid media,[28a] while Mn–Mn bond cleavage products can dominate in fluid solution.[24a,28] At this point we are not in a position to say whether the low-temperature rigid media change the *primary* chemical decay paths of the photoexcited species; only the *net* chemical results have been observed. Establishment of whether the medium and temperature affect anything other than recombination processes requires flash photolysis and transient spectroscopy techniques.

Finally, it would appear that the new reactivity associated with $(C_5R_5)Fe(CO)_2$ stems from the extraordinary tendency of $Fe(CO)_3$ to bind 1,3-dienes. Additional elaboration of this finding will be attempted in this laboratory.

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Registry No. $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-Bz})$, 12093-91-3; $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-Bz})$, 95420-89-6; $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^1\text{-Bz})$, 33135-99-8; $(\eta^4\text{-}C_5H_5Bz)Fe(CO)_3$, 95585-26-5; $(\eta^4\text{-}C_5H_5Bz)Fe(CO)_2PPh_3$, 73089-33-5; $(\eta^4\text{-}C_5H_6)Fe(CO)_3$, 40729-83-7; $(\eta^5\text{-}C_5H_4Bz)Fe(CO)_2H$, 95420-90-9; $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, 35913-82-7; $(\eta^5\text{-}C_5H_4Bz)Fe(CO)_2Cl$, 95420-91-0; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, 12107-04-9; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-Bz})$, 43157-75-1; $(\eta^5\text{-}C_5Me_5)Fe(CO)(\eta^3\text{-Bz})$, 95420-92-1; $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)(\eta^1\text{-Bz})$, 95420-93-2; $(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_3$, 95420-94-3; $(\eta^5\text{-}C_5Me_4Bz)Fe(CO)_2Me$, 95420-95-4; $(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_2PPh_3$, 95420-96-5; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$, 52409-66-2; $(\eta^4\text{-}C_5Me_6)Fe(CO)_3$, 95420-97-6; $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, 12154-95-9; $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Bz)Fe_2(CO)_4$, 53335-09-4; $(\eta^5\text{-}C_5H_4Bz)_2Fe_2(CO)_4$, 95585-27-6; $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$, 35344-11-7; $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4$, 95420-98-7; $(\eta^5\text{-}C_5Me_4Bz)_2Fe_2(CO)_4$, 95420-99-8; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_5$, 12088-73-2; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Mn(CO)_5$, 95421-00-4; $Mn_2(CO)_{10}$, 10170-69-1; $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]Na$, 52409-74-2; $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)Me$, 12108-22-4; $(\eta^4\text{-}C_5H_5Me)Fe(CO)_3$, 95421-02-6; $(\eta^3\text{-}C_5H_5)Fe(CO)_3Me$, 95464-48-5; $(\eta^4\text{-}C_5H_5(Mn(CO)_5))Fe(CO)_3$, 95421-03-7; $Fe_2(CO)_9$, 15321-51-4; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$, 12080-06-7; $(\eta^4\text{-}C_5Me_5(Mn(CO)_5))Fe(CO)_3$, 95421-04-8; $C_5H_5(CH_2C_6H_5)$, 60170-73-2; $C_5Me_4H(CH_2C_6H_5)$, 95421-01-5; $Li[C_5H_5]$, 16733-97-4; CO, 630-08-0; $C_6H_5CH_2Br$, 100-39-0; CH_3I, 74-88-4; $C_6H_5CH_2Cl$, 100-44-7; C_5H_6, 542-92-7; CCl_4, 56-23-5; $HCCl_3$, 67-66-3; $PhCH_2\cdot$, 2154-56-5; bibenzyl, 103-29-7; *cis*-2-bromo-2-butene, 3017-68-3; *trans*-2-bromo-2-butene, 3017-71-8.

Supplementary Material Available: Tables of crystal data, bond lengths and angles, positional and thermal parameters, and listings of structure factor amplitudes for $(\eta^4\text{-}C_5Me_5(CH_2C_6H_5))Fe(CO)_3$ (7 pages). Ordering information is given on any current masthead page.

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