A third yellow band was eluted off the column with 3% diethyl ether/97% pentane to afford an orange oily solid identified as (1-((trimethylsilyl)ethynyl)-2-ethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (8 mg, 27 μmol, 10.6% yield): m/e (relative intensity) 296 (M^+, 47.76), 85 (100.00); NMR (CCl_4) δ 4.88 (s, 5 H), 3.96 (s, 2 H), 2.95 (s, 1 H), 0.19 (s, 9 H).

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Registry No. 9, 67378-04-5; **13**, 80471-04-1; **14**, 80471-05-2; **15**, 80471-06-03; **16**, 18823-04-6; **17**, 18765-46-3; **18**, 80471-03-0; **19**, 67378-02-3; **20**, 67378-01-2; **21**, 77347-34-3; **22**, 69991-02-2; **23**, 80471-02-9; **24**, 80471-16-5; **25**, 80471-17-6; **26**, 80471-01-8; **27**, 80471-18-7; **28**, 80471-19-8; **29**, 80471-20-1; **30**, 67378-03-4; **49**, 80470-99-1; **50**, 80471-00-7; **53** isomer 1, 80470-98-0; **53** isomer 2, 80513-56-0; **54** isomer 1, 80470-97-9; **54** isomer 2, 80513-54-8; **54** isomer 3, 80513-55-9; bis(trimethylsilyl)butadiyne, 4526-07-2; 1,2,4,5-tetraethylbenzene, 635-81-4; 1,6-dichlorohexa-2,4-diyne, 16260-59-6; bis(trimethylsilyl)hexatriyne, 21751-86-3; (1,2,3-tris(trimethylsilyl)-4-((1-hydroxy-1-methyl)ethyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt, 80485-79-6; (1-(trimethylsilyl)-2,3-bis(trimethylsilyl)etnynyl)-4-((1-hydroxy-1-methyl)ethyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt, 80471-55-2; (2-butadiynyl-2′-ethynyl-3,3′,4,4′-tetrakis(trimethylsilyl)-1:1′-bi(η^4-cyclobutadienyl))bis((η^5-cyclopentadienyl)cobalt), 80471-56-3; (1,2,3-tris(trimethylsilyl)-4-((trimethylsilyl)ethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt, 70657-45-3; (1-((trimethylsilyl)ethynyl)-2-ethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt, 80470-96-8; $CpCo(CO)_2$, 12078-25-0.

Supplementary Material Available: Listing of complete low- and high-resolution mass and infrared spectral data as well as elemental analysis values for 22 compounds (16 pages). Ordering information is given on any current masthead page.

Photochemistry of Alkyldicarbonyl(η^5-cyclopentadienyl)iron and -ruthenium. Ligand Substitution and Alkene Elimination via Photogenerated 16-Valence-Electron Intermediates

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Photoreaction of (η^5-C_5H_5)M(CO)$_2$R (M = Fe, Ru; R = CH_3, C_2H_5, n-C_5H_{11}) and (η^5-C_5Me_5)Fe(CO)$_2C_2H_5$ involves dissociative loss of CO as the primary photoprocess following near-UV excitation. The quantum yield for photosubstitution of (η^5-C_5H_5)M(CO)$_2CH_3$ is independent of the incoming ligand or its concentration (above 10^{-3} M); the quantum yield is 0.4 ± 0.05 for M = Ru and 0.7 ± 0.03 for M = Fe. All of the complexes for R having β-hydrogens yield the analogous (η^5-$C_5R'_5$)M(CO)$_2$H (R′ = H, Me) complexes upon near-UV irradiation at 298 K in fluid, alkane solution. For the (η^5-C_5H_5)Fe(CO)$_2C_2H_5$ complex the photochemical formation of the hydride occurs even at 77 K in alkane matrices, and there are no infrared detectable intermediates at an extent conversion of <5%. Irradiation of (η^5-C_5H_5)Ru(CO)$_2C_2H_5$ yields photoreaction at 77 K, initially giving infrared spectral changes consistent with the formation of (η^5-C_5H_5)Ru(CO)(C_2H_4)(H) followed by spectral changes consistent with the formation of the (η^5-C_5H_5)Ru(CO)$_2$H. Likewise in rigid (paraffin) media at 298 K, initial spectral changes accompanying near-UV irradiation of (η^5-C_5H_5)Ru(CO)$_2C_2H_5$ are consistent with the formation of the ethylene–hydride complex. At 298 K, high concentrations of PPh_3 suppress the formation of iron–hydride products from irradiation of (η^5-C_5H_5)Fe(CO)$_2C_2H_5$ in a manner consistent with the intermediacy of (η^5-C_5H_5)Fe(CO)C_2H_5 from the dissociative loss of CO from the starting dicarbonyl. For the (η^5-C_5H_5)Ru(CO)$_2CH_3$, irradiation at 77 K in an alkane matrix yields infrared spectral changes consistent with the formation of (η^5-C_5H_5)Ru(CO)CH_3, providing direct evidence for the photogeneration of a 16-valence-electron intermediate. The rate of β-hydrogen transfer for the Fe species created by light is estimated to be >3 × 10^2 s^{-1} at 298 K, and 77 K data suggest that the activation energy for β-hydrogen transfer from photogenerated intermediates is less than ~6 kcal/mol for both the Fe and Ru complexes.

The lowest excited state of many mononuclear transition element complexes undergoes decay by a ligand dissociation process.[1] In some cases the excited-state ligand dissociation has a very low thermal activation energy that allows the generation of coordinatively unsaturated species at low temperature.[2] We have recently exploited photochemistry of this sort to generate the 16-valence-electron alkyl complex (η^5-C_5H_5)W(CO)$_2$(n-pentyl) by extrusion of CO from the 18-valence-electron (η^5-C_5H_5)W(CO)$_3$(n-pentyl).[3] The low-temperature generation of the 16-electron species allowed us to spectroscopically monitor its thermal reaction (eq 1). The principle is that photolysis

$$(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl}) \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H) \quad (1)$$

may allow the generation and characterization of species that would be thermally unstable at temperatures where it would ordinarily be thermally accessible. For example, thermal routes to (η^5-C_5H_5)W(CO)$_2$(n-pentyl) would likely involve more activation energy than does the β-hydrogen-transfer process represented by eq 1. Generally, using light to change the rate-limiting step in a reaction sequence may have consequence with respect to possible reaction products and can provide insight into reaction mechanisms.

Our follow-up studies of the (η^5-C_5H_5)W(CO)$_3$(n-pentyl) and related complexes have confirmed that the alkene hydride product is the trans isomer,[3,4] and this may ac-

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count for the fact that the process represented by eq 2 is

$$(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H) \rightarrow (\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl}) \quad (2)$$

slow.[3] The thermal activation energy for the chemistry represented by eq 1 is ~10 kcal/mol, consistent with a fast, reversible transformation of $(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl})$ to the *cis*-$(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H)$ with a subsequent cis → trans isomerization actually being the rate-limiting step.

With the hope of clarifying aspects of the mechanism of the reaction of 16-valence-electron alkyls, we undertook an investigation of the photochemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ and related complexes. An $(\eta^5\text{-}C_5H_5)Fe(CO)(1\text{-pentene})(H)$ must have a cis disposition of the hydride and alkene. In this case, it has already been proposed that photoexcitation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = CH_3, C_2H_5) yields dissociative loss of CO,[5] as proposed for other $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ systems.[1,5-8] For R = C_2H_5, photoexcitation of the complex yields $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ even at 10 K in an Ar matrix![9] Study of the thermal chemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$ showed the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H)$ and ethylene at ~60 °C.[10] The thermal mechanism was proposed to involve PPh_3 dissociation as the initiating step to give $(\eta^5\text{-}C_5H_5)Fe(CO)(C_2H_5)$ as proposed in the photochemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_2H_5)$.[5] At least for $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$, the loss of CO has a large activation energy. Our data actually show that the β-hydrogen transfer and its reverse occur with great facility at low temperature, consistent with loss of a two-electron donor from an 18-valence-electron alkyl as the rate-limiting step in thermally induced reactions of the starting alkyl complex. Thus, photoexcitation brings about a change in the nature of the rate-limiting step of $(\eta^5\text{-}C_5H_5)Fe(CO)(L)(H)$ formation from $(\eta^5\text{-}C_5H_5)Fe(CO)(L)(C_2H_5)$. From the studies thus far of the Fe complexes there are no data establishing the rate of the β-hydrogen transfer of the presumed 16-electron intermediate. Further, there are no data concerning a mechanism involving an $\eta^5\text{-}C_5H_5 \rightarrow \eta^3\text{-}C_5H_5$ "ring slippage" to open the coordination site that would appear to be necessary to effect the β-hydrogen transfer. The Ru analogues of the Fe complexes have not been previously studied. We find that these Ru complexes yield intermediates than cannot be observed for the Fe species and provide more direct evidence for the mechanism of β-hydrogen transfer.

Experimental Section

Instruments. UV–visible spectra were recorded by using a Cary 17 spectrophotometer; infrared spectra were recorded by using a Perkin-Elmer 180 or Nicolet 7199 Fourier transform spectrometer; NMR spectra were recorded by using a Varian T-60, a JEOL FX90Q Fourier transform, or a Brucker 250 MHz Fourier transform spectrometer. Gas–liquid chromatographic separations were accomplished by using a Varian 2440 or 1440 gas chromatograph with flame ionization detectors and interfaced with a Hewlett-Packard Model 3380S electronic integrator. *n*-Pentane and the linear pentenes were separated by using a 0.3 cm × 9.2 m column of 20% propylene carbonate on Chromasorb P at 25 °C. *n*-Decane analysis was done by using a 0.3 cm × 7.7 m column of Poropak Q at 190 °C with *n*-heptane as an internal standard. All manipulations of the organometallic complexes were done under N_2 by using a Vacuum Atmospheres drybox or under Ar by using conventional Schlenk line techniques unless otherwise noted.

Chemicals. Hexane and toluene were reagent grade and were freshly distilled from CaH_2 under N_2. Tetrahydrofuran (THF) was freshly distilled from benzophenone dianion under N_2. Spectroquality isooctane was further purified by stirring over concentrated H_2SO_4/HNO_3 overnight, washing with H_2O and dilute $NaHCO_3$ and then repeating the acid wash 2 more times. Isooctane was then stirred over 2% $KMnO_4$ in 10% H_2SO_4 overnight, washed, dried over $MgSO_4$, and distilled under N_2 from CaH_2. Finally, the distilled isooctane was passed down grade No. 1 alumina (neutral, Woelm) before use. Methylcyclohexane was washed twice with concentrated H_2SO_4 for several hours and then with fuming H_2SO_4, washed with H_2O, dilute $NaHCO_3$, and saturated NaCl, predried over $CaCl_2$, and then passed down grade No. 1 Al_2O_3. PPh_3 (Aldrich) was recrystallized three times from absolute C_2H_5OH. P(O-*o*-tolyl)$_3$ (Strem), 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (Strem), 90% ^{13}CO (Merck), and paraffin (Fischer) were used as received. Tricyclohexylphosphine (Strem) was recrystallized from hexanes under N_2 prior to use. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (Strem) was recrystallized from CH_2Cl_2/hexanes. $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ was available from previous work.[11] $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)CH_3$ was a gift from A. Davison's research group. Literature procedures were used to prepare $(\eta^5\text{-}C_5H_5)M(CO)_2CH_3$,[12] $(\eta^5\text{-}C_5H_5)M(CO)_2CH_2CH_3$,[13] $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2CH_3$,[14] and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$.[15] $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(2\text{-pentyl})$, and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_3$ were prepared by procedures analogous to those for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ by reducing the appropriate dimer with 1% sodium amalgam in THF followed by addition of 1-iodopentane, 2-bromopentane, or ethyl bromide. The compounds were purified by column chromatography on neutral alumina, eluting with hexanes. $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$: ^1H NMR (60 MHz, C_6D_6) δ 4.88 (s), 1.7–0.6 (m), integration 5:11. Mass spectrum (70 eV) shows a parent ion at *m/z* 248 (calcd 248). The 2-pentyl complex is similar in the ^1H NMR, but the 2-pentyl complex and the *n*-pentyl complex were determined to be different by using ^{13}C NMR (62.8 MHz, C_6D_6). For the *n*-pentyl complex we find peaks (in δ, Me_4Si δ 0) at 218.2 for the CO's, at 85.3 for the C_5H_5, and at 38.3, 37.5, 22.7, 14.4, and 3.8 for the *n*-pentyl group. For the 2-pentyl complex we find peaks at 218.6 for the CO's, at 85.8 for the C_5H_5, and at 49.4, 29.3, 23.7, 20.6, and 14.3 for the 2-pentyl group. The five different resonances for *n*-pentyl are different from those for 2-pentyl, confirming the structural assignments. Infrared and UV–visible absorption properties of compounds relevant to this study are given in Table I.

Irradiations. Two GE blacklight bulbs (355 ± 20 nm, ~2 × 10^{-6} einstein/min) were used for irradiation unless otherwise noted. Quantum yields at 366 or 313 nm were carried out by using ~10^{-3} M $(\eta^5\text{-}C_5H_5)M(CO)_2R$ with the appropriate ligand concentration. Samples (3.0 mL) in 13 × 100 mm test tubes were freeze–pump–thaw degassed and hermetically sealed prior to irradiation. The light source was a 550-W medium-pressure Hg lamp equipped with Corning glass filters and filter solutions to isolate the 366- or 313 nm Hg emissions. Ferrioxalate actinometry[16] was used to determine light intensity which was typically ~10^{-7} einstein/min. Quantum yields are corrected to account for incomplete light

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Table I. Spectroscopic Data for Relevant Compounds[a]

compd	ν_{CO}, cm^{-1} (ϵ, M^{-1} cm^{-1} or rel abs)	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	2015 (5540), 1960 (6360)	345 (770), 275 (sh)
$(\eta^5\text{-}C_5H_5)Fe(^{13}CO)_2CH_3$	1969 (1.00), 1918 (1.2)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$	2011 (4700), 1957 (5420)	352 (744), 275 (sh)
$(\eta^5\text{-}C_5H_5)Fe(CO)_2$(*n*-pentyl)	2009 (5100), 1955 (5770)	351 (749), 275 (sh)
$(\eta^5\text{-}C_5H_5)Fe(CO)_2$(2-pentyl)	2007 (1.00), 1953 (1.2)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2H$	2024 (1.0), 1967 (~1.0)	
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	2006 (3000), 1962 (6400), 1794 (6200)	535 (650), 410 (1700), 348 (7700)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$	1916 (3200) or 1906 (2300)[b]	400 (sh), 280 (sh, ~6200)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$	1921	
$(\eta^5\text{-}C_5H_5)Fe(CO)(P(OPh)_3)CH_3$	~1943	
$(\eta^5\text{-}C_5H_5)Fe(CO)(P(OCH_2)_3CCH_2CH_3)CH_3$	~1952	
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$[c]	1923	
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)CH_3$	1923 (1.0), 1620 (0.14)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)CH_2CH_3$	2020 (1.0), 1963 (2.0), 1666 (0.4)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$[d]	2056 (3700), 2004 (3400)	480 (sh), 396 (690), 338 (1020), 285 (1830)
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_3$	1990 (5600), 1935 (6600)	358 (880), 285 (sh, 4200)
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$	2004 (1.0), 1946 (0.8)	
$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$	1933 (1.0), 1765 (0.6)	
$(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_2CH_3$	2021 (1.0), 1961 (1.1)	
$(\eta^5\text{-}C_5H_5)Ru(CO)_2H$	2035 (1.0), 1975 (1.0)	
$(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$	2025 (5400), 1967 (6700)	280 (2500), 235 (sh)
$(\eta^5\text{-}C_5H_5)Ru(CO)(P(c\text{-}Hx)_3)CH_3$	1917	
$(\eta^5\text{-}C_5H_5)Ru(CO)(P(OCH_2)_3CCH_2CH_3)CH_3$	1963	

[a] All measurements were made in isooctane solution at 25 °C unless otherwise noted. [b] Toluene solution. [c] Benzene solution from: Su, S. R.; Wojcicki, A. *J. Organomet. Chem.* 1971, *27*, 231. [d] Isooctane/CH_2Cl_2 solution.

absorption, typically only 90%.

Low-Temperature Spectra. Low-temperature IR spectra were obtained by using either a Precision Cell, Inc., Model P/N 21.000 variable-temperature cell with NaCl outer windows using liquid nitrogen as coolant or a low-temperature cell built in-house based on a published design[17] using CaF_2 windows mounted in a Cryogenics Technology, Inc., Spectrim II cryocooler with NaCl windows. Temperature was measured by using a thermocouple (chromel vs. Au –0.7 at % Fe) with the reference junction at room temperature. The thermocouple was attached to the copper body of the IR cell with Ag epoxy. Thermocouple output was measured with a Hewlett-Packard 3465A digital multimeter and converted to temperature by using published calibration curves[18] which were checked with liquid nitrogen, dry ice/acetone, and ice/water. Temperatures are considered accurate to ±2 °C at fixed temperatures and ±10 °C while being warmed or cooled. The data for Figures 3 and 4 were obtained by using ~1 mM $(\eta^5\text{-}C_5H_5)M(CO)_2CH_2CH_3$ dissolved in liquid paraffin (mp ~52 °C) and coated (~1 mm) onto a KBr pellet.

Results and Discussion

a. Photosubstitution of $(\eta^5\text{-}C_5H_5)M(CO)_2CH_3$ (M = Fe, Ru). Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, as is known from previous work,[1,5,7] results in the substitution of CO by P-donor groups. We have examined the 366-nm quantum yield for the ligand substitution represented by eq 3 in isooctane solutions of different ligands L and at

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3 \xrightarrow[L]{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)(L)(CH_3) + CO \quad (3)$$

variable concentrations of L. Representative quantum yield data are given in Table II. In the presence of the P-donor ligands or ^{13}CO we find no other primary products other than the substitution product. Thus, disappearance yields can be equated with formation quantum yields of product. The quantum yields establish ligand substitution to account for most of the excited-state decay, and there is no effect on quantum yield, within experimental error, upon variation in the concentration of L or upon variation in the electronic character or structural demands of the entering P-donor ligand.[19]

Table II. Quantum Yields for Disappearance of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ at 366 nm in the Presence of L[a]

L, M	$\Phi \pm 0.03$
PPh_3, 5.2×10^{-3}	0.71
PPh_3, 4.9×10^{-2}	0.68
P(O-*o*-tolyl)$_3$, 4.7×10^{-3}	0.72
P(O-*o*-tolyl)$_3$, 5.1×10^{-2}	0.71
$P(OCH_2)_3CCH_2CH_3$, 4.7×10^{-3}	0.72
$P(OCH_2)_3CCH_2CH_3$, 5.1×10^{-2}	0.71
^{13}CO, 1.0×10^{-2}	0.67

[a] All experiments carried out in deoxygenated isooctane solutions of L and 10^{-3} M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$. All samples are 3.00 mL in Pyrex ampules and were analyzed by infrared spectroscopy after <15% conversion to product. Irradiation carried out at 25 °C in a 366-nm merry-go-round at a light intensity of ~10^{-7} einstein/min. The only detectable product is $(\eta^5\text{-}C_5H_5)Fe(CO)(L)CH_3$.

The lack of variation in quantum yield upon variation in L or its concentration requires the intermediacy of a relatively long-lived and indiscriminate coordinatively unsaturated species. An $(\eta^3\text{-}C_5H_5)Fe(CO)_2CH_3$ intermediate, a ring slippage product, would seemingly be short-lived and structurally demanding compared to the 16-electron $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ formed by dissociative loss of CO from the photoexcited complex (eq 4 and 5).

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3 \xrightarrow[366\ nm]{h\nu} [(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3]^* \quad (4)$$

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$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3]^* \xrightarrow{k_5} (\eta^5\text{-}C_5H_5)Fe(CO)CH_3 + CO \quad (5)$$

Consistent with photochemical generation of $(\eta^5\text{-}C_5H_5)$-$Fe(CO)CH_3$ we find that $(\eta^5\text{-}C_5H_5)Fe(^{13}CO)(CO)CH_3$ is rapidly formed when $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ is irradiated in isooctane solution exposed to 1 atm of 90% ^{13}CO (15-fold excess of ^{13}CO compared to amount required to completely exchange the ^{12}CO in the starting complex). Inasmuch as ^{13}CO cannot be regarded as a nucleophile, it represents a very different entering group compared to the P-donor ligands. The rapid, efficient ^{13}CO exchange during irradiation is most consistent with dissociative loss of CO as the mechanism of ligand substitution. The fact that the ^{13}CO substitution quantum yield is the same as for P-donor entering groups is especially convincing. If the intermediate in the substitution were the ring slippage product, the quantum yield for substitution by the ^{13}CO would be lower than for the P donors provided the CO's equilibrate at the $(\eta^3\text{-}C_5H_5)Fe(CO)_2(^{13}CO)CH_3$ stage.

The chemical efficiency for the formation of simple substitution products in the presence of L rules out two other conceivable primary photoreactions: homolytic $Fe\text{–}CH_3$ cleavage and $\text{–}CH_3$ migration. We do not observe the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_n(L)_{4-n}$ products that would be expected[20] if $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ was formed as a primary product from $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$. Nor do we observe $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C(O)CH_3)$ that would be formed if $(\eta^5\text{-}C_5H_5)Fe(CO)(C(O)CH_3)$ was a result of excited-state decay.

Our studies of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ thus lead to the straightforward and expected conclusion that photoexcitation in solution leads to dissociative loss of CO. The photochemistry of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ may proceed by ring slippage as a result of photoexcitation,[21] but we find that the data are most consistent with CO loss as the principal result of excited-state decay in solution for the $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ species. The quantum yield of 0.7 is the lower limit for the quantum efficiency for the loss of CO; the actual quantum yield for CO loss could be higher with the net quantum yield for substitution being attenuated by inefficient cage escape of the photoejected CO. In toluene solvent that can be weakly coordinated to 16-electron metal carbonyls, we find that the quantum yield for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$ formation is 1.0 ± 15% at 366 nm. This means that the previous finding[5] of CH_4 formation from the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ does not proceed via loss of CH_3 as a primary photoproduct. Completely efficient loss of CO from the excited species, (eq 5) means that k_5 dominates all other rate constants for excited-state decay. The lowest excited state of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ is likely ligand field in character and involves the population of an orbital that is strongly σ antibonding.[22] Apparently, the degree of labilization of the CO is sufficiently great that virtually every excited species loses CO within its lifetime. Such is not uncommon for mononuclear metal carbonyls having ligand field lowest excited states.[1]

The disappointing finding concerning the photochemistry is that we have not been able to observe the 16-electron $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ by irradiating $(\eta^5\text{-}C_5H_5)Fe$-$(CO)_2CH_3$ in inert (paraffin) matrices at low temperature (40–77 K). Duplicating experimental conditions that have proven successful with $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ to observe $(\eta^5\text{-}C_5H_5)W(CO)_2CH_3$ have failed to yield spectroscopically detectable $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$. The reason for this failure is not clear, particularly inasmuch as we do see the analogous Ru species (vide infra). It may be that k_5 is strongly temperature dependent, giving a quantum yield that is too low to observe product on the timescale of our photolyses. Another possibility is that CO loss is indeed quite efficient but that the back-reaction is fast and cage escape of CO at low temperature in the rigid medium is too slow to compete with regeneration of the $(\eta^5\text{-}C_5H_5)$-$Fe(CO)_2CH_3$. Experiments with $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ (vide infra) suggest that it is the latter explanation that accounts for our inability to photogenerate spectroscopically detectable quantities of $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ in low-temperature paraffin matrices. Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in an Ar matrix at 10 K also does not yield a monocarbonyl product, even though $^{12}CO/^{13}CO$ exchange can be induced photochemically when ^{13}CO is present in the 10 K matrix.[9] Consistent with this finding, irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in neat 1-pentene at 77 K leads to loss of the two CO absorptions due to the dicarbonyl (2005, 1948 cm^{-1}), the growth of absorption due to free CO (2135 cm^{-1}), and the growth of a single absorption at ~1948 cm^{-1} under the lower energy absorption of the dicarbonyl. We attribute the single product peak at ~1948 cm^{-1} to $(\eta^5\text{-}C_5H_5)Fe(CO)(1\text{-pentene})CH_3$. Irradiations at low temperature in fluid solutions confirm this assignment, as described in the following paragraph.

Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in 1-pentene-containing solution at low temperature also shows that CO loss can occur at temperatures as low as −90 °C. Figure 1a shows infrared spectral changes resulting from irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in the presence of 1 M 1-pentene. The decline of the two CO absorptions due to the starting complex is not the same, and the growth of absorbance on the low-energy side of the 1959 cm^{-1} starting material absorption indicates that there is a single CO infrared absorption for a product at ~1957 cm^{-1}. We attribute the ~1957-cm^{-1} absorption to $(\eta^5\text{-}C_5H_5)Fe(CO)(1\text{-pentene})$-$CH_3$. Warming the solution to −20 °C results in nearly complete regeneration of the absorptions attributable to $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ concomitant with decline of the ~1957-cm^{-1} absorption. These data suggest that the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ is not only photolabile at −90 °C but that the $(\eta^5\text{-}C_5H_5)Fe(CO)(alkene)CH_3$ complexes are very thermally labile. Note that in the experiment summarized in Figure 1a the photoreleased CO is no more than 5×10^{-3} M while the 1-pentene concentration is 1 M and still nearly complete regeneration of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ occurs at −20 °C. To confirm that the ~1957 cm^{-1} is a substitution labile product, we generated it in a second experiment by irradiating at −78 °C and then introduced PPh_3 and warmed the sample to 25 °C. Infrared analysis (Figure 1b) shows the net formation of the inert $(\eta^5\text{-}C_5H_5)Fe(CO)$-$(PPh_3)CH_3$.

The photosubstitution behavior of $(\eta^5\text{-}C_5H_5)Ru$-$(CO)_2CH_3$ at 25 °C parallels that detailed above for the Fe analogue. The quantum yields for substitution (Table III) are again independent of the nature of the ligand or its concentration. This result is in full accord with a mechanism that involves the dissociative loss of CO. The quantum efficiency, 0.40 ± 0.05, is somewhat lower than for the Fe complex, but this value still gives what would be regarded as an efficient photoreaction. The quantum yields for the Ru complex are reported for 313 nm, since the principal absorption for the Ru complexes is higher

(20) The substitution lability and coupling reactions of 17-electron metal-centered radicals are well established. See ref 11 and references therein.

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(22) (a) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50. (b) Alway, D. G.; Barnett, K. W. *Adv. Chem. Ser.* **1978**, *No. 168*, 115.

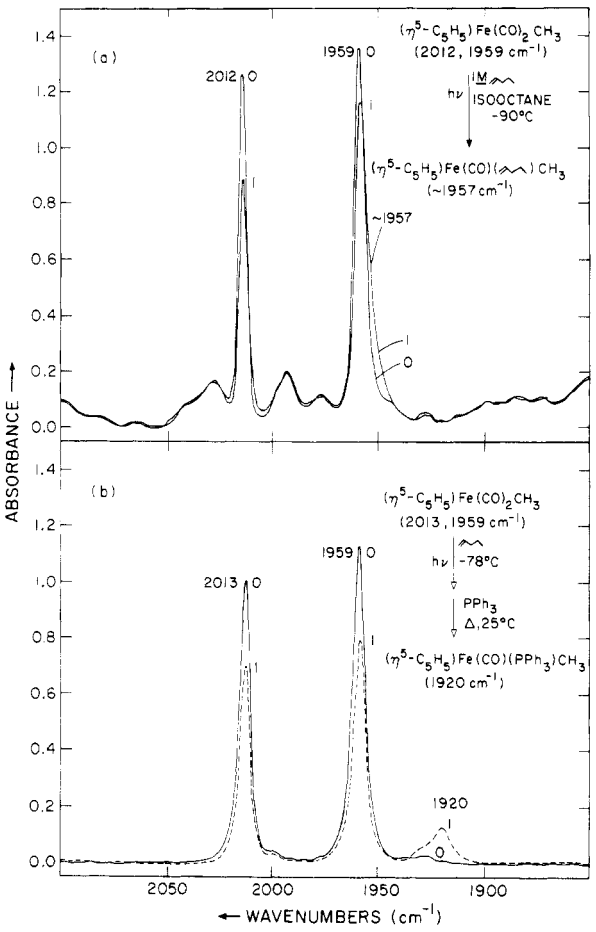

Figure 1. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$. (a) Trace 0 shows $\sim 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in degassed 1 M 1-pentene in isooctane at −90 °C. Trace 1 is after 6-min irradiation. (b) Trace 0 shows $\sim 5 \times 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in 1-pentene. Trace 1 is after cooling to −78 °C, irradiation for 5 min, and then addition of PPh_3 followed by warming to 25 °C. Unidentified peaks in (a) are due to solvent in this single-beam measurement.

Table III. Quantum Yields for Photosubstitution of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$[a]

L, M	Φ ± 0.05
P(c-Hx)$_3$, 5.7×10^{-3}	0.40
P(c-Hx)$_3$, 5.2×10^{-2}	0.47
P(OCH$_2$)$_3$CCH$_2$CH$_3$, 4.9×10^{-3}	0.43
P(OCH$_2$)$_3$CCH$_2$CH$_3$, 5.5×10^{-2}	0.38

[a] All experiments carried out in deoxygenated isooctane solutions of L and $\sim 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$. All samples are 3.00 mL in Pyrex ampules and were analyzed by infrared spectroscopy after <15% conversion to $(\eta^5\text{-}C_5H_5)Ru(CO)(L)(CH_3)$. Irradiation was carried out at 25 °C in a 313-nm merry-go-round at a light intensity of $\sim 10^{-7}$ einstein/min.

in energy than for the Fe species.

Fortunately, and in contrast to the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, we find that UV irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ at 77 K in a methylcyclohexane matrix gives infrared spectral changes that are consistent with the formation of $(\eta^5\text{-}C_5H_5)Ru(CO)CH_3$, the proposed intermediate in light-induced substitution. Bands for the dicarbonyl (2018, 1958 cm^{-1}) smoothly decline while a single absorption grows at $\sim$1937 cm^{-1} (77 K in methylcyclohexane) that we would associate with the 16-valence-electron species. In accord with this assertion we also observe the growth of a feature at $\sim$2135 cm^{-1} that is the absorption of free CO. In a methylcyclohexane solution containing 0.1 M P(c-Hx)$_3$ (c-Hx = cyclohexyl) we find that irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ at 77 K yields two infrared features, one that we attribute to the 16-valence-electron species and one that we attribute to $(\eta^5\text{-}C_5H_5)Ru(CO)(P(c\text{-}Hx)_3)CH_3$. Warm-up to 298 K yields a diminution in the feature attributable to the 16-valence-electron species, leaving the one absorption feature at 1916 cm^{-1} (alkane, 298 K) for the monosubstitution product. Consistent with the lability of CO in methylcyclohexane, we find that irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ in neat 1-pentene at 77 K yields disappearance of the dicarbonyl at 2015 and 1952 cm^{-1}, growth of the free CO absorption at $\sim$2135 cm^{-1}, and the growth of a single absorption at 1943 cm^{-1} (1-pentene, 77 K) attributable to $(\eta^5\text{-}C_5H_5)Ru(CO)(1\text{-pentene})CH_3$. The 77 K experiments with $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$ directly establish the mechanism for photosubstitution to begin with the dissociative loss of CO, as we found for $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ by similar means.[3]

b. Photochemistry of Alkyl Complexes Where the Alkyl Group Has β-Hydrogens. Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in isooctane solution proceeds according to eq 6. Figure 2 compares the infrared spectral

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)_2H + C_2H_4 \quad (6)$$

changes accompanying photoreaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in toluene/0.5 M PPh_3 and photoreaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in isooctane containing no deliberately added entering groups. Like the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ included in Figure 2 for comparison, irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ in the presence of 0.5 M PPh_3 results in efficient CO substitution. The product is $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$ and specifically not $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H)$ or $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C(O)C_2H_5)$, since the infrared spectrum for the product does not correspond to these species. In the absence of entering group in isooctane, photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ yields the $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$. Likewise, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ yields the same metal carbonyl species, as deduced from the infrared spectrum. The $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ exhibits infrared absorptions at 2024 and 1967 cm^{-1} (Table I) that are the same as those for an authentic sample prepared from reaction of acetic acid with Na$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$.[23] Further, as shown in Figure 2 the $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ reacts with CCl_4 to form $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, as expected. A hydride signal is detectable in the ^{1}H NMR of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ at δ −11.88 (s) in C_6D_6, and this signal is found upon irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ in C_6D_6.

Although $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ is observed in dilute ($\sim 10^{-2}$ M) solutions, decomposition of the hydride to form $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ does occur. Indeed, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ is found as a secondary photoproduct. After prolonged photolysis the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ is the only detectable metal carbonyl, and it accounts for all of the starting $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$, within experimental error. After extensive irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl})$ we find n-pentane and the linear pentenes, mainly 1-pentene, as the products from the n-pentyl group. The ratio of n-pentane to linear pentenes is $\sim$1/1. No n-decane was detected (<0.1% of n-pentyl) by gas chromatography from irradiation of the

(23) Sodium borohydride reduction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ has been used to prepare $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ on a synthetic scale. However, anion acidification such as that used to prepare $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Cr, Mo, W) (ref. 12) is more convenient when separation of acetic acid and the volatile hydride is not required.

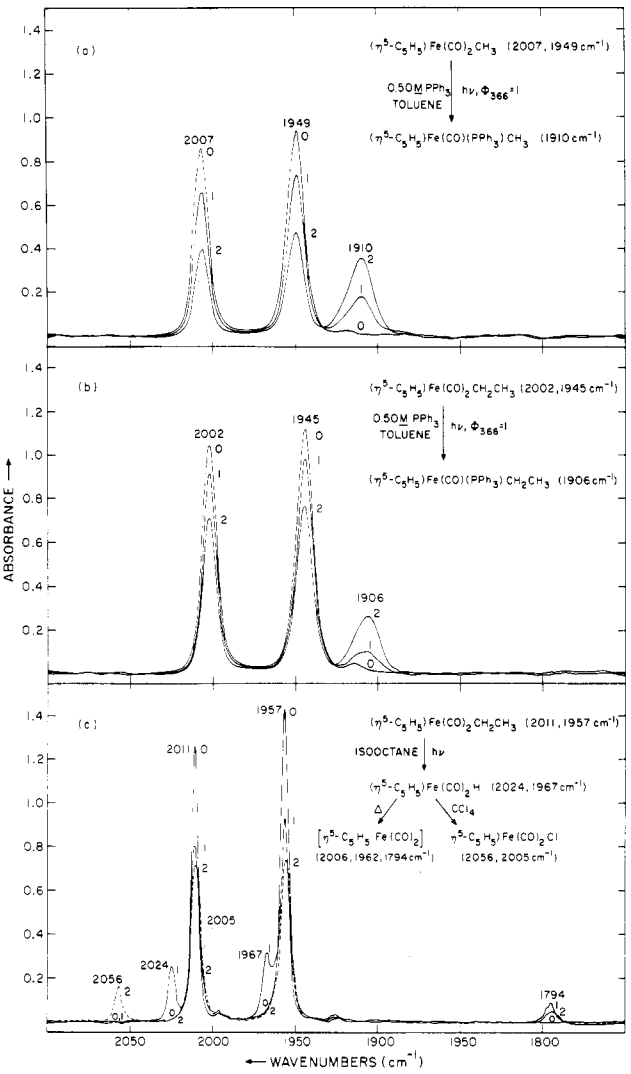

Figure 2. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$. (a) Trace 0 shows $\sim 3 \times 10^{-2}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ in degassed toluene containing 0.50 M PPh_3. Traces 1 and 2 are after 30- and 90-s irradiation, respectively. The observed product is $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$. (b) Trace 0 shows $\sim 8 \times 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in degassed toluene containing 0.50 M PPh_3. Traces 1 and 2 are after 15- and 60-s irradiation, respectively. The observed product is $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2CH_3$. The ordinate has been expanded 2.0 times for these spectra. (c) Trace 0 shows $\sim 1 \times 10^{-2}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in degassed isooctane. Trace 1 is after one flash from a Xenon flash lamp. Trace 2 is after addition of 10 μL degassed CCl_4 to the IR cell.

n-pentyl complex in toluene solution.

While they have not been investigated in detail, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_3$ and $(\eta^5\text{-}C_5H_5)Ru(CO)_2C_2H_5$ both yield clean photoreaction in isooctane at 25 °C to give $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ and $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$, respectively. Thus, like $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(*n*-pentyl) the initially observable product from photolysis in isooctane is not an alkene–hydride complex as found in the irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3$(*n*-pentyl).[3] The 366-nm quantum yields for disappearance of the ethyl and *n*-pentyl Fe complexes in isooctane solution are significantly higher than for the methyl complex (Table IV). For the methyl complex the irradiation does not cleanly yield tractable product; a small amount (~15%) of $(\eta^5\text{-}C_5H_5)_2Fe(CO)_4$ is formed and ~20% CH_4 is detected, but there is no C_2H_6 or C_2H_4 detected. The mechanism of the formation of these products is under study. The low quantum yield for dissappearance of the methyl complex

Table IV. Disappearance Quantum Yields for $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(alkyl)[a]

complex	solvent	entering group, M	Φ ± 15%
$(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$	isooctane	none	0.36
$(\eta^5\text{-}C_5H_5)Fe(CO)_2$(*n*-pentyl)	isooctane	none	1.00
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	isooctane	none	0.07
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	isooctane	PPh_3, 0.049	0.68[b]
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	toluene	PPh_3, 0.5	1.00
$(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$	toluene	PPh_3, 0.5	1.00

[a] All samples irradiated in deoxygenated, 3.00 mL, 25 °C, solutions at $\sim 10^{-2}$ M of complex. Irradiation was at 366 nm, $\sim 10^{-7}$ einstein/min, and quantum yields are for <15% conversion. Irradiations in the presence of PPh_3 yield only $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$. In isooctane alone the ethyl and *n*-pentyl complexes yield $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$; the methyl complex yields some decomposition to unidentified products and some $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. [b] This value has a smaller error, ±0.03; cf. Table II.

is consistent with the primary process represented by eq 5 and the finding that photolysis under ^{13}CO leads to facile exchange. Larger disappearance quantum yields for the ethyl and *n*-pentyl complexes in isooctane are consistent with the possibility of the β-hydrogen transfer allowed by loss of alkene (eq 7–9). The $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ then

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{alkyl}) \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkyl}) + CO \quad (7)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkyl}) \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkene})(H) \quad (8)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkene})(H) \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(H) + \text{alkene} \quad (9)$$

forms by capture of CO (eq 10). Apparently, the sequence

$$(\eta^5\text{-}C_5H_5)Fe(CO)(H) + CO \xrightarrow{k_{10}} (\eta^5\text{-}C_5H_5)Fe(CO)_2H \quad (10)$$

of (8) and (9) to yield loss of alkene is faster than the back-reaction of the 16-electron alkyl complex with photoreleased CO, (eq 11), since the quantum yields are very

$$(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkyl}) + CO \xrightarrow{k_{11}} (\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{alkyl}) \quad (11)$$

high. It is perhaps not surprising that we do not observe the $(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkene})(H)$ at 25 °C, since our data for $(\eta^5\text{-}C_5H_5)Fe(CO)(\text{alkene})CH_3$ show the alkene to be only weakly bound and that it will react at −20 °C (or lower) with the photoreleased CO from its formation, even with 1 M 1-pentene present (vide supra and Figure 1). Nor is it surprising that the photoreleased CO cannot efficiently recapture the 16-electron alkyl complex at 25 °C; the β-hydrogen transfer is a unimolecular process that can occur at a fast rate.[3,4]

Consistent with the mechanistic proposal represented by eq 7–10, we find that photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(*n*-pentyl) in isooctane that contains added PPh_3 yields two additional products (in a ratio and amount that depends on added PPh_3 concentration) from reaction of the proposed 16-electron species with PPh_3 (eq 12 and 13). Indeed, at sufficiently high

$$(\eta^5\text{-}C_5H_5)Fe(CO)(alkyl) + PPh_3 \xrightarrow{k_{12}} (\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(alkyl) \quad (12)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(H) + PPh_3 \xrightarrow{k_{13}} (\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H) \quad (13)$$

PPh_3 concentration the product is mainly the substitution product $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(alkyl)$ (alkyl = C_2H_5 or *n*-pentyl) (Figure 2). Thus, sufficient concentrations of nucleophile can apparently intercept the primary 16-electron photoproduct to suppress the product from β-hydrogen transfer (Table V). Likewise, P-donor ligands in solution can effectively suppress β-hydrogen transfer products for the ruthenium ethyl species, though a higher concentration of the P-donor group is needed.

We propose that the transfer of the β-hydrogen is reversible (eq 8), since we find some of the 2-pentenes from photolysis of the *n*-pentyl complex. Study of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(alkyl)$ also led to this conclusion.[10] However, we do not find extensive isomerization of 1-pentene to the 2-pentenes by irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(*n*-pentyl) in the presence of added 1-pentene, but there is enough in the way of catalysis (greater than five turnovers based on molecules of 2-pentene formed per molecule of Fe complex) to invoke the same mechanism involved in the thermolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(alkyl)$, where loss of PPh_3 yields the same 16-electron species that we invoke here. The photoassisted isomerization of 1-pentene is proposed to proceed as in eq 14–20. In principle, the

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2(n\text{-pentyl}) \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(n\text{-pentyl}) + CO \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(1\text{-pentene})(H) + CO \quad (14)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(1\text{-pentene})(H) \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(2\text{-pentyl}) \quad (15)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(2\text{-pentyl}) \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(cis\text{-2-pentene})(H) \quad (16)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(2\text{-pentyl}) \underset{k_{-17}}{\overset{k_{17}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(trans\text{-2-pentene})(H) \quad (17)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(cis\text{-2-pentene})(H) \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(H) + cis\text{-2-pentene} \quad (18)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(trans\text{-2-pentene})(H) \underset{k_{-19}}{\overset{k_{19}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(H) + trans\text{-2-pentene} \quad (19)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(1\text{-pentene})(H) \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Fe(CO)(H) + 1\text{-pentene} \quad (20)$$

quantum efficiency for the isomerization could be greater than unity, but, in fact, there is a very low quantum yield for isomerization ($<10^{-2}$). The low extent conversion for the isomerization and the low quantum yields do not mean that the thermal steps in the catalytic cycle are slow. Rather, the low quantum efficiency is likely due to the fact that the hydride effects reduction of pentene to *n*-pentane while $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ is formed. The Fe dimer is not an active isomerization catalyst at 25 °C either in the dark or under irradiation.[24]

Further confirmation of the reversibility of the alkene–hydride formation is provided by results from the irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(2-pentyl) in toluene. We find the formation of *n*-pentane, 1-pentene, *cis*-2-pentene, and *trans*-2-pentene in a distribution at ~50% conversion very similar to that from irradiating the *n*-pentyl complex under the same conditions. Presumably, rapid isomerization catalysis of an added alkene would result if the consumption of hydride could be prevented. Studies aimed at preventing the dimer formation are now underway employing surface-confined $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ catalyst precursors.

c. Low-Temperature Irradiation of $(\eta^5\text{-}C_5H_5)M(CO)_2C_2H_5$. W find that the $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ is photoreactive in inert matrices at low temperature. Irradiation of the ethyl complex at 77 K in a paraffin matrix results in the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ (Figure 3). Even at the very low conversions illustrated in Figure 3, we observe no infrared absorptions attributable to an intermediate $(\eta^5\text{-}C_5H_5)Fe(CO)(C_2H_4)(H)$. The photochemical reaction of the ethyl complex at 77 K is consistent with the fact that others have observed the same reaction to occur even at 10 K in an Ar matrix.[9] Since the logical intermediate in the reaction is the $(\eta^5\text{-}C_5H_5)Fe(CO)(C_2H_4)(H)$, having only one CO stretch in the infrared that may be close to the low-energy CO absorption in $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$, we have carefully compared the relative diminution in the two bands due to the $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ (Figure 3b). We find no evidence for any hidden absorption; both bands of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ decline at the same rate. The only primary product that is detectable is $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$.

Irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2C_2H_5$ at 77 K in an alkane matrix also results in reaction (Figure 4). In this case the initial spectral changes show that $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ is *not* the primary photoproduct. Indeed, spectra at low conversion show a significant difference compared to what would be expected for the $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$. The noteworthy feature of the spectra at low conversion is the single CO stretching frequency at 1966 cm^{-1}, consistent with a monocarbonyl photoproduct. The constancy of the ratio of the two negative peaks (2017, 2055 cm^{-1}) for the disappearing $(\eta^5\text{-}C_5H_5)Ru(CO)_2C_2H_5$ reveals that there are no peaks associated with product under those for the starting material. The position of the single product peak, higher in energy than the low-energy peak of the dicarbonyl, is inconsistent with it being the coordinatively unsaturated $(\eta^5\text{-}C_5H_5)Ru(CO)C_2H_5$, inasmuch as $(\eta^5\text{-}C_5H_5)M(CO)CH_3$ has its single CO absorption below that for the dicarbonyl. Further, $(\eta^5\text{-}C_5H_5)M(CO)(alkene)CH_3$ has its absorption below that for $(\eta^5\text{-}C_5H_5)Ru(CO)_2CH_3$. We therefore assign the 1966 cm^{-1} absorption to the $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$. Continued irradiation at 77 K results in the formation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ (2032, 1971 cm^{-1}). The observation of the 1966-cm^{-1} photoproduct peak that we associate with $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ provides direct proof that one-step formation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ does not occur; the results are consistent with a mechanism involving the dissociative loss of CO as the primary photoprocess. Unfortunately, the $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ is photochemically and thermally labile and has not been fully characterized. It is noteworthy that relatively inert complexes $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(alkene)(H)$ can be formed from an 80 °C thermolysis of the $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(alkyl)$ precursor.[25]

(24) Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6769.
(25) Lehmkuhl, H.; Grundke, J.; Benn, R.; Schroth, G.; Mynott, R. *J. Organomet. Chem.* **1981**, *217*, C5.

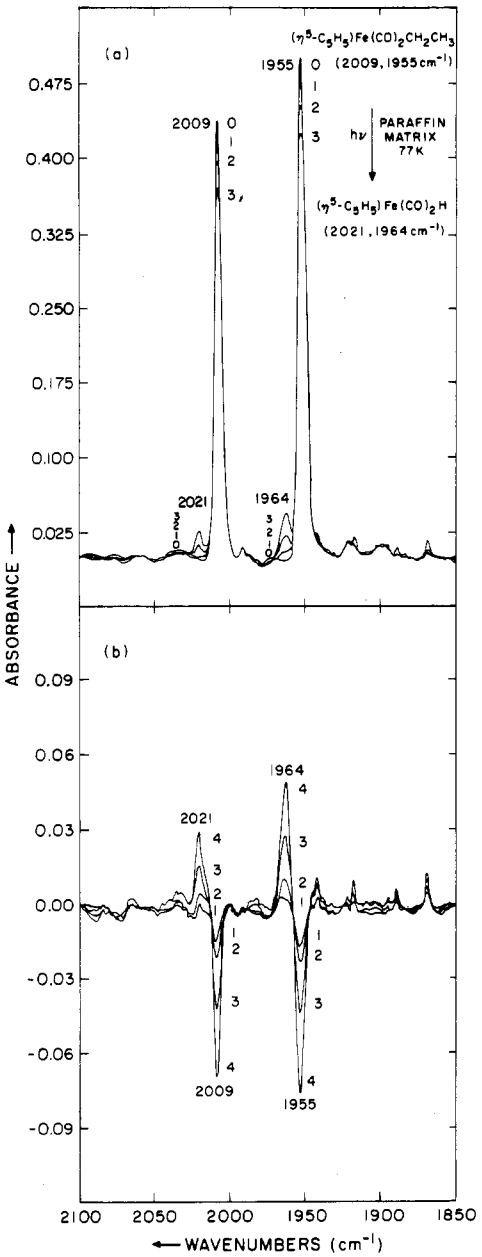

Figure 3. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$. (a) Trace 0 shows $\sim 10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in a paraffin matrix at 77 K. Traces 1, 2, and 3 are after 15-, 40-, and 80-min irradiation, respectively. (b) Traces 1, 2, 3, and 4 show subtraction spectra obtained by subtracting the initial spectrum from spectra obtained after 5-, 15-, 40-, and 80-min irradiation, respectively.

Apparently, the PPh_3 stabilizes the alkene–hydride complex. It is also noteworthy that the monocarbonyl photoproduct that we assign as $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ can also be observed in a paraffin matrix at 25 °C at low conversion. However, irradiation in isooctane at 25 °C yields $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ as the only detectable product at <5% conversion. These findings are consistent with a cage effect on the loss of C_2H_4 from the Ru.

To confirm the existence of the $(\eta^5\text{-}C_5H_5)Ru(CO)$(alkene)(H), we prepared $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ and irradiated it in neat 1-pentene at 77 K. In neat 1-pentene the two bands for $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ are at 2015 and 1952 cm^{-1}. The infrared spectral changes are in accord with CO substitution: the free CO absorption grows, the dicarbonyl features decline, and a single absorption at $\sim$1954 cm^{-1} (1-pentene, 77 K) grows in that we attribute to $(\eta^5\text{-}C_5H_5)Ru(CO)$(1-pentene)(H). The $\sim$1954-cm^{-1} position

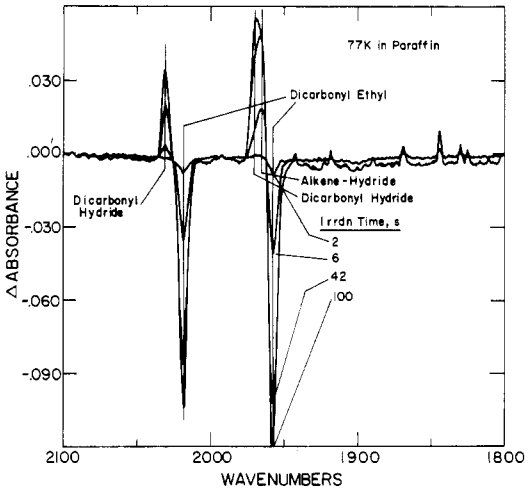

Figure 4. Infrared spectral changes accompanying the irradiation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2C_2H_5$ at 77 K in a paraffin matrix. Note that the starting material peaks at $\sim$2020 and 1960 cm^{-1} represent consumption and the peak ratios are independent of irradiation time. The primary product peak is at $\sim$1970 cm^{-1} that we associate with $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ and longer irradiation yields peaks at $\sim$2040 and $\sim$1980 cm^{-1} characteristic of $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$.

is $\sim$12 cm^{-1} lower in energy than for the ethylene–hydride but this is expected on the basis of the fact that the 1-pentene complex will likely absorb at a lower frequency and the 1-pentene vs. methylcyclohexane matrix gives a 3–6-cm^{-1} shift to lower frequencies for these complexes. Thus, irradiation of the $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ provides an independent entry to alkene hydride products as we found for $(\eta^5\text{-}C_5H_5)W(CO)_3H$.[3]

Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(*n*-pentyl) in neat 1-pentene solution at −140 °C leads to a diminution in the two bands due to the *n*-pentyl complex and the growth of a new absorption at $\sim$1947 cm^{-1} (Figure 5). Warming the solution to −40 °C yields $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ at the expense of the product associated with the $\sim$1947-cm^{-1} absorption. Specifically, we do not observe the regeneration of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = alkyl) as was observed for R = CH_3 (vide supra). Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ at −78 °C in neat 1-pentene followed by addition of PPh_3 at −78 °C followed by warm-up to 25 °C yields $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$ (R = alkyl), not $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H)$. ^1H NMR of the product shows it to be $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(*n*-pentyl), not the ethyl complex. These results suggest that the $\sim$1947-cm^{-1} absorption is due to $(\eta^5\text{-}C_5H_5)Fe(CO)$(1-pentene)(*n*-pentyl) that is very substitution labile, as is $(\eta^5\text{-}C_5H_5)Fe(CO)$(1-pentene)$(CH_3)$ (vide supra).

Irradiation of $(\eta^5\text{-}C_5H_5)M(CO)_2C_2H_5$ (M = Fe, Ru) at 77 K in neat 1-pentene leads to rapid photoreaction. For M = Fe the principal product appears to be $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ with an alkene monocarbonyl as a possible minor product. By way of contrast we find that the Ru complex appears to give mainly $(\eta^5\text{-}C_5H_5)Ru(CO)$(alkene)(H). Interestingly, it does not appear that the neat 1-pentene matrix suppresses β-hydrogen transfer. While the matrix is a pure two-electron donor that could capture a photogenerated, 16-valence-electron intermediate prior to β-hydrogen transfer as with PPh_3 in fluid solution, apparently the rigidity of the matrix prevents suppression of the β-hydrogen transfer.

At the present time we are still not in a position to unambiguously rule out $\eta^5\text{-}C_5H_5 \rightarrow \eta^3\text{-}C_5H_5$ ring slippage as the pathway for β-hydrogen transfer, but results for the Ru methyl complex compel us to adopt the mechanism

Table V. Effect of PPh_3 Concentration on Photoproduct Distribution from $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$

	photoproducts,[a] %		
$[PPh_3]$, M	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$	$(\eta^5\text{-}C_5H_5)Fe(CO)(L)(H)$ (L = CO or PPh_3)	(substitution/hydride)[b]
0	0	100	0
0.002	3.8	96.2	0.04
0.012	14.5	85.5	0.17
0.020	24.8	75.2	0.33
0.029	29.6	70.4	0.42
0.035	30.6	69.4	0.44
0.055	40.1	59.9	0.67

[a] Photoproducts determined, quantitatively by IR, cf. Table I. All irradiations were carried out in deoxygenated isooctane solutions containing ~0.01 M $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ and PPh_3. The irradiation was a single flash from a pair of Xenon flash lamps (~10-μs flash) to avoid secondary photolysis. The hydride products are a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$; cf. text eq 10 and 13. [b] Ratio of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$ to the sum of the two hydride products. Assuming k_{-8} to be small, the ratio should equal $k_{12}[PPh_3]/k_8$; a plot of the ratio vs. $[PPh_3]$ is a straight line with an intercept of zero.

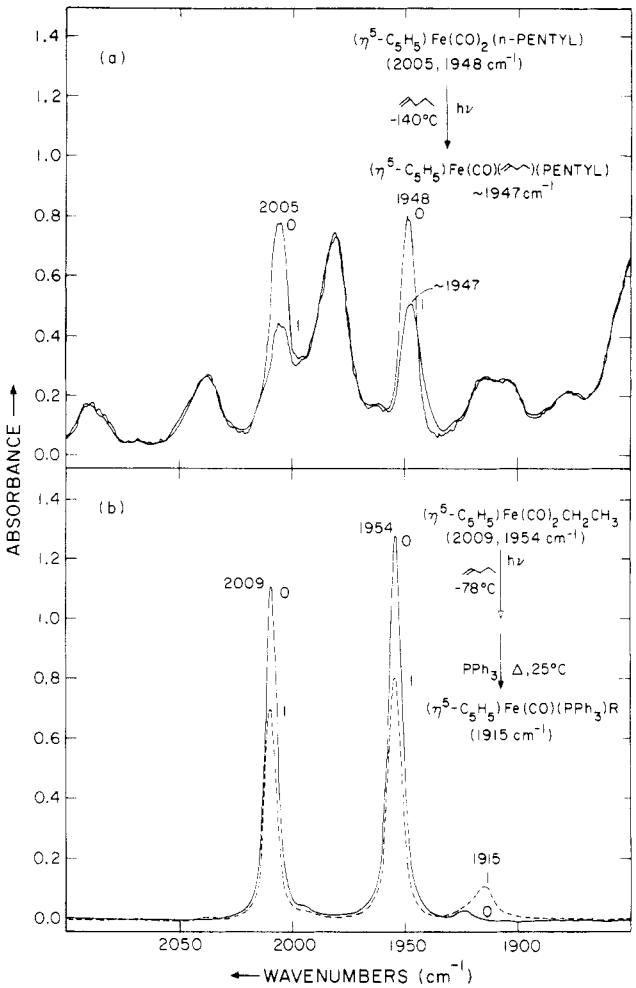

Figure 5. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$. (a) Trace 0 shows ~$10^{-3}$ M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in degassed 1-pentene at −140 °C. Trace 1 is after 22-min irradiation. (b) Trace 0 shows ~5 × 10^{-3} M $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_3$ in 1-pentene. Trace 1 is after cooling to −78 °C, irradiation for 5 min, and then addition of PPh_3 followed by warming to 25 °C. The unidentified peaks in (a) are due to solvent in the single-beam measurement.

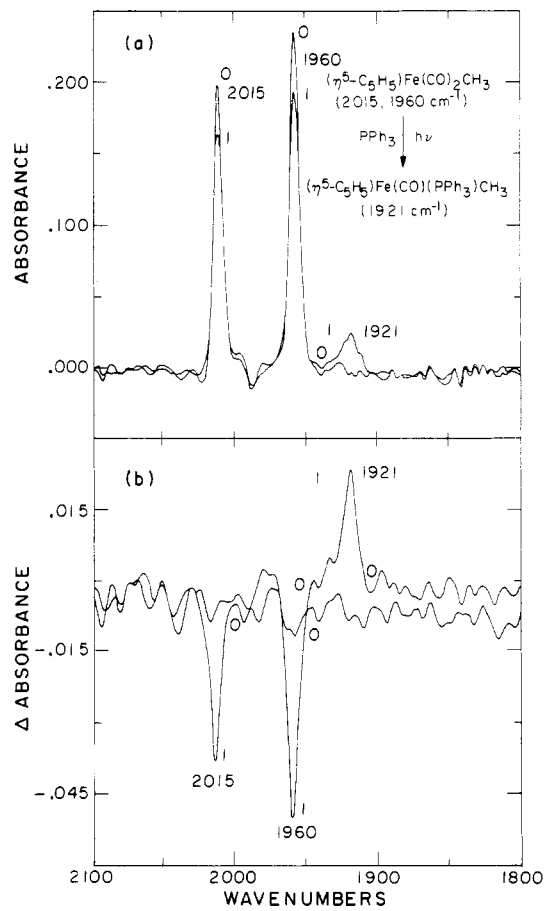

Figure 6. Spectra of ~1 mM $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$/1 mM PPh_3/isooctane before (0) and <200 ms after (1) a flash photolysis to generate $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$. In (a) the spectra are shown and in (b) difference spectra are shown. No $(\eta^5\text{-}C_5H_5)Fe(CO)CH_3$ intermediate, expected to absorb between 1960 and 1921 cm^{-1} is observed, indicating that capture of the 16-electron species occurs in <200 ms. A spectrum recorded 25 s after the flash is the same as scan 1, indicating that reaction is complete in <200 ms.

involving dissociative CO loss as the preferred path. For Fe complexes, the low-temperature experimentation does indicate that photoejected CO does not efficiently escape into the matrix. The 25 °C studies of the methyl complexes show no entering group structural effects in substitution (Tables II and III), and there is no reason to suspect that results for the ethyl and *n*-pentyl complexes would be different. The lack of entering group effects in substitution is most consistent with the dissociative loss of CO.

Having concluded that the immediate precursor to β-hydrogen transfer is the 16-electron $(\eta^5\text{-}C_5R'_5)M(CO)R$, we now consider the rate of β-hydrogen transfer. The inability to observe $(\eta^5\text{-}C_5H_5)Ru(CO)C_2H_5$ under conditions where $(\eta^5\text{-}C_5H_5)Ru(CO)CH_3$ is observable indicates that β-hydrogen transfer is very fast and much faster than for Mo and W complexes.[3,4] At 77 K, we find that $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ or $(\eta^5\text{-}C_5H_5)Ru(CO)(C_2H_4)(H)$ can be formed

photochemically in a time that depends on the intensity of the light source. Conservatively, we can say that the half-time for photoreaction at 77 K can be <60 s. We can thus put a limit on the rate constant associated with the thermal conversion of the photogenerated 16-valence-electron intermediate I to the metal hydride (eq 21). We

$$\mathrm{I} \xrightarrow{k_{21}} \text{metal hydride} \qquad (21)$$

conclude that k_{21} must be $\sim 10^{-2}$ s^{-1} at 77 K. Assuming the highest frequency factor possible for a unimolecular reaction, $A = 10^{14}$ s^{-1}, this leads to the conclusion that the activation energy for the metal hydride formation from I is <6 kcal/mol. This is in accord with the data for the β-hydrogen transfer in the Mo and W complexes (η^5-C_5H_5)M(CO)$_2$R,[3,4] where the activation energy is $\sim$10 kcal/mol; these complexes do not give significant rates for β-hydrogen transfer at 77 K.

Assuming that (η^5-C_5H_5)Fe(CO)C_2H_5 can be directly intercepted by PPh_3 to give substitution prior to any β-hydrogen transfer and assuming the substitution of the methyl complex proceeds by the same kind of intermediate with the same rate, allow us to place a limit on the 25 °C rate of β-hydrogen transfer. Using the rapid scan (7 scans/s) Fourier transform infrared technique, we have shown that the substitution of CO in the iron–methyl complex by 1×10^{-3} M PPh_3 is at least 75% complete within 200 ms after a flash excitation to produce $\sim 10^{-4}$ M I (Figure 6). This gives us a lower limit on the rate constant for capturing the 16-electron species by PPh_3, k_{22}, eq 22, of $\sim 3 \times 10^3$ M^{-1} s^{-1}. Under the same conditions,

$$(\eta^5\text{-}C_5H_5)\mathrm{Fe(CO)R} + \mathrm{PPh_3} \xrightarrow[\text{isooctane}]{k_{22}} (\eta^5\text{-}C_5H_5)\mathrm{Fe(CO)(PPh_3)R} \qquad (22)$$

$$\mathrm{R} = \mathrm{CH_3}$$

$\sim$0.1 M PPh_3 is required to observe (η^5-C_5H_5)Fe(CO)(PPh_3)(C_2H_5) at 50% of the product mixture from irradiation of (η^5-C_5H_5)Fe(CO)$_2C_2H_5$ in isooctane solution (Table V). These results suggest that k_{21} at 25 °C is $>3 \times 10^2$ s^{-1} consistent with the extrapolation of our 77 K lower limit for k_{21} and the activation energy. The value of k_{22} is probably much higher that 3×10^3 M^{-1} s^{-1}, on the basis of flash photolysis studies;[26] this means that k_{21} would be much larger than 3×10^2 s^{-1}.

These considerations of the 16-valence-electron species indicate that transfer of a β-hydrogen from the alkyl group onto the metal occurs with facility even at very low temperatures. Direct monitoring of the progress of the transfer of the β-hydrogen atom has not proven to be possible with the techniques that we used for the (η^5-C_5H_5)W(CO)$_3$(*n*-pentyl). Flash photolysis with a time resolution of at least nanoseconds and perhaps picoseconds is required to directly monitor reaction to give a hydride product at 298 K. Conventional, greater than microsecond timescale, flash photolysis could prove useful in obtaining good rate constants for conversion of 16-valence-electron alkyls to hydride product by using the interception by PPh_3 as an internal clock. Development of the instrumentation for monitoring the products from flash photolysis by Raman spectroscopy and infrared spectroscopy is now in progress.

Acknowledgment. We thank the National Science Foundation for support of this research by grant support to M.S.W. and a predoctoral fellowship to R.J.K. (1978–1981).

Note Added in Proof. We wish to call attention to the recently reported claim of ring-slippage upon radiation of η^5-C_5H_5Fe(CO)$_2$CH$_3$ at 12 K in a CO matrix: *J. Chem. Soc., Dalton Trans.* **1981**, 2311.

Registry No. (η^5-C_5H_5)Fe(CO)$_2$CH$_3$, 12080-06-7; (η^5-C_5H_5)Fe(^{13}CO)$_2$CH$_3$, 80409-88-7; (η^5-C_5H_5)Fe(CO)$_2$CH$_2$CH$_3$, 32611-65-7; (η^5-C_5H_5)Fe(CO)$_2$(*n*-pentyl), 69005-48-7; (η^5-C_5H_5)Fe(CO)$_2$(2-pentyl), 69661-75-2; (η^5-C_5H_5)Fe(CO)$_2$H, 35913-82-7; [(η^5-C_5H_5)Fe(CO)$_2$]$_2$, 12154-95-9; (η^5-C_5H_5)Fe(CO)(PPh_3)CH$_2$CH$_3$, 32824-72-9; (η^5-C_5H_5)Fe(CO)(PPh_3)CH$_3$, 12100-51-5; (η^5-C_5H_5)Fe(CO)(P(OPh)$_3$)CH$_3$, 12290-98-1; (η^5-C_5H_5)Fe(CO)(P(OCH$_2$)$_3$CCH$_2$CH$_3$)CH$_3$, 80409-89-8; (η^5-C_5H_5)Fe(CO)(PPh_3)H, 32660-22-3; (η^5-C_5H_5)Fe(CO)(PPh_3)C(O)CH$_3$, 12101-02-9; (η^5-C_5H_5)Fe(CO)$_2$C(O)CH$_2$CH$_3$, 53403-10-4; (η^5-C_5H_5)Fe(CO)$_2$Cl, 12107-04-9; (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$CH$_3$, 80409-90-1; (η^5-C_5Me_5)Fe(CO)$_2$H, 80409-91-2; [(η^5-C_5Me_5)Fe(CO)$_2$]$_2$, 35344-11-7; (η^5-C_5H_5)Ru(CO)$_2$CH$_2$CH$_3$, 72042-46-7; (η^5-C_5H_5)Ru(CO)$_2$H, 57349-59-4; (η^5-C_5H_5)Ru(CO)$_2$CH$_3$, 53449-90-4; (η^5-C_5H_5)Ru(CO)(P(CH$_3$)$_3$)CH$_3$, 80409-92-3; (η^5-C_5H_5)Ru(CO)(P(OCH$_2$)$_3$CCH$_2$CH$_3$)CH$_3$, 80409-93-4.

(26) (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.