ligands are 14- and 19-membered rings.

Trans monomers are formed in solution even with the dphp ligand (10-membered chelate ring), albeit in small amounts. The percentage of trans monomer increases from dphp to dpdod (15-membered chelate ring) in agreement with literature reports for the trans-bonded cobalt(III) complexes with long-chain diammines. Ring contributions, Δ_R, for the trans monomers decrease with increasing ring size and reach zero at a ring size of 15 members—thus we conclude that Δ_R in trans monomeric complexes is a measure of ring strain for these large-ring chelates. For ligands with short chelate backbones such as *cis*-[Pt(dpe)Cl_2] the anomalous coordination chemical shift observed for this and other five-membered ring systems cannot be due to "ring strain", as the complex *trans*-[Pt(dpe)Cl_2] has been isolated, which also possesses an anomalous coordination chemical shift but which cannot be chelated.

Finally, trans-bonded monomeric complexes appear to be unstable for 19-membered chelate rings and above.

Registry No. *cis*-Pt(dpe)Cl_2, 14647-25-7; *cis*-Pt(dph)Cl_2, 83095-87-8; *cis*-Pt(dphp)Cl_2, 83095-88-9; *cis*-[Pt(dpo)Cl_2]$_2$, 83095-89-0; *cis*-Pt(dpn)Cl_2, 83095-90-3; *cis*-Pt(dpd)Cl_2, 83095-91-4; *cis*-Pt(dpu)Cl_2, 83095-92-5; *cis*-[Pt(dpdod)Cl_2]$_2$, 83151-17-1; *cis*-Pt(dphd)Cl_2, 83095-93-6; *cis*-[Pt(dpe)Cl_2]$_2$, 83095-94-7; *cis*-[Pt(dpn)Cl_2]$_2$, 83095-95-8; *cis*-[Pt(dpd)Cl_2]$_2$, 83095-96-9; *cis*-[Pt(dpu)Cl_2]$_2$, 83095-97-0; *cis*-[Pt(dphd)Cl_2]$_2$, 83095-98-1; *trans*-[Pt(dpe)Cl_2]$_x$, 83095-84-5; *trans*-[Pt(dph)Cl_2]$_x$, 83095-86-7; *trans*-Pt(dphp)Cl_2, 83149-21-7; *trans*-Pt(dpo)Cl_2, 83095-99-2; *trans*-Pt(dpn)Cl_2, 83149-22-8; *trans*-Pt(dpd)Cl_2, 83149-23-9; *trans*-Pt(dpu)Cl_2, 83149-24-0; *trans*-Pt(dpdod)Cl_2, 83096-00-8; *trans*-[Pt(dphd)Cl_2]$_2$, 83149-25-1; *trans*-[Pt(dphp)Cl_2]$_2$, 83096-01-9; *trans*-[Pt(dpo)Cl_2]$_2$, 83149-26-2; *trans*-[Pt(dpn)Cl_2]$_2$, 83149-27-3; *trans*-[Pt(dpd)Cl_2]$_2$, 83149-28-4; *trans*-[Pt(dpu)Cl_2]$_2$, 83149-29-5; *trans*-[Pt(dpdod)Cl_2]$_2$, 83096-02-0; $K_2[PtCl_4]$, 10025-99-7; $K[Pt(C_2H_4)Cl_3]$, 12012-50-9.

Photochemistry of Metal Carbonyl Alkyls. Study of Thermal β-Hydrogen Transfer in Photogenerated, 16-Valence-Electron Alkyldicarbonylcyclopentadienylmolybdenum and -tungsten Complexes

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Abstract: Near-UV irradiation of $(\eta^5\text{-}C_5R'_5)M(CO)_3R$ (R′ = H, Me; M = Mo, W; R = CH_3, C_2H_5, *n*-pentyl) results in efficient ($\Phi_{366} > 0.1$) dissociative loss of CO. If the photoreaction is carried out at 77 K, the 16-valence-electron species resulting from CO loss can be accumulated and characterized by infrared spectroscopy. Relative intensities of the two carbonyl stretching absorptions suggest that the structure of these species is similar to that of the 18-valence-electron $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$, that is, a relaxed structure. Upon warming, $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ reacts with CO or added PPh_3 to regenerate starting material or form $(\eta^5\text{-}C_5R'_5)M(CO)_2(PPh_3)R$, respectively. In the case where R contains β-hydrogens, warming in the absence of ligand results in β-hydrogen transfer to form *trans*-$(\eta^5\text{-}C_5R'_5)M(CO)_2$(alkene)(H). For the R groups having β-hydrogens, optical and infrared spectroscopy give evidence for a second $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ species that is not completely coordinatively unsaturated and is proposed to be the immediate precursor to β-hydrogen transfer. This species can be formed by warming or irradiating samples of the photogenerated 16-valence-electron complex and is thought to have a weak M–(β-H) bond. This species does not react rapidly with CO or PPh_3 at 195 K as do the $(\eta^5\text{-}C_5R'_5)M(CO)_2CH_3$ complexes. The activation energy $\Delta G^\ddagger$ for the conversion of all such 16-valence-electron species to an alkene–hydride is 10 ± 2 kcal/mol, and the C_2H_5 and C_2D_5 species react at the same rate. Irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3CD_2CH_3$ gives a mixture of *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_3D)(D)$ and *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_2D_2)(H)$ at a temperature where both are inert. The β-hydrogen transfer is proposed to involve a preequilibrium between the 16-valence-electron species and a cis-alkene–hydride complex that isomerizes to the trans alkene–hydride in the rate-determining step. $(\eta^5\text{-}C_5R'_5)M(CO)_2$(alkene)(H) reacts with PPh_3 at 298 K to form $(\eta^5\text{-}C_5R'_5)M(CO)_2(PPh_3)$(alkyl). For $(\eta^5\text{-}C_5H_5)W(CO)_2(C_5H_{10})(H)$ the reaction rate is proportional to PPh_3 concentration up to ~0.1 M, after which little further increase in rate is observed. The kinetics for this reaction are treated as a preequilibrium between the 16-valence-electron dicarbonyl–alkyl and an 18-valence-electron alkene–hydride with the PPh_3 reacting with the dicarbonyl–alkyl. The rate constant for the conversion of the pentene–hydride to the dicarbonyl–pentyl is determined to be $1.7 \times 10^{-3}\ s^{-1}$ at 298 K. In the case of M = Mo, R = C_2H_5 the equilibrium constant for this interconversion is ~2 and both species are observed in alkane solution at temperatures as high as 250 K.

Introduction

Photochemistry can serve as a useful tool for the generation and characterization of reactive organometallic intermediates. Among the organometallic intermediates that can be formed photochemically are 17-valence-electron metal-centered radicals via metal–metal bond cleavage and 16-valence-electron coordinatively unsaturated metal carbonyls via ligand dissociation or reductive elimination.[1] Generally, an intermediate is a transient molecular entity formed in the course of a reaction and is not accumulated in appreciable amounts, since the activation energy for the formation is larger than the activation energy for the decomposition or further reaction. Photochemistry offers an alternative pathway for generation of certain thermally reactive intermediates having the advantage that at sufficiently low temperatures an intermediate can be accumulated.[2] This study

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represents an application of this and other techniques to the characterization of intermediates in the reaction of metal carbonyl alkyls. A preliminary account of this work has appeared.[3]

β elimination of an alkene, eq 1, from a metal alkyl or the

$$L_nM(\text{alkyl}) \rightarrow L_nM\text{–}H + \text{alkene} \tag{1}$$

reverse reaction, often termed olefin insertion, is a step in transition-metal-catalyzed reactions of olefins such as hydrogenation and hydroformylation. In fact, β elimination exists as either a desirable or an undesirable reaction step in virtually all catalyzed reactions involving metal alkyls. Not surprisingly, therefore, a large amount of effort, both experimental[4] and theoretical,[5] has gone into elucidating factors controlling this reaction. In general, β-elimination occurs on a single metal center and requires an open coordination site on the metal (preferably cis to the alkyl) and a small M–C–C–H dihedral angle allowing access to the metal by the hydrogen to be transferred. Experimental work has generally not allowed the direct observation of intermediates in the β-elimination reaction because thermal extrusion of a ligand, eq 2, generally requires higher temperature than does the subsequent

$$L_nM(\text{alkyl}) \rightarrow L_{n-1}M(\text{alkyl}) + L \tag{2}$$

$$L_{n-1}M(\text{alkyl}) \rightarrow L_{n-1}(\text{alkene})M\text{–}H \tag{3}$$

step, β-hydrogen transfer, eq 3, to produce an alkene hydride. Further, the low thermal activation energy associated with the final step, eq 4, often even precludes observation of the alkene

$$L + L_{n-1}(\text{alkene})M\text{–}H \rightarrow L_nM\text{–}H + \text{alkene} \tag{4}$$

hydride. Our earlier communication[3] has established that both coordinatively unsaturated alkyls and alkene hydrides can be observed by near-UV irradiation of appropriate metal carbonyl alkyl complexes at low temperature. Photoinduced CO dissociation from $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-}C_5H_{11})$ results in a 16-valence-electron $(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-}C_5H_{11})$, which can be characterized by its spectra at low temperatures and by its reaction chemistry at higher temperatures. Warming this species results in β-hydrogen transfer forming *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_5H_{10})(H)$. This paper reports our study of the kinetics and mechanism of this and related systems.

Experimental Section

Instruments. UV-vis spectra were recorded with a Cary 17 spectrophotometer; infrared spectra were recorded with a Perkin-Elmer 180 grating or Nicolet 7199 Fourier transform spectrometer; NMR spectra were recorded with a Varian T-60, a JEOL FX90Q Fourier transform, or Bruker 250-MHz Fourier transform spectrometer. Gas–liquid chromatographic separations were accomplished using a Varian 2440 gas chromatograph with flame ionization detectors interfaced with a Hewlett-Packard Model 3380S electronic integrator. Pentane and linear pentenes were separated with a 0.3 cm × 9.2 m column of 20% propylene carbonate on Chromasorb P at 25 °C with hexane as an internal standard. Generally, all manipulations of the organometallic complexes were done under N_2 using a Vacuum Atmospheres drybox or under Ar using conventional Schlenk line techniques unless otherwise noted. However, the compounds $(\eta^5\text{-}C_5R'_5)W(CO)_3R$ ($R' = H, CH_3$; $R = CH_3, C_2H_5$, *n*-pentyl) are air stable in the dark and were stored and transferred in air. Melting points were determined in sealed capillaries under N_2 on a Mel-Temp melting point apparatus and are uncorrected.

Chemicals. Hexane, toluene, and CH_2Cl_2 were reagent grade and freshly distilled from CaH_2 under N_2. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone under N_2. Spectroquality isooctane was further purified by stirring over concentrated H_2SO_4/HNO_3 overnight, washing with H_2O and NaOH solution, and then repeating the acid wash two more times. Isooctane was then stirred over 2% $KMnO_4$ in 10% H_2SO_4 overnight, washed, predried over $MgSO_4$, and distilled from CaH_2 under N_2. Finally, the distilled isooctane was passed down grade 1 alumina (neutral, Woelm). PPh_3 (Aldrich) was recrystallized three times from absolute EtOH. $P(OPh)_3$ was used as received from commercial sources.

Literature procedures were used to synthesize $(\eta^5\text{-}C_5H_5)M(CO)_3CH_3$,[6a] $(\eta^5\text{-}C_5H_5)M(CO)_3C_2H_5$,[6b] $(\eta^5\text{-}C_5H_5)M(CO)_3(H)$,[6c] and $[(\eta^5\text{-}C_5Me_5)W(CO)_3]_2$.[6d] $(\eta^5\text{-}C_5H_5)M(CO)_3(n\text{-}C_5H_{11})$ was synthesized by a method analogous to that for the methyl and ethyl derivatives. $(\eta^5\text{-}C_5H_5)M(CO)_3Na$ in THF was treated with an excess of *n*-pentyl iodide and stirred overnight. THF was removed by vacuum and the yellow-brown residue extracted with hexane. The extract was filtered, concentrated, and cooled to crystallize $(\eta^5\text{-}C_5H_5)M(CO)_3(n\text{-}C_5H_{11})$, which was recrystallized an additional time from hexane. $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-}C_5H_{11})$ is a yellow solid (mp 65 °C). The elemental analysis is satisfactory (Alfred Bernhart, West Germany). Anal. Calcd: C, 38.64; H, 3.99. Found: C, 38.50; H, 3.91. ^1H NMR ($CDCl_3$): δ 5.32 (s, 5 H, C_5H_5), 1.0–1.5 (m, 11 H, *n*-C_5H_{11}). $(\eta^5\text{-}C_5Me_5)W(CO)_3C_2H_5$ was synthesized by Na/Hg reduction of $[(\eta^5\text{-}C_5Me_5)W(CO)_3]_2$ under CO in THF followed by addition of C_2H_5Br and worked up as for the *n*-pentyl complex. $(\eta^5\text{-}C_5Me_5)W(CO)_3CH_2CH_3$ is a yellow crystalline solid (mp 131–133 °C). ^1H NMR (C_6D_6): δ 1.88 (t, 3 H, CH_3), 1.54 (s, 15 H, ring CH_3), 0.98 δ (q, 2 H, CH_2). ^{13}C NMR (C_6D_6, ^1H decoupled): δ –9.9 δ (ring CH_3), –6.0 (CH_2), 20.5 (CH_3), 102.5 (ring C), 223.3, 232.8 (CO). $(\eta^5\text{-}C_5Me_5)W(CO)_3(H)$ was synthesized by addition of acetic acid to a THF solution of $(\eta^5\text{-}C_5Me_5)W(CO)_3Na$ prepared as above. $(\eta^5\text{-}C_5Me_5)W(CO)_3(H)$ was purified by recrystallization from hexanes (yellow crystals, mp 110–112 °C, some darkening) ^1H NMR (C_6D_6): δ 1.75 (s, 15 H, ring CH_3), –6.52 (s, 1 H, hydride; $J_{H\text{–}^{183}W}$ = 19.4 Hz). $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CH_2CH_3$ was synthesized by reaction of C_2H_5Br with $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)Na$[6e] formed by the reduction of $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)Cl$ with Na/Hg in THF followed by the workup above. The compound forms yellow crystals (mp 180 °C, decomposes with effervescence) after crystallization from CH_2Cl_2. ^1H NMR ($CDCl_3$): δ 7.3 (m, 15 H, phenyl), 4.70 (d, $J \approx 1$ Hz, 5 H, C_5H_5), 1.60 (s, br, 5 H, CH_2CH_3).

$(\eta^5\text{-}C_5H_5)W(CO)_3C_2D_5$ was synthesized as above with C_2D_5Br (Merck, 99 atom % D). When compared to that of $(\eta^5\text{-}C_5H_5)W(CO)_3C_2H_5$, the IR spectrum shows changes consistent with replacement of C_2H_5 with C_2D_5 $\nu_{C_2H_5}$, $\nu_{C_2D_5}$(calcd), $\nu_{C_2D_5}$(found): 2978, 2174, 2225; 2960, 2161, 2205; 2930, 2139, 2142; 2876, 2099, 2170, 1460, 1066, 1070; 1380, 1007, 935, cm^{-1}. Isotopic purity was established as at least 99.3 atom % D by ^1H NMR techniques corresponding to ~2% of molecules having a light hydrogen in the β position.

$(\eta^5\text{-}C_5H_5)W(CO)_3CH_2CD_3$ was synthesized as above with CD_3CH_2I (Stohler, 99 atom % D). The ^1H NMR spectrum does not straightforwardly lead to determination of isotopic purity since the α- and β-hydrogens are not separated even at 250 MHz. The isotopic purity of the starting material, CD_3CH_2I, was established as at least 98 atom % D by ^1H NMR spectroscopy corresponding to ~8% of the molecules having a light hydrogen in the β position. The gated $^{13}C\{^1H\}$ NMR spectrum establishes that H and D do not scramble between α and β positions upon attachment to the tungsten center since the $^{13}C\text{–}^1H$ couplings are observed only for the α-carbon, and correspondingly $^{13}C\text{–}^2H$ couplings are observed only for the β-carbon: δ –17.5 (t, α-carbon, $^1J_{C\text{–}H}$ = 130 Hz), 19.5 (m, β-carbon, $^1J_{C\text{–}D}$ = 18 Hz). ^1H NMR (toluene-d_8) δ 4.50 (s, 5 H, C_5H_5), 1.50 (s, 2 H, CH_2CD_3).

$(\eta^5\text{-}C_5H_5)W(CO)_3CD_2CH_3$ was synthesized as above with CH_3CD_2I (Stohler, 99 atom % D). Proof of structure was established by the ^{13}C NMR spectrum as for the complex labeled on the β-carbon.

Concentrated solutions of $(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)(H)$ for ^{13}C NMR spectroscopy were prepared by irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3C_2H_5$ in THF-d_8 at –78 °C. At these temperatures the β-hydrogen-transfer reaction is slow even in an alkane solvent ($t_{1/2}$ is on the order of 10 s), and we believe $(\eta^5\text{-}C_5H_5)W(CO)_2(THF)C_2H_5$ is formed, which could slow the β-hydrogen-transfer process. Warming to room temperature results in the formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)(H)$. ^1H NMR (THF-d_8): δ 4.42 (s, 5 H, C_5H_5), –5.5 (s, 1 H, –H) (bound ethylene obscured by alkyl resonance of starting material at δ 1.54). ^{13}C NMR (THF-d_8, –5 °C): δ 217.5 (CO), 90.9 (C_5H_5), 21.0 (ethylene). The spectrum is unchanged upon cooling to –50 °C. More dilute solutions of (η^5-

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$C_5H_5)W(CO)_2(C_2H_4)(H)$ were generated by flash photolysis (Xenon flash tubes, 5000 V, 2000 J) of $(\eta^5\text{-}C_5H_5)W(CO)_3C_2H_5$ in isooctane or toluene.

Irradiations. Two General Electric Blacklight bulbs (355 ± 20 nm, $\sim 2 \times 10^{-6}$ einstein/min) were used for irradiation unless otherwise noted. Quantum yields at 366 nm were measured in a merry-go-round[7a] using $\sim 10^{-3}$ M $(\eta^5\text{-}C_5R'_5)M(CO)_3R$ with the appropriate ligand concentration. Three-milliliter samples in 13 × 100 mm test tubes were freeze-pump-thaw degassed ($<10^{-5}$ torr, 3 cycles) and hermetically sealed prior to irradiation. 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[7b] was used to determine light intensity, which was typically $\sim 10^{-7}$ einstein/min.

Kinetic Studies. Rates of $(\eta^5\text{-}C_5R'_5)M(CO)_2(\text{alkene})(H)$ formation or $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ disappearance were measured by infrared spectroscopy in the carbonyl region for the temperature range 150-195 K. Temperature was maintained by a Cryogenics Technology, Inc., Spectrim II cryocooler equipped with NaCl outer windows. The sample was either a solid paraffin solution coated onto a KBr or sapphire disk or a fluid alkane solution contained in a cell with CaF_2 windows built in-house based on a published design.[8] The temperature was measured with a thermocouple (chromel vs. Au/0.7 atom % Fe) with the reference junction at room temperature. The thermocouple was either embedded in the paraffin solution or attached with silver epoxy to the copper body of the solution cell. The thermocouple output was measured with a Hewlett-Packard 3465A digital multimeter and converted to temperature by using published calibration curves[9] which were checked with liquid nitrogen, dry ice/acetone, and ice water. In some cases, artifactually fast rates were measured, especially for the paraffin samples, which we attribute to poor thermal contact resulting in warming of some sample preparations. Thus, only the slowest rates measured at any particular temperature are included in the calculations. The solution measurements were not plagued by thermal contact problems and gave clean kinetic behavior. Temperatures are considered accurate to ±2 K. A silicon wafer was used to filter out the visible light from the infrared source.

Data for Figure 5 were obtained with a solution sample held in a Precision Cell, Inc., Model P/N 21.000 variable-temperature cell with NaCl outer windows using dry ice/acetone as the coolant. Spectra were accumulated at 2-cm^{-1} resolution with use of the rapid-scan mode of the Nicolet 7199 FT IR spectrometer corresponding to approximately 1 scan/s at this resolution. Spectra presented are single-scan difference spectra that have been corrected for base line flatness but without any curve smoothing. Reactions of $(\eta^5\text{-}C_5H_5)M(CO)_2R$ with PPh_3 at 195 K were studied analogously. Deoxygenated alkane solutions of $(\eta^5\text{-}C_5H_5)M(CO)_3R$ (~0.7 mM) and PPh_3 (~1 mM) were cooled to 195 K in the P/N 21.000 cell (~1 mm path length) and briefly irradiated (~4 s) with a Bausch and Lomb SP200 high-pressure Hg lamp (output filtered with ~10 cm of water to remove infrared radiation). The sample assembly was replaced in the spectrometer, and spectra were accumulated with the rapid-scan mode.

The reactivity of $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ was also investigated by ^1H NMR methods. A deoxygenated toluene-d_8 solution of $(\eta^5\text{-}C_5H_5Mo(CO)_2C_2H_5$ (~50 mM) was irradiated for 1 h at 77 K with the high-pressure Hg lamp and then warmed to 223 K. ^1H NMR obtained at this temperature shows peaks consistent with the formation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_2H_4)(H)$ [δ 4.18 (s, ~5 H), 1.50 (s, ~4 H), -5.2 (s, ~1 H)] and $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ [δ 3.93 (s, ~5 H), 1.24 (s, ~5 H)]. Addition of $P(OPh)_3$ (to make 0.14 M) to the sample at 223 K does not result in reaction within ~30 min. After the sample is warmed to 273 K overnight, the ^1H NMR spectrum shows disappearance of the above products along with the formation of peaks consistent with $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OPh)_3)C_2H_5$ [δ 4.37 (d, J = 1 Hz, 5 H), 1.54, 1.46 (other peaks obscured by starting material)]. The infrared spectrum of this solution confirms this assignment [1950, 1876 cm^{-1} (toluene-d_8)].

Irradiation of $(\eta^5\text{-}C_5R'_5)M(CO)_3R$ Monitored by UV-Vis Spectroscopy. Deoxygenated methylcyclohexane solutions of $(\eta^5\text{-}C_5R'_5)M(CO)_3R$ ($\sim 10^{-3}$ M) in a 1-cm path length quartz cell held in a large copper holder were immersed in coolants (liquid nitrogen or dry ice/ethanol) contained in a Dewar flask equipped with quartz flats. For a UV-vis spectrum the level of coolant was lowere to just below the optical path of the spectrometer, making sure that the copper holder was immersed in coolant at all times. Both cell and holder were kept immersed in coolant during irradiation with the high- or medium-pressure Hg lamp or the beam expanded output (~5 mW) from an Aerotech, Inc., Model LS5P He-Ne laser operated at 632.8 nm.

Photoreaction of $(\eta^5\text{-}C_5H_5)W(CO)_3CD_2CH_3$ and $\text{-}CH_2CD_3$. Specifically labeled complexes were studied to determine whether there can be scrambling of α- and β-hydrogens during photochemical formation of the thermally inert *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(\text{alkene})(H)$. For $(\eta^5\text{-}C_5H_5)W(CO)_3CD_2CH_3$, photolysis of a THF solution of the complex (~0.1 M) containing CD_2Cl_2 internal standard was monitored by ^2H NMR. The irradiation was carried out at 195 K; the sample was warmed to 298 K briefly (<60 s) to allow formation of *trans*-$(\eta^5\text{-}C_5H_5)W(C_2H_4)(H)$ and then cooled to 258 K to record the ^2H NMR spectrum. The spectrum showed a deuteride signal at δ -5.7 consistent with formation of 33 ± 10% *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_3D)(D)$ and 67 ± 10% *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_2D_2)(H)$. The $(\eta^5\text{-}C_5H_5)W(CO)_3(CH_2CD_3)$ complex (~0.01 M) was studied similarly except toluene-d_8 was used as solvent, irradiation was at 77 K, β-hydrogen transfer was allowed to occur at 195 K, and the ^1H NMR spectrum (248 K) was used to monitor the reaction: the ^1H NMR spectrum showed a resonance at δ -5.7 consistent with formation of 36 ± 10% *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2HD_3)(H)$ and 64 ± 10% *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_2D_2)(D)$. In these experiments the temperature was kept sufficiently low that scrambling by secondary thermal reaction of *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(\text{alkene})(H)$ could not occur.

Results and Discussion

Nature of the Primary Photoprocess of $(\eta^5\text{-}C_5R'_5)M(CO)_3R$. Near-UV irradiation of $(\eta^5\text{-}C_5R'_5)M(CO)_3R$ results in the dissociative loss of CO (eq 5). Evidence supporting this as the only

$$(\eta^5\text{-}C_5R'_5)M(CO)_3R \xrightarrow[\text{alkane}]{\text{near-UV}} (\eta^5\text{-}C_5R'_5)M(CO)_2R + CO \quad (5)$$

detectable chemistry has been previously reported by us.[3] The 16-valence-electron species from the M = W, R' = H, R = CH_3 and $n\text{-}C_5H_{11}$ complexes is detectable by infrared spectroscopy upon irradiation in rigid media at low temperature.[3] Figure 1 shows infrared spectral data providing the same direct evidence for the M = Mo, R' = H, R = CH_3 and C_2H_5 complexes.

Irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ in solution at 298 K containing $P(OPh)_3$ leads to the decline of starting material absorptions and the growth of absorptions attributable to the substitution product $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OPh)_3)CH_3$ (Figure 1a). At 75 K in rigid media irradiation results in the diminution of starting material bands, the growth of a feature at ~2135 cm^{-1} associated with free CO, and new features at 1967 and 1882 cm^{-1} (Figure 1b). Irradiation in low-temperature matrices also results in significant optical spectral changes: the matrix turns from colorless to blue (Figure 2). Warmup of the matrix results in uptake of the CO and regeneration of starting material. Warmup of an irradiated matrix containing a ligand such as $P(OPh)_3$ results in some regeneration of starting material and some formation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OPh)_3)CH_3$. These data lead to the conclusion that the species absorbing at 1967 and 1882 cm^{-1} after irradiation is the 16-valence-electron species. The band positions and relative intensities are similar to those for the analogous W species (Table I).

Irradiation of the C_2H_5 species (Figure 1c) at 77 K in a rigid medium also appears to give a 16-valence-electron species absorbing at 1958 and 1879 cm^{-1}. The small shift in the band positions relative to those in the CH_3 complex is attributable to the electronic differences associated with CH_3 vs. C_2H_5. Interestingly, the optical spectral changes accompanying the lower temperature irradiation differ somewhat from those for the CH_3 complexes. As illustrated in Figure 2 for the W-C_2H_5 complex compared to the W-CH_3 species, there is a definite feature at ~405 nm in addition to a lower energy feature at 565 nm for $(\eta^5\text{-}C_5H_5)W(CO)_2C_2H_5$. The ~400-nm feature is not present in the CH_3 species. Further, irradiation with light at 632.8 nm absorbed by $(\eta^5\text{-}C_5H_5)W(CO)_2C_2H_5$ leads to the diminution of the 565-nm absorption and the obvious growth of the 405-nm feature. Exhaustive visible light irradiation of $(\eta^5\text{-}C_5H_5)W$-

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[7] (a) Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

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[10] $(\eta^5\text{-}C_5H_5)M(CO)_3H$: Hoffmann, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613. $(\eta^5\text{-}C_5H_5)M(CO)_3X$, X = halide: Alway, D. G.; Barnett, K. W. *Ibid.* **1980**, *19*, 1533. $(\eta^5\text{-}C_5H_5)M(CO)_3R$, R = CH_3, C_2H_5, benzyl: Severson, R. G.; Wojcicki, A. *J. Organomet. Chem.* **1977**, *124*, 167. Alt, H. F.; Eichner, M. E. *Ibid.* **1981**, *212*, 397. Tyler, D. R. *Inorg. Chem.* **1981**, *20*, 2257.

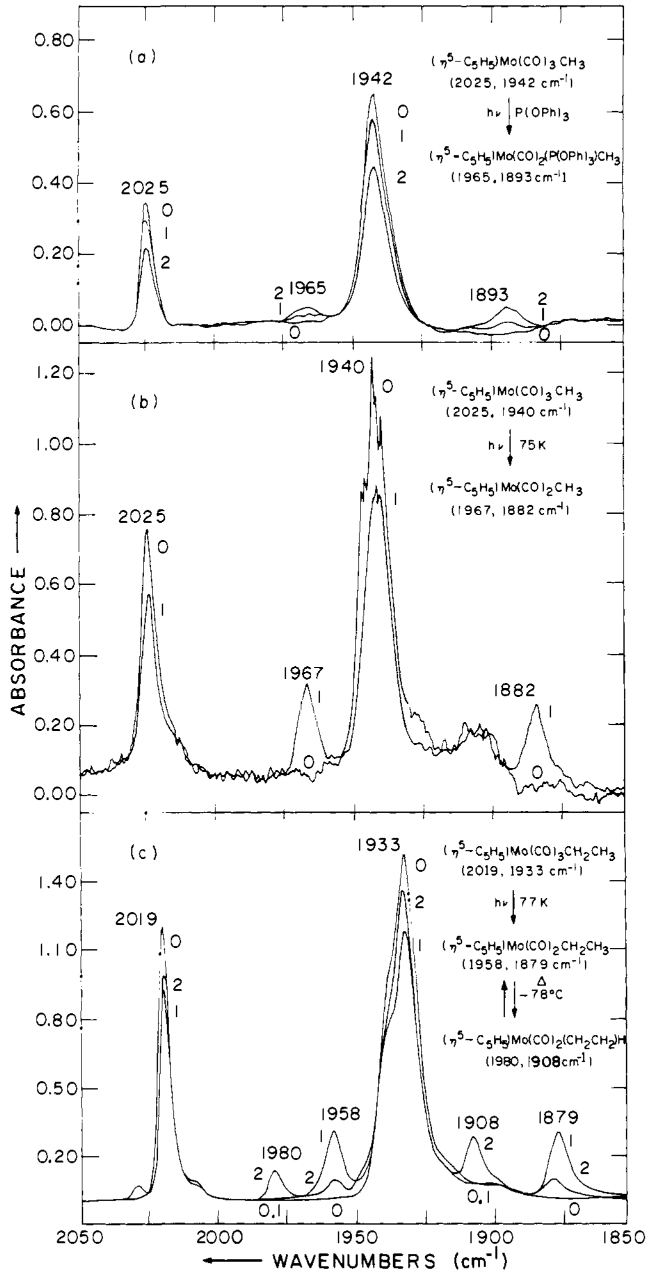


Figure 1. Infrared spectral changes accompanying the irradiation of (η^5-C_5H_5)Mo(CO)$_3$R: (a) Trance 0 shows the spectrum of ~5 mM (η^5-C_5H_5)Mo(CO)$_3$CH$_3$ in isooctane containing 0.2 M P(OPh)$_3$ at 300 K. Traces 1 and 2 are after 10- and 30-s irradiation, respectively. (b) Trace 0 shows the spectrum of ~1.0 mM (η^5-C_5H_5)Mo(CO)$_3$CH$_3$ in a paraffin matrix at 75 K. Trace 1 shows the formation of (η^5-C_5H_5)Mo(CO)$_2$CH$_3$ after 12-min irradiation. (c) Trace 0 shows the spectrum of (η^5-C_5H_5)Mo(CO)$_3$C$_2$H$_5$ in a paraffin matrix at 77 K. Trace 1 shows the formation of (η^5-C_5H_5)Mo(CO)$_2$C$_2$H$_5$ after 15-min irradiation. Trace 2 shows the results of warming this species to 195 K. (η^5-C_5H_5)Mo(CO)$_2$(ethylene)(H) is formed in addition to the regeneration of some starting material.

(CO)$_2$CH$_3$ does not lead to detectable spectral changes of this sort. Generally, as shown by the data in Table I, the C_2H_5 species all give an ~400-nm feature that is absent in the analogous CH$_3$ complexes. The additional feature at ~400 nm is not as prominent in the W-n-C_5H_{11} complex, but there appears to be a shoulder at ~435 nm. The presence of only one visible absorption feature for the CH$_3$ complexes and two for the other alkyls suggests that the C_2H_5 and n-C_5H_{11} species can exist as at least two different structures, one of which is the structure of the CH$_3$ species. However, the infrared spectra of the dicarbonyl-alkyl species are not very different in the CO stretching region and suggest that the geometries of all dicarbonyl species are quite similar. We proposed that, for R having β-hydrogens, the two geometries are as represented in I and II. The structure I is a completely

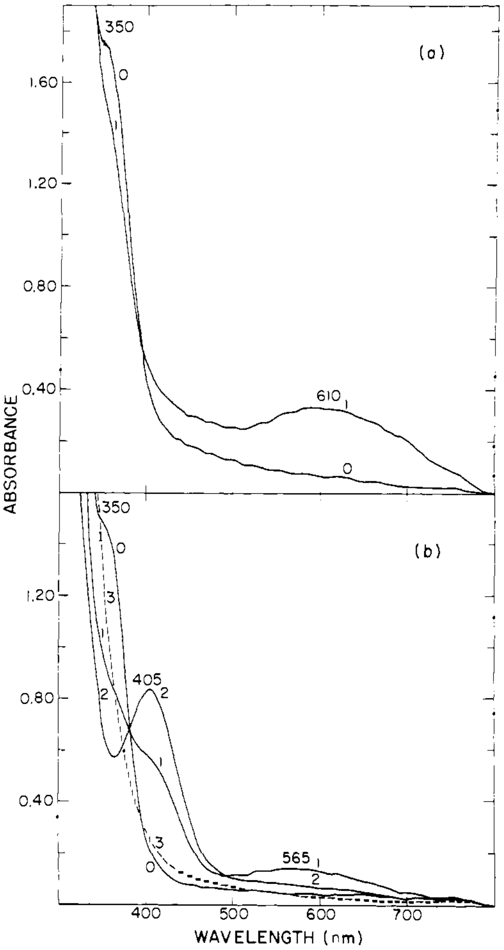
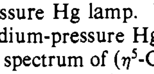


Figure 2. UV-vis spectral changes observed upon irradiation of (η^5-C_5H_5)W(CO)$_3$R at 77 K: (a) Trave 0 shows the spectrum of (η^5-C_5H_5)W(CO)$_3$CH$_3$ in a methylcyclohexane glass at 77 K. Trace 1 shows the spectrum obtained after 20-min irradiation with a 550-W medium-pressure Hg lamp. No further changes occur upon irradiation with a medium-pressure Hg lamp or with a He-Ne laser. (b) Trace 0 shows the spectrum of (η^5-C_5H_5)W(CO)$_3$C$_2$H$_5$ in a methylcyclohexane glass at 77 K. Trace 1 shows the spectrum after 20-min irradiation with a 550-W medium-pressure Hg lamp. Trace 2 shows the spectrum after an additional 40-min Hg lamp irradiation followed by 30-min irradiation with a 5-mW He-Ne laser (632.8 nm). Trace 3 shows the spectrum after warming to 300 K. All 77 K spectra are uncorrected for solvent contraction.



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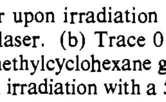

II

coordinatively unsaturated species that we associate with the blue color (λ_{max} 555–625 nm) of the dicarbonyl-alkyl species. Structure II is proposed to be one having a weak interaction of M and a β-hydrogen. It is well-known that coordinatively unsaturated metal carbonyls can interact weakly with donor groups to give large optical spectral changes while influencing the CO stretching frequencies only modestly, e.g., W(CO)$_5$Ne vs. W(CO)$_5$CH$_4$.[2b] We propose structure II on the additional basis of the reaction chemistry upon warmup (vide infra).

For all of the complexes studied, irradiation in low-temperature matrices gives free CO (2135 cm^{-1}) and a product having a two-band pattern in a nearly 1:1 ratio associated with the 16-valence-electron metal dicarbonyl (eq 5). Data for each case are included in Table I. The relative intensity of the two bands at

Table I. Spectroscopic Data for Relevant Complexes[a]

compd	IR, cm^{-1} (ϵ or rel abs)	UV-vis, nm (ϵ)
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{CH}_3$	2021 (2600), 1932 (13 600)	350 (sh), 310 (2500)
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{CH}_3$[b]	1955 (1.0), 1865 (1.0)	600
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{PPh}_3)\text{CH}_3$	1936 (1.0), 1861 (1.2)	
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{C}_2\text{H}_5$	2018 (6000), 1927 (9800)	348 (sh), 310 (2400), 250 (sh)
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{C}_2\text{H}_5$[b]	1952 (1.0), 1865 (0.8)	405, 565
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{PPh}_3)\text{C}_2\text{H}_5$	1936 (2400), 1858 (7300)	380 (sh, 1600), 315 (sh, 4600), 260 (sh, 8600)
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{C}_2\text{H}_4)(\text{H})$	1980 (1.0), 1905 (2.0)	~350 (sh)
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3(n\text{-C}_5\text{H}_{11})$	2016 (6800), 1926 (11 000)	350 (sh), 310 (2700), 250 (sh)
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(n\text{-C}_5\text{H}_{11})$[b]	1948 (1.0), 1862 (1.0)	~435, 565
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{PPh}_3)(n\text{-C}_5\text{H}_{11})$	1934 (1.0), 1855 (2.2)	
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{pentene})(\text{H})$	1973 (1.0), 1900 (1.9)	
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3(\text{H})$	2026 (1.0), 1936 (2.2)	
$[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3]_2$	1958 (9800), 1910 (7700)	493 (2400), 362 (20 200)
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{CH}_3$	2025 (1.0), 1940 (1.5)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{CH}_3$[b]	1967 (1.0), 1882 (0.9)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2(\text{P(OPh)}_3)\text{CH}_3$	1965 (1.0), 1893 (2.0)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{C}_2\text{H}_5$	2021 (5200), 1936 (8900)	360 (sh), 312 (2190)
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{C}_2\text{H}_5$[b]	1958 (1.0), 1879 (1.0)	420, 600
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2(\text{P(OPh}_3))\text{C}_2\text{H}_5$	1959 (1.0), 1886 (2.2)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2(\text{C}_2\text{H}_4)(\text{H})$[c]	1980 (1.0), 1908 (2.0)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3(n\text{-C}_5\text{H}_{11})$	2020 (1.0), 1937 (1.4)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3(\text{H})$	2019 (5300), 1946 (9200)	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$	1960 (7500), 1915 (4900)	512 (1700), 388 (20 400)
$(\eta^5\text{-C}_5\text{Me}_5)\text{W(CO)}_3\text{C}_2\text{H}_5$	2004 (6000), 1912 (11 000)	353 (sh), 322 (2400), 245 (sh)
$(\eta^5\text{-C}_5\text{Me}_5)\text{W(CO)}_2\text{C}_2\text{H}_5$	1934 (1.0), 1848 (0.8)	410, 555
$(\eta^5\text{-C}_5\text{Me}_5)\text{W(CO)}_2(\text{PPh}_3)\text{C}_2\text{H}_5$	1919 (1.0), 1842 (0.6)	
$(\eta^5\text{-C}_5\text{Me}_5)\text{W(CO)}_2(\text{C}_2\text{H}_4)(\text{H})$	1968 (1.0), 1891 (1.6)	
$(\eta^5\text{-C}_5\text{Me}_5)\text{W(CO)}_3(\text{H})$	2013 (1.0), 1924 (1.9)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{CH}_3$[d]	2015 (5540), 1960 (6360)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{C}_2\text{H}_5$[d]	2011 (4700), 1957 (5420)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(n\text{-C}_5\text{H}_{11})$[d]	2009 (5100), 1955 (5770)	
$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2\text{C}_2\text{H}_5$[d]	1990 (5600), 1935 (6600)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{CH}_3$[d]	2021 (1.0), 1961 (1.1)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{C}_2\text{H}_5$[d]	2025 (5400), 1967 (6700)	

[a] In isooctane solution at 298 K unless otherwise noted. All alkene-hydride complexes of Mo and W have a trans structure. [b] Paraffin matrix at 77 K. [c] Paraffin matrix at 195 K. [d] Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* 1982, *1*, 602.

Table II. Reaction Quantum Yields of Representative Complexes

compd	$\Phi \pm 10\%$[a]	$\Phi \pm 10\%$[b]	compd	$\Phi \pm 10\%$[a]	$\Phi \pm 10\%$[b]
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{CH}_3$	0.24	0.38	$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3(n\text{-C}_5\text{H}_{11})$	0.58	0.42
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{C}_2\text{H}_5$	0.34		$(\eta^5\text{-C}_5\text{Me}_5)\text{W(CO)}_3\text{C}_2\text{H}_5$	0.32	

[a] Φ's are for 366-nm irradiation of complexes dissolved in isooctane for <10% conversion. For the CH_3 complex the only W-carbonyl product detected is a substoichiometric amount of $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3]_2$ whereas for the C_2H_5 and $n\text{-C}_5\text{H}_{11}$ complexes the corresponding *trans*-$(\eta^5\text{-C}_5\text{R}'_5)\text{W(CO)}_2(\text{alkene})(\text{H})$ is formed in >90% yield. [b] In toluene solution with 0.5 M PPh_3. The observed product (>90% yield) in each case is the PPh_3-substituted alkyl: $(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_2(\text{PPh}_3)\text{R}$.

1:1 is quite close to that in the structurally characterized $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{R}$ complexes (Table I). Thus, it can be concluded that the structure of the photogenerated 16-valence-electron $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\text{R}$ (M = Mo, W) complexes is quite similar to that of the 18-valence-electron $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{R}$. The ejection of CO from the tricarbonyl is followed by a structural relaxation. In quantitative terms, the OC–M–CO angle can be calculated on the basis of the relative intensity of the symmetric and asymmetric carbonyl stretches for the dicarbonyl. For the M = Mo, R′ = H, R = CH_3 case the OC–Mo–CO angle is 88°, taking the 1967-cm^{-1} band to be the symmetric stretch.[11] By comparison, the starting tricarbonyl has angles of 78° between cis CO's and 108° between trans CO's on the basis of its X-ray structure.[12a] The infrared spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{CH}_3$ leads to a calculated OC–Fe–CO angle of 94° in excellent agreement with X-ray structures for similar $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{R}$ species[12b] and in accord with the structure deduced for $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{CH}_3$.

Irradiation of $(\eta^5\text{-C}_5\text{R}'_5)\text{M(CO)}_3\text{R}$ in solutions containing a ligand L yields clean, quantum efficient substitution of CO by L presumably via the sequence represented by eq 5 and 6. Table II includes some quantum yield data for representative complexes for L = PPh_3. Others have reported clean, efficient photosubstitution for related complexes.[10] The ability to quantitatively from $(\eta^5\text{-C}_5\text{R}'_5)\text{M(CO)}_2\text{LR}$, in 298 K fluid solutions and by low-temperature irradiations of rigid solutions, leads to the conclusion that dissociative loss of CO is the only primary photoprocess of consequence for the systems studied. In particular, there is no evidence for prompt homolysis of the M–R bond to form alkyl- and metal-centered radicals. Expected products from these radicals are not observed. Thus, despite the fact that the lowest excited state[10,13] of the $(\eta^5\text{-C}_5\text{R}'_5)\text{M(CO)}_3\text{R}$ species is σ antibonding with respect to all σ-bonded ligands, the loss of CO is empirically the main chemical consequence of photoexcitation.

$$(\eta^5\text{-C}_5\text{R}'_5)\text{M(CO)}_2\text{R} + \text{L} \xrightarrow{\Delta} (\eta^5\text{-C}_5\text{R}'_5)\text{M(CO)}_2\text{LR} \quad (6)$$

Two recent reports[14,15] concern the low-temperature photochemistry of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{CH}_3$ in frozen-gas matrices at 12 K[14] and in poly(vinyl chloride) films.[15] In the main, our findings

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[11] Based on arguments similar to those in: Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

[12] (a) Bennett, M. J.; Mason, R. *Proc. Chem. Soc., London* **1963**, 273. (b) $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\eta^1\text{-C}_5\text{H}_5)$, OC–Fe–CO = 96°: Bennett, M. J.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S. J.; Morehouse, S. M. *J. Am. Chem. Soc.* **1966**, *88*, 4371. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{CH}_2\text{COOH}$, OC–Fe–CO = 89°: Green, M. L. H.; Ariyaratne, J. K. P.; Bjereuni, A. M.; Ishaq, M.; Prout, C. K. *Chem. Commun.* **1967**, 430. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2\text{C}_4\text{H}_4$, CO–Fe–CO = 94.1°: Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1969**, *8*, 1936.

[13] Green, J. C.; Jackson, S. E. *J. Chem. Soc., Dalton Trans.* **1976**, 1698.

[14] Mahmoud, K. A.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2199.

[15] Hitam, R. B.; Hooker, R. H.; Mahmoud, K. A.; Narayanaswamy, R.; Rest, A. J. *J. Organomet. Chem.* **1981**, *222*, C9.

in hydrocarbon matrices accord well with these other studies. The irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ in a CO matrix[14] provides the valuable result that $(\eta^3\text{-}C_5H_5)Mo(CO)_4CH_3$ is *not* formed; rather, even in the CO matrix $(\eta^5\text{-}C_5H_5)Mo(CO)_2CH_3$ can be photogenerated.[14] Photolysis in the poly(vinyl chloride) film[15] appears to give new products for which we see no evidence in the hydrocarbon matrices; these presumably arise from the reaction with the matrix.

The ability to photogenerate the 16-valence-electron $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ species is representative of the ability to prepare and characterize thermally sensitive intermediates at a temperature where such species are inaccessible by thermal routes. As in the numerous examples previously reported,[2] metal carbonyls generally have a fairly large activation energy for loss of CO from the ground state and only a small activation energy for loss of CO upon population of the lowest excited state.

Thermal Reaction of $(\eta^5\text{-}C_5R'_5)M(CO)_2R$. The low-temperature photochemistry of all of the complexes studied is the same: dissociative loss of CO occurs subsequent to photoexcitation to lead to the generation of a spectroscopically detectable 16-valence-electron species. However, the thermal chemistry of the 16-valence-electron species for R having β-hydrogens differs from that for R = CH_3. Figure 1c illustrates the result from warming the photogenerated $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ species from 77 to 195 K. The two features at 1958 and 1879 cm^{-1} decline while two new features, 1980 and 1908 cm^{-1}, grow and are associated with $(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_2H_4)(H)$. The band positions and relative intensities for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_2H_4)(H)$ accord very well with those for $(\eta^5\text{-}C_5H_5)W(CO)_2$(1-pentene)(H) that has been characterized previously.[3] During the warmup of $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ there is some regeneration of starting $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_2H_5$. For the $(\eta^5\text{-}C_5R'_5)M(CO)_2CH_3$ species the only metal carbonyl detected upon warmup is the $(\eta^5\text{-}C_5R'_5)M(CO)_3CH_3$ starting material, whereas all $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ (R = C_2H_5, $n\text{-}C_5H_{11}$) complexes yield detectable $(\eta^5\text{-}C_5R'_5)M(CO)_2$(alkene)(H) (Table I). However, it appears that the dicarbonyls adopt structure II prior to formation of the alkene–hydride, since precursor solutions are yellow, not blue. Thus, the β-hydrogen transfer process, eq 7, is a significant thermal process.

$$\underset{\text{structure II}}{(\eta^5\text{-}C_5R'_5)M(CO)_2R} \xrightarrow[\text{R has }\beta\text{-H}]{\Delta,\ k_7} (\eta^5\text{-}C_5R'_5)M(CO)_2(\text{alkene})(H) \qquad (7)$$

For the $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ system (Figure 1c) it appears that the dicarbonyl and the alkene hydride are in equilibrium, eq 8, with an equilibrium constant of about 2 at 195 K. The

$$\underset{\text{structure II}}{(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5} \rightleftarrows (\eta^5\text{-}C_5H_5)Mo(CO)_2(C_2H_4)(H) \qquad (8)$$

equilibrium constant of 2 is estimated from the ratio of concentration of the two species determined by infrared absorbance data collected from irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_2H_5$ after thermal reaction ceased. Also, the same ratio is obtained from irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ in the presence of C_2H_4 (vide infra). We propose that the dicarbonyl is in fact the one represented by structure II. Solutions of $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ at 195 K are not blue; rather they are yellow. Moreover, the dicarbonyl does not readily back-react with the photoejected CO to re-form $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_2H_5$, whereas the corresponding CH_3 complex does not persist in solution at 195 K, presumably owing to fast back-reaction with CO according to eq 9. the di-

$$\underset{\text{structure I}}{(\eta^5\text{-}C_5R'_5)M(CO)_2R} + CO \xrightarrow[\text{fast}]{\Delta} (\eta^5\text{-}C_5R'_5)M(CO)_3R \qquad (9)$$

carbonyl ethyl species having structure I can lead to formation of structure II, eq 10, in competition with reaction with ligands such as CO. In fact, the 632.8-mm-induced I → II conversion represented in Figure 2 may be a consequence of local heating effects from absorption of light. Reference 2 and references therein discuss aspects of visible-light-induced reactions of photogenerated, coordinatively unsaturated metal carbonyls. Careful examination of the infrared spectrum of $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ photogenerated at 77 K and the spectra obtained after warmup to 195 K does reveal small shifts in the CO absorptions for the dicarbonyl consistent with the existence of two structures. In Figure 1c, for example, the 1879- and 1958-cm^{-1} features are for the dicarbonyl species. The 1879-cm^{-1} feature at 77 K shifts ~2 cm^{-1} and diminishes upon warming, whereas the 1958-cm^{-1} band does not shift. The ~2-cm^{-1} shift is attributed to the generation of structure II from I. We propose that I and II can interconvert, since the dicarbonyl alkyl having β-hydrogens will slowly react with entering groups (vide infra). However, the equilibrium lies far toward structure II. Thus, UV–vis and infrared spectra and differences in the rate of reaction with CO establish at least two structures for the dicarbonyl species. Note that the sluggish kinetics for reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ (structure II) at 195 K with CO cannot be attributable to either interactions with solvent or impurities therein or dinuclear species (such as $Cr_2(CO)_{11}$ from $Cr(CO)_5$ and $Cr(CO)_6$ in that system[16]) because the less sterically demanding dicarbonyl–CH_3 complexes back-react rapidly with CO in the same media. The data are wholly consistent with an intramolecular interaction in structure II that blocks the open coordinate site surprisingly well when R is ethyl or *n*-pentyl.

$$\underset{\substack{\text{structure I}\\ \lambda_{max}\ \text{blue 555–625 nm}}}{(\eta^5\text{-}C_5R'_5)M(CO)_2R} \underset{k_{-10}}{\overset{\Delta,\ k_{10}}{\rightleftharpoons}} \underset{\substack{\text{structure II}\\ \lambda_{max}\ \text{yellow 400–435 nm}}}{(\eta^5\text{-}C_5R'_5)M(CO)_2R} \qquad (10)$$

We invoke the equilibrium represented by eq 8, since conversion of the dicarbonyl to the ethylene hydride is incomplete, unlike the situation for the W complexes. The equilibrium distribution is nearly temperature insensitive up to 250 K, where the dicarbonyl and the ethylene hydride disappear together. In alkane solutions $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ is formed as the temperature is raised. Consistent with the existence of the equilibrium represented by eq 8 we have shown that it is possible to enter the equilibrium by irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ at 232 K in isooctane purged with C_2H_4. The same set of product peaks are generated but in a slightly different ratio, consistent with a small temperature effect on the equilibrium. Consistent with the structure II for $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$ we do not find evidence for a significant reaction with the excess C_2H_4 in the medium, providing further evidence for the blocked coordination site.

Irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_2H_5$ or the *n*-pentyl analogue in alkane solution at 300 K yields $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ presumably via the loss of CO, β-hydrogen transfer, loss of alkene, and uptake of CO. The reaction also yields small amounts of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ presumably accompanied by H_2 and/or alkane formation. For $(\eta^5\text{-}C_5H_5)Mo(CO)_3(n\text{-}C_5H_{11})$ we do find pentane and 1-pentene after long irradiation times. Similarly, the W species yields pentane and pentene, but the pentene is partially isomerized to *cis*- and *trans*-2-pentene. The point is that the alkene hydrides of Mo are labile with respect to alkene loss. Assuming a correlation here of lability and thermodynamics, we can conclude that the alkene is weakly bound to Mo relative to W, since the alkene–hydrides of W (Table I) are inert at 300 K. Consistent with a more firmly bound alkene in the W complexes, the 16-valence-electron W–C_2H_5 or –$n\text{-}C_5H_{11}$ complexes react completely to initially form the ethylene–hydride or pentene–hydride complex, respectively. It is well established that low-valent W complexes of this wort are more substitution inert than their Mo analogues,[17] and we have established this to be true for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_2H_4)CH_3$ compared to the W analogue. Irradiation (355 nm) of the $(\eta^5\text{-}C_5H_5)M(CO)_3CH_3$ complexes at 1 mM in C_2H_4-purged isooctane at 195 K results in the formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)CH_3$ (ν_{CO} = 1979, 1904 cm^{-1})[18] and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_2H_4)CH_3$ (ν_{CO} = 1964, 1909 cm^{-1}). Addition of PPh_3 (to a concentration of 5 mM) followed by warmup to 300 K yields

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[16] Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.

[17] Darensbourg, D. J. *Adv. Organomet. Chem.*, in press.

[18] (a) Alt, H. G.; Schwarzle, J. A.; Kreiter, C. G. *J. Organomet. Chem.* **1978**, *153*, C7. (b) Kreiter, C. G.; Nist, K.; Alt, H. G. *Chem. Ber.* **1981**, *114*, 1845.

$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2(\text{PPh}_3)\text{CH}_3$ in <30 min whereas the W species is completely inert on this time scale.

As a representative of all of the alkene–hydride complexes, the relatively inert $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{C}_2\text{H}_4)(\text{H})$ has been characterized by its reactions and by its spectroscopies. First, the species can be formed from warming photogenerated $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{C}_2\text{H}_5$ from 77 to 195 K. Two infrared features, 1980 and 1905 cm^{-1}, in a 1:2 ratio are characteristic. The same infrared bands are formed when $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{H}$ is irradiated in an ethylene-saturated alkane solution (eq 11). It is known that loss of CO is the principal result from photoexcitation of $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_3\text{H}$.[19] $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{C}_2\text{H}_4)(\text{H})$ reacts with CCl_4 to form CHCl_3, a known reaction for such hydrides.[20] The ^1H and ^{13}C NMR spectra accord well with the proposed formulation (cf. Experimental Section). The infrared band in the CO stretching region is consistent with that of a dicarbonyl. The OC–W–CO angle from the relative band intensities is 108°, consistent with a trans geometry, *trans*-$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{C}_2\text{H}_4)(\text{H})$. The ^{13}C NMR spectrum at −5 °C shows a single, sharp resonance for the CO's, confirming the trans geometry of the complex. This feature is unchanged upon cooling the solution to −50 °C. On the basis of the spectroscopic similarities (Table I), we conclude that all $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{R}$ ($\text{R} = \text{C}_2\text{H}_5$, $n\text{-C}_5\text{H}_{11}$) species thermally react to form *trans*-$(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2$(alkene)(H). Such reaction can be detected at temperatures less than 195 K, but the extent of conversion depends on whether M = Mo or W: reaction goes to completion for M = W but only to ~65% for M = Mo.

$$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{H} \xrightarrow[\text{C}_2\text{H}_4/\text{alkane}]{355\text{ nm}} (\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{C}_2\text{H}_4)(\text{H}) + \text{CO} \quad (11)$$

The fact that the alkene–hydride complexes are the *trans* isomers raises the question of whether the yellow species that we have assigned as the dicarbonyl–alkyl of structure II is in fact the cis alkene hydride. Both the UV–vis and the IR spectra of the yellow species are inconsistent with it being the cis-alkene–hydride complex. The IR spectra of *cis*- and *trans*-$(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{LR}$ complexes in the CO stretching region are very similar,[10,11,21] whereas structure II and the trans-alkene–hydride complexes have very different spectra in this region. Also, the ~400-nm absorption for II is too low in energy to be associated with a cis alkene hydride, since the trans alkene hydride (Figure 2b) absorbs well above this energy. Finally, irradiation of the Mo–C_2H_5 complex at 77 K followed by warmup to 223 K only yields one hydride resonance, δ −5.2, for the trans alkene hydride despite the presence of species of structure II.

To summarize the thermal chemistry of $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{R}$ so far, we note that (i) back-reaction with CO is apparently facile for dicarbonyl alkyls of structure I, (ii) for the C_2H_5 and $n\text{-C}_5\text{H}_{11}$ species conversion of structure I to II occurs in competition with the back-reaction with CO, and (iii) the structure II species appear to thermally react to give *trans*-$(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{R}$(alkene)(H). To further substantiate the reactivity differences associated with structures I and II, we have carried out photosubstitution of 0.7 mM $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_3\text{R}$ in 195 K isooctane solutions containing 1 mM PPh_3. The procedure is to irradiate the sample in an infrared cell with an intense UV source for a short period and then to rapidly analyze to determine the thermal rate of formation of $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2(\text{PPh}_3)\text{R}$ and $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2$(alkene)(H) (where possible) from reaction of the photogenerated $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{R}$. For R = CH_3 we find that $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2(\text{PPh}_3)\text{CH}_3$ is formed immediately (<10 s). For R = C_2H_5 we find that a certain amount of $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2(\text{PPh}_3)\text{C}_2\text{H}_5$ is formed instantly, but this is accompanied by the presence of $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{C}_2\text{H}_5$ that slowly gives $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2(\text{C}_2\text{H}_4)(\text{H})$ but no additional PPh_3 substitution product. The slow reaction to give alkene–hydride is presumably via the dicarbonyl of structure II that only sluggishly reacts with PPh_3 because the open site is blocked. Immediate formation of PPh_3 substitution products is via the dicarbonyl alkyl of structure I, the primary product from loss of CO. Monitoring the photochemistry of the $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{C}_2\text{H}_5$ at 223 K in toluene-d_8 by ^1H NMR spectroscopy reveals the same information as obtained from the infrared data. At sufficiently high concentrations of entering groups L in 298 K solution the efficiency for scavenging the coordinatively unsaturated species I becomes unity, since only $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{LR}$ is formed photochemically at high L concentration.

At least for the W species, the rate of reaction of the alkene hydride with L is too slow to account for the complete formation of $(\eta^5\text{-C}_5\text{R'}_5)\text{W(CO)}_2\text{LR}$ via the prior formation of $(\eta^5\text{-C}_5\text{R'}_5)\text{W(CO)}_2$(alkene)(H). The $(\eta^5\text{-C}_5\text{R'}_5)\text{W(CO)}_2$(alkene)(H) species do react with L to form $(\eta^5\text{-C}_5\text{R'}_5)\text{W(CO)}_2\text{LR}$, but the rate is low. Monitoring by infrared allows quantitative analysis of such reaction. Data in Figure 3 are for reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2$(1-pentene)(H) with PPh_3. As shown in the inset, good initial rate data can be obtained at 298 K. For low PPh_3 concentrations, the rate depends strongly on PPh_3 concentration and is first order in PPh_3, since plots of initial rate vs. [PPh_3] are linear. At sufficiently high PPh_3 concentration the rate of formation of $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{PPh}_3)(n\text{-C}_5\text{H}_{11})$ is nearly independent of PPh_3 concentration. These data are consistent with the mechanistic sequence represented by eq 12–14 Thus, when $k_{14}[\text{L}] >> k_{10}k_7/k_{-10}$ the rate of formation of $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{LR}$ gives k_{12} as the intercept of the plot of (initial rate)$^{-1}$ vs. [L]$^{-1}$, if the **II** $\rightleftarrows$ **I** interconversion is assumed to be fast. Figure 4 shows the effect of varying PPh_3 concentration on the initial ratio of $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{PPh}_3)\text{C}_2\text{H}_5$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{C}_2\text{H}_4)(\text{H})$ formed from irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{C}_2\text{H}_5$ in isooctane solution at 298 K. These data accord well with the data for the thermal reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2$(1-pentene)(H) with PPh_3 via eq 12–14 in that the PPh_3, at a given concentration, suppresses the β-hydrogen-transfer products by an amount near that expected on the basis of the intermediacy of a common 16-valence-electron species I in the thermal reaction of the alkene hydride with L and in the photochemical substitution of the tricarbonyl.

$$(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2(\text{alkene})(\text{H}) \underset{k_7}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{structure II}}{(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{R}} \quad (12)$$

$$\underset{\text{structure II}}{(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{R}} \underset{k_{10}}{\overset{k_{-10}}{\rightleftharpoons}} \underset{\text{structure I}}{(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{R}} \quad (13)$$

$$\underset{\text{structure I}}{(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{R}} + \text{L} \xrightarrow{k_{14}} (\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2\text{LR} \quad (14)$$

The ability to photochemically prepare the *trans*-$(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2$(alkene)(H) complexes illustrates another example of a thermally inaccessible species. Thermal chemistry of $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_3\text{R}$ requires temperatures well above 298 K to obtain a significant rate of reaction, and the product from the metal carbonyl is mainly $(\eta^5\text{-C}_5\text{R'}_5)_2\text{M}_2(\text{CO})_6$, not an alkene hydride. The temperatures necessary to promote dissociative loss of CO from $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_3\text{R}$ are apparently sufficiently great to lead to good rates for further reaction of the alkene–hydride or to other thermal processes of $(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_3\text{R}$. *trans*-$(\eta^5\text{-C}_5\text{R'}_5)\text{Mo(CO)}_2$(alkene)(H) is obviously quite thermally labile (decomposes above ~250 K), and the W complexes are quite labile above 350 K. The thermal chemistry at high temperatures requires detailed study in order to comment further on the photochemistry at low temperature vs. thermal chemistry.

Mechanisms of Formation of *trans*-$(\eta^5\text{-C}_5\text{R'}_5)\text{M(CO)}_2$(alkene)(H). Formation of the alkene–hydride complexes from irradiation of the tricarbonyl precursors involves first the loss of CO to form the coordinatively unsaturated intermediate. The absorption of light produces an electronically excited state that undergoes facile loss of CO at temperatures as low as 77 K, whereas, significant thermal reaction of the tricarbonyl species

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[19] (a) Mills III, W. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 5832. (b) Kazlauskas, R. J.; Robbins, J. L.; Wrighton, M. S., to be submitted for publication.

[20] Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 635, 7902 and references therein.

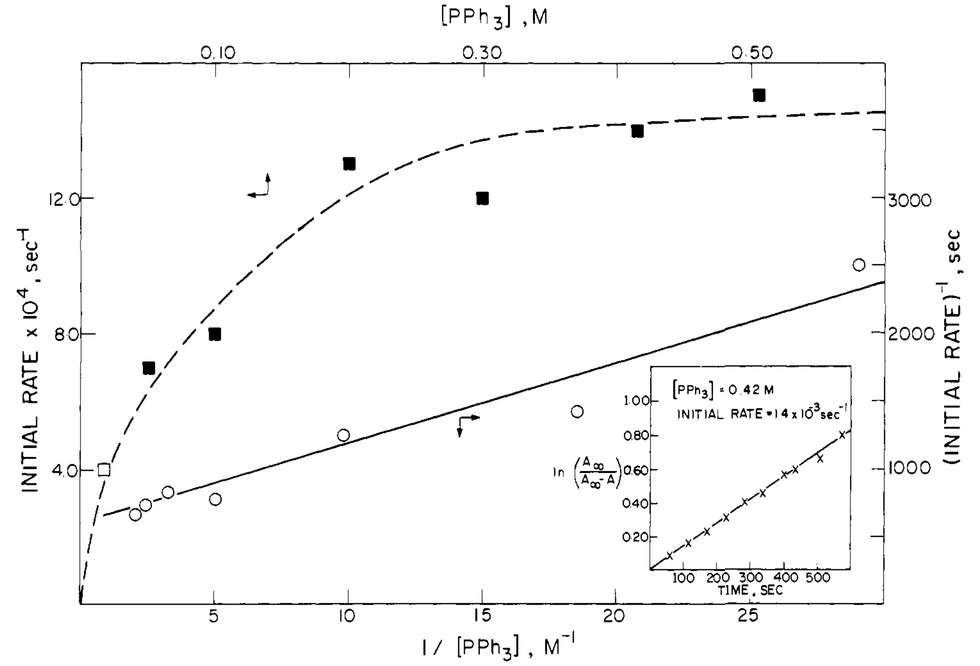


Figure 3. Kinetic analysis for the reaction of PPh_3 with $(\eta^5\text{-}C_5H_5)W(CO)_2(\text{pentene})(H)$. The inset shows the natural logarithm of absorbance changes for initial formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(n\text{-}C_5H_{11})$ as a function of time in toluene containing 0.42 M PPh_3. The slope corresponds to a pseudo-first-order rate constant of 1.4×10^{-3} s^{-1}. The dashed curve represents a plot of initial rate vs. PPh_3 concentration (use top and left scale), showing a limiting rate of 1.7×10^{-3} M. The open symbols represent data obtained in isooctane, while the darkened symbols represent data obtained with toluene as a solvent. The smooth curve represents a plot of (initial rate)$^{-1}$ vs. $[PPh_3]^{-1}$ (bottom and right scales).

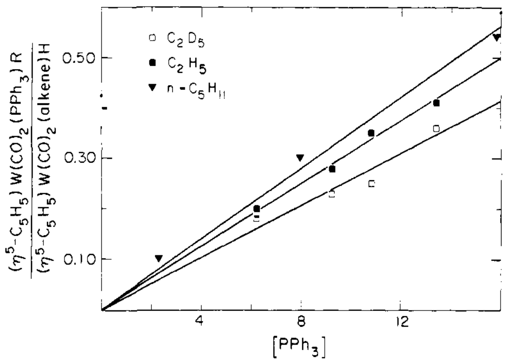
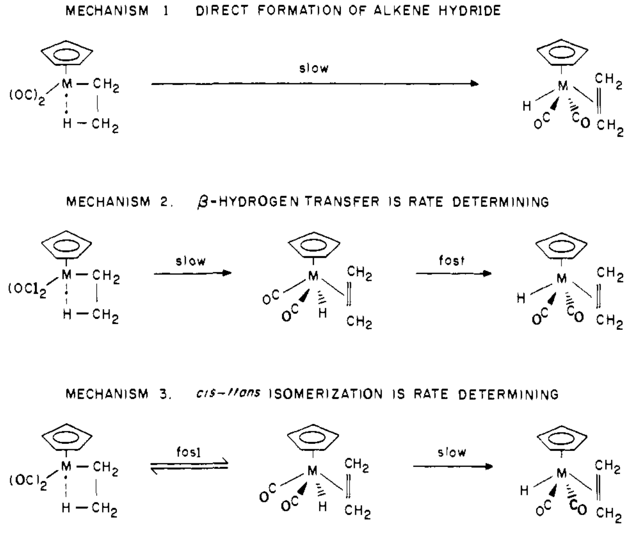


Figure 4. Relative rates of β-hydrogen transfer and capture by PPh_3. The ratio (±15%) of $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)R$ and $(\eta^5\text{-}C_5H_5)W(CO)_2(\text{alkene})(H)$ (or D) is plotted as a function of PPh_3 concentration from 0 to 16 mM. Measurements were done in isooctane solution at 300 K with ~1 mM starting complex irradiated with a single flash from a GTE Sylvania flashcube. Spectra were obtained within 60 s of reaction to minimize any contribution from secondary thermal reaction of alkene hydride with PPh_3.

Scheme I. Possible Mechanisms for Formation of Alkene Hydride from Dicarbonyl Alkyl[a]



requires a temperature in excess of 298 K. Thus, it is clear that irradiation allows the β-hydrogen transfer to occur at low temperature because CO loss is not rate limiting. The issue we now address is whether the rate of formation of *trans*-$(\eta^5\text{-}C_5R'_5)M(CO)_2(\text{alkene})(H)$ from the dicarbonyl–alkyl, k_7, is in fact limited by the rate of the β-hydrogen-transfer processes.

We consider the three mechanistic possibilities as represented in Scheme I. In the first, where the β-hydrogen transfer is rate limiting, *trans*-$(\eta^5\text{-}C_5R'_5)M(CO)_2(\text{alkene})(H)$ is generated directly from the dicarbonyl–alkyl. In the second, a slow β-hydrogen transfer to form a cis-alkene–hydride complex is followed by a fast cis → trans isomerization. In the third mechanism, there is a fast interconversion between the dicarbonyl–alkyl and a cis alkene–hydride, and cis → trans isomerization of the alkene–hydride is rate limiting. We have measured the rate of reaction of the dicarbonyl alkyl for a variety of systems and conditions. The data to be elaborated below are best interpreted as supporting the third mechanism, where cis → trans isomerization is the rate-determining step in the formation of the trans alkene hydride.

In order to measure the rate of reaction of the dicarbonyl–alkyl complexes, we have used infrared spectroscopy to monitor the metal carbonyl species. Figure 5 shows spectral changes following the irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-}C_5H_{11})$ at 195 K in isooctane solution. The irradiation initially produces the 16-valence-electron species (structure II) that reacts slowly in a subsequent thermal step to form the trans alkene hydride. The rapid-scan FT IR method allows simultaneous monitoring of product and starting material with molecular specificity. The inset shows that good kinetics can be obtained.

Figure 6 shows a summary of rate data collected as a function of temperature for a variety of complexes with either the FT IR rapid-scan or conventional single-wavelength monitoring vs. time. In all cases the rate of reaction is directly proportional to concentration of the dicarbonyl alkyl. It should be realized that the rate data have relatively large experimental errors. Any given determination has an error in the temperature of ±2 K and in the observed rate of ±20%. Table III summarizes the activation

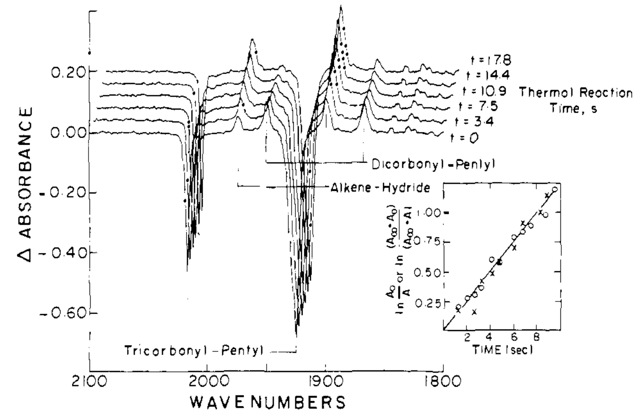


Figure 5. Infrared spectral changes accompanying the thermal reaction of (η^5-C_5H_5)W(CO)$_2$(n-C_5H_{11}) as shown by difference infrared spectra. (η^5-C_5H_5)W(CO)$_3$(n-C_5H_{11}) in isooctane (~1 mM) at approximately 195 K is irradiated briefly with a xenon arc lamp. The spectrum immediately after irradiation is the trace marked $t = 0$ and shows large negative peaks corresponding to the disappearance of starting material. Positive peaks are seen at 1948 and 1862 cm^{-1} corresponding to the formation of (η^5-C_5H_5)W(CO)$_2$(C_5H_{11}) and also at 1973 and 1900 cm^{-1} corresponding to (η^5-C_5H_5)W(CO)$_2$(pentene)(H). The successive spectra show in real time the thermal conversion of the dicarbonyl pentyl (structure II) to the alkene hydride. The inset shows a plot of the natural logarithm of an absorbance ratio vs. time for the appearance of the alkene hydride at 1900 cm^{-1} (×) and the disappearance of the dicarbonyl alkyl at 1950 cm^{-1} (0). Both result in the same line whose slope corresponds to the first-order rate constant for reaction.

Table III. Kinetic Parameters for Conversion of (η^5-$C_5R'_5$)M(CO)$_2$R to *trans*-(η^5-$C_5R'_5$)M(CO)$_2$(alkene)(H)

starting compd[a]	$\Delta G^{\ddagger}$, kcal/mol (± 25%)	$\Delta H^{\ddagger}$, kcal/mol (± 25%)	$\Delta S^{\ddagger}$, eu (±25%)	k_7, s^{-1} (195 K, ±20%) ($t_{1/2}$, s)
(η^5-C_5H_5)W(CO)$_2C_2H_5$	11	11	−8	0.06 (11)
(η^5-C_5H_5)W(CO)$_2C_2D_5$	11	11	−8	0.1 (7)
(η^5-C_5H_5)W(CO)$_2$(n-C_5H_{11})	9	8	−23	0.02 (30)
(η^5-C_5Me_5)W(CO)$_2C_2H_5$	11	11	−10	0.04 (17)
(η^5-C_5H_5)Mo(CO)$_2C_2H_5$	10	10	−18	0.004 (170)

[a] All compounds indicated have been photogenerated by 355-nm irradiation of the parent tricarbonyl in alkane media in an infrared cell at low temperature. Under the conditions of the thermal reactions the dicarbonyl alkyls have structure II.

parameters and k_7 and $t_{1/2}$ at 195 K for the systems studied.

It is noteworthy that all of the complexes have approximately the same activation parameters. Further, the dicarbonyl–C_2H_5 and –C_2D_5 complexes react at a similar rate. The similarity in rate for the dicarbonyl–C_2H_5 and –C_2D_5 complexes is also reflected in the data in Figure 4 associated with the capture of the dicarbonyl alkyl by PPh_3 to suppress the products resulting from a β-hydrogen transfer. If the C_2H_5 and C_2D_5 complexes reacted to form alkene hydride at significantly different rates, then the efficiency for suppressing the β-hydrogen-transfer product would differ for the two cases. The data in Figures 4 and 6 do seem to suggest that the C_2D_5 complex reacts faster than the C_2H_5 complex. However, the experimental error is such that the differences observed are not significant. But we have carried out additional experiments to minimize systematic errors that show that the isotope effect is negligible. First, we have examined the rate of formation of alkene hydride following the irradiation of a 1:1 mixture of the C_2D_5 and C_2H_5 complexes at low temperature (170 K). We found that there was only one decay curve (concentration vs. time) for the disappearance of dicarbonyl alkyl and only one appearance curve for the alkene hydride. This rules out any major differences in rate of reaction for the dicarbonyl–C_2H_5 and dicarbonyl–C_2D_5 complexes. The PPh_3-capture experiments at 298 K allow a better measure of whether there is an isotope effect, and careful comparison of the C_2H_5, C_2H_5, and CH_2CD_3 complexes has been done in parallel under rigorously controlled conditions. With the complex at 1.7 × 10^{-3} M, PPh_3 at 1.5 × 10^{-2} M, in Ar-purged isooctane we find that there is no effect from replacing ^1H by ^2H on the ratio of (η^5-C_5H_5)W(CO)$_2$(PPh_3)(ethyl) to hydride products. Likewise, there is no effect when a 1:1 mixture of the C_2H_5 and C_2D_5 complexes are used. In these experiments the error on the product ratios is less than 10%, and to this extent we conclude that there is no isotope effect. The lack of a significant isotope effect is consistent with a rate-limiting step that does not involve C–H bond breaking and excludes a mechanism where the β-hydrogen transfer is rate determining.

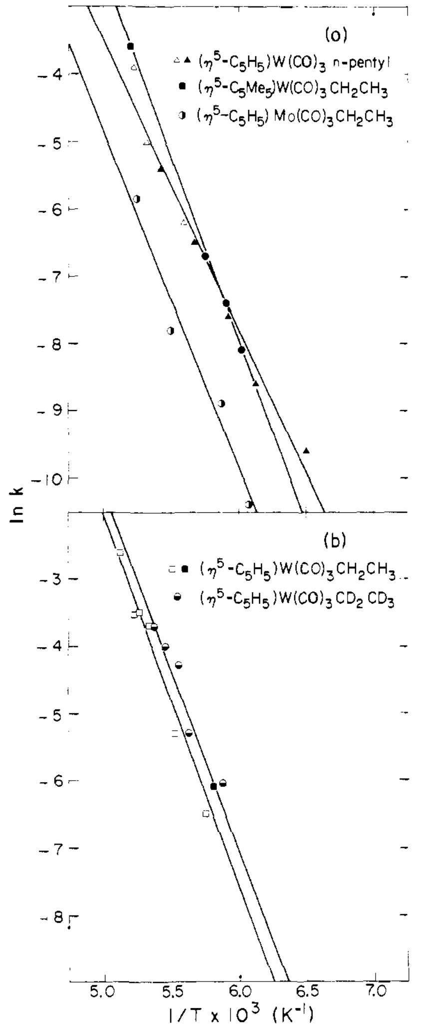


Figure 6. Arrhenius plots for reaction 7 for alkane media. For (η^5-C_5H_5)W(CO)$_3$(n-C_5H_{11}) and (η^5-C_5H_5)W(CO)$_3C_2H_5$ measurements were done in both paraffin solution and fluid 2-methylbutane solution. The open symbols represent fluid solution data; the closed symbols represent paraffin solution. All other complexes were studied in paraffin. The errors are ±2 K in temperature and ±20% in rate for a given data point.

The activation energies in Table III are in a range similar to those for the interconversion of *cis*- and *trans*-(η^5-C_5H_5)M(CO)$_2$LH complexes, and the rate of such interconversions has no measurable hydrogen isotope effect.[21] The data so far are thus consistent with reaction proceeding to first form a cis-alkene–hydride complex. The compelling experiments concern the distribution of products originating from (η^5-C_5H_5)W(CO)$_3CD_2CH_3$ and (η^5-C_5H_5)W(CO)$_3CH_2CD_3$. For (η^5-C_5H_5)W(CO)$_3CD_2CH_3$, having no D on the β-carbon, we find a significant yield (33 ± 10%) of *trans*-(η^5-C_5H_5)W(CO)$_2$(C_2H_3D)(D) by ^2H NMR when the irradiation is carried out and reaction monitored at a temperature where the trans alkene hy-

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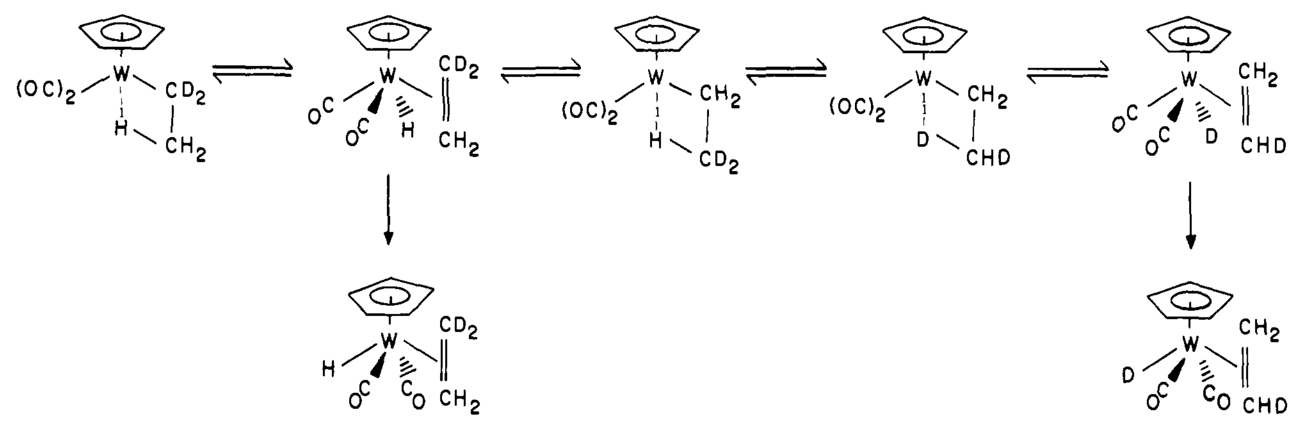
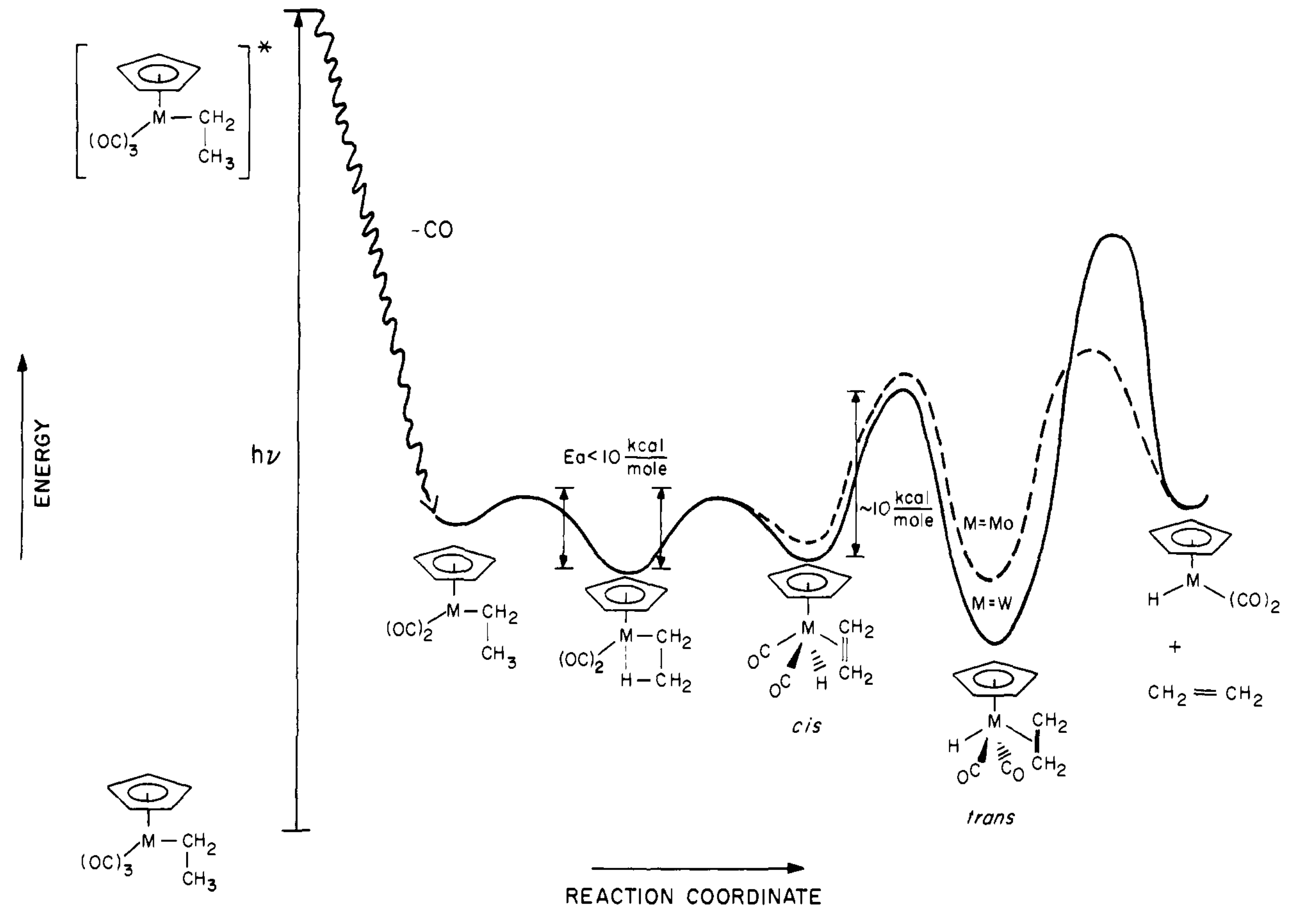
[21] Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

Scheme II. Mechanism for Equilibration of α- and β-Carbons in (η^5-C_5H_5)W(CO)$_2$CD$_2$CH$_3$



Scheme III. Mechanism and Energetics for Photoinduced Reactions of (η^5-C_5H_5)M(CO)$_3$R



dride is completely thermally inert with respect to formation of dicarbonyl alkyl as determined by the PPh$_3$-capture reactions (Figures 3 and 4). Consistently, (η^5-C_5H_5)W(CO)$_3$CH$_2$CD$_3$, having no H on the β-carbon, yields a significant amount of (η^5-C_5H_5)W(CO)$_2$(C$_2$HD$_3$)(H) (36 ± 10%) under the same conditions. Others[3b] have reported the absence of ^{2}H in (η^5-C_5H_5)W(CO)$_3$H formed from exhaustive photolysis of (η^5-C_5H_5)W(CO)$_3$CD$_2$CH$_3$. However, our ^{1}H and ^{2}H NMR data unequivocally establish a metal deuteride at the alkene–hydride (deuteride) stage in approximately a statistical (~40%) amount. Inasmuch as the trans-alkene–hydride complexes are inert under the conditions of these experiments (protons are not equilibrating between alkene and hydride), the conclusion is that scrambling between α- and β-carbons occurs, as illustrated in Scheme II, involving the interconversion between the cis alkene–hydride and the dicarbonyl alkyl. Such scrambling requires equilibration of the alkene carbon atoms at the cis-alkene–hydride stage to equilibrate the α- and β-carbons. We conclude that the tungsten alkene hydride that is isolated is inert since it reacts to form the alkyl–PPh$_3$ complexes at a very slow rate and is definitely not labile on the NMR time scale (vide supra).

The direct transfer of a β-hydrogen to form the trans alkene hydride as the exclusive mechanism is specifically ruled out by the experiments with the labeled compounds. The fast β-hydrogen transfer to form a cis-alkene–hydride complex is a reasonable explanation for the data. Study of the β-hydrogen transfer of (η^5-$C_5R'_5$)M(CO)$_2$R (M = Fe, Ru; R = C_2H_5, n-C_5H_{11}) following irradiation shows that the β-hydrogen transfer to form a cis alkene hydride can be as fast as is necessary[22] for cis → trans isomerization to be the rate-determining step in forming *trans*-(η^5-

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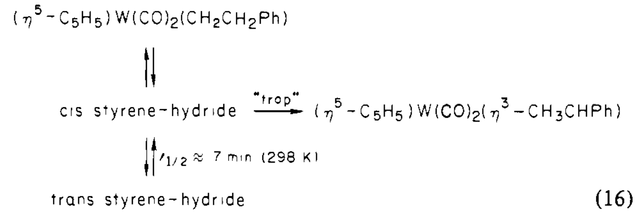
(22) (a) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics*, **1982**, *1*, 602. (b) Gerhartz, W.; Ellerhorst, G.; Dahler, P.; Eilbracht, P. *Justus Liebigs Ann. Chem.* **1980**, 1296.

$C_5R'_5)M(CO)_2$(alkene)H from $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ in the complexes studied here. The cis $\rightleftarrows$ trans interconversion of related complexes have activation parameters similar to those found here,[21] consistent with our mechanistic proposal.

Consistent with the proposed mechanism, we and others[23] find that 298 K irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2CH_2Ph$ in hydrocarbon solution gives the product indicated in eq 15, along with some *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(CH_2CHPh)(H)$.[24] Further, the

$$(\eta^5\text{-}C_5H_5)W(CO)_3CH_2CH_2Ph \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}CH_3CHPh) + CO \quad (15)$$

trans-$(\eta^5\text{-}C_5H_5)W(CO)_2(CH_2CHPh)(H)$, which can also be formed, along with $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}CH_3Ph)$, upon irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(H)$ in the presence of styrene, is relatively thermally inert at 298 K. On the same time scale ($t_{1/2} \approx 7$ min) that high concentration of PPh_3 reacts with $(\eta^5\text{-}C_5H_5)W(CO)_2$(pentene)(H) to form $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(n\text{-}C_5H_{11})$ (cf. Figure 3), we find that *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(CH_2CHPh)(H)$ reacts to give $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}CH_3CHPh)$. These data are thus consistent with inert trans-alkene–hydride complexes, and the CH_2CH_2Ph system shows that the preequilibrium can be "trapped" by formation of the stable $\eta^3\text{-}CH_3CHPh$ complex as shown in eq 16. These results are elaborated elsewhere.[24]



(16)

Conclusions

Scheme III represents a summary of the information obtained in this study. All $(\eta^5\text{-}C_5R'_5)M(CO)_3R$ (M = Mo, W; R′ = H, CH_3; R = CH_3, C_2H_5, $n\text{-}C_5H_{11}$) complexes undergo dissociative loss of CO as the principal result of photoexcitation. The resulting 16-valence-electron dicarbonyl complexes can be spectroscopically characterized at low temperature, and the infrared spectrum suggests that the structure of $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ is similar to that for the 18-valence-electron species $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$. The 16-valence-electron species can be captured by two-electron donor ligands to form substitution products $(\eta^5\text{-}C_5R'_5)M(CO)_2LR$. For R = C_2H_5, C_5H_{11}, having β-hydrogens, the 16-valence-electron species can adopt a structure where the coordination site is blocked, inhibiting reaction with incoming ligands. The dicarbonyl–alkyl species where the alkyl has β-hydrogens react to form *trans*-$(\eta^5\text{-}C_5R'_5)M(CO)_2$(alkene)(H). The mechanism for formation of the alkene hydrides is apparently one where a fast β-hydrogen transfer occurs, after photogeneration of the 16-valence-electron species, to form a cis-alkene–hydride complex that then, in the slow step, isomerizes to *trans*-$(\eta^5\text{-}C_5R'_5)M(CO)_2$(alkene)(H). Significant formation rates of the alkene hydride from the 16-valence-electron species obtain at temperatures as low as 195 K. Photochemistry thus allows observation and characterization of two species, $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ and *trans*-$(\eta^5\text{-}C_5R'_5)M(CO)_2$(alkene)(H), that would not be observable by thermal chemistry of $(\eta^5\text{-}C_5R'_5)M(CO)_3R$ where the activation energy for dissociative loss of CO is significantly greater than for reaction of $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ to form *trans*-$(\eta^5\text{-}C_5R'_5)M(CO)_2$(alkene)(H) or to decompose the alkene hydride. But since the rate-determining step is a cis → trans isomerization of the alkene hydride in the thermal conversion of the dicarbonyl alkyl to the alkene hydride, we do not gain rate information for the β-hydrogen-transfer process. We can only conclude that ΔG^* is less than 10 ± 2 kcal/mol for the β-hydrogen transfer and the rate is greater than the rate for the cis → trans isomerization of the cis alkene hydride.

Interestingly, the photogenerated 16-valence-electron $(\eta^5\text{-}C_5R'_5)M(CO)_2R$ (R has β-hydrogens) apparently can adopt a structure, II, that involves a "light saturation" of the metal center via an interaction with the β-hydrogen. Structure II is apparently the immediate precursor to the alkene–hydride β-hydrogen-transfer product. Other examples of transition-metal interactions with the saturated C–H bonds of coordinated ligands have been documented.[25-27]

Acknowledgment. We thank the National Science Foundation for support of this research. R.J.K. acknowledges support as an NSF Predoctoral Fellow, 1978–1981. We thank the National Institutes of Health (Grant GM 27551) for support for the Nicolet 7199 FT IR spectrometer used in these studies.

Registry No. $(\eta^5\text{-}C_5)W(CO)_3CH_3$, 12082-27-8; $(\eta^5\text{-}C_5H_5)W(CO)_2CH_3$, 73715-35-2; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CH_3$, 12115-41-2; $(\eta^5\text{-}C_5H_5)W(CO)_3C_2H_5$, 51232-59-8; $(\eta^5\text{-}C_5H_5)W(CO)_2C_2H_5$, 82615-21-2; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(C_2H_5)$, 82615-23-4; $(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)(H)$, 80376-16-5; $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-}C_5H_{11})$, 59307-58-3; $(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-}C_5H_{11})$, 73715-34-1; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(n\text{-}C_5H_{11})$, 73715-33-0; $(\eta^5\text{-}C_5H_5)W(CO)_2$(pentene)(H), 83198-83-8; $(\eta^5\text{-}C_5H_5)W(CO)_3(H)$, 12128-26-6; $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$, 12566-66-4; $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$, 12082-25-6; $(\eta^5\text{-}C_5H_5)Mo(CO)_2CH_3$, 80441-96-9; $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PCOPh)_3)CH_3$, 33056-74-5; $(\eta^5\text{-}C_5H_5)Mo(CO)_3C_2H_5$, 12083-68-0; $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_2H_5$, 83152-31-2; $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OPh)_3)C_2H_5$, 33111-93-2; $(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_2H_4)(H)$, 83152-32-3; $(\eta^5\text{-}C_5H_5)Mo(CO)_3(n\text{-}C_5H_{11})$, 83152-33-4; $(\eta^5\text{-}C_5H_5)Mo(CO)_3(H)$, 12176-06-6; $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, 12091-64-4; $(\eta^5\text{-}C_5Me_5)W(CO)_3C_2H_5$, 83152-34-5; $(\eta^5\text{-}C_5Me_5)W(CO)_2C_2H_5$, 83152-35-6; $(\eta^5\text{-}C_5Me_5)W(CO)_2(PPh_3)C_2H_5$, 83152-36-7; $(\eta^5\text{-}C_5Me_5)W(CO)_2(C_2H_4)(H)$, 83152-37-8; $(\eta^5\text{-}C_5Me_5)W(CO)_3(H)$, 32839-62-6; $(\eta^5\text{-}C_5H_5)(CO)_3Na$, 12107-36-7; $[(\eta^5\text{-}C_5Me_5)W(CO)_3]_2$, 83152-38-9; C_2H_5Br, 74-96-4; $(\eta^5\text{-}C_5Me_5)W(CO)_3Na$, 83152-39-0; $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)Na$, 65255-15-4; $(\eta^5\text{-}C_5H_5)W(CO)_3C_2D_5$, 83152-40-3; C_2D_5Br, 3675-63-6; $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2CD_3$, 83159-79-9; CD_3CH_2I, 7439-87-4; $(\eta^5\text{-}C_5H_5)W(CO)_3CD_2CH_3$, 80376-17-6; CH_3CD_2I, 3652-82-2; $(\eta^5\text{-}C_5H_5)W(CO)_2C_2D_5$, 83152-41-4; *n*-pentyl iodide, 628-17-1; acetic acid, 64-19-7.

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