Photochemical Dehydrogenation of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CH_2CH_2CH_3)$ to $[C_5H_5(CO)Fe](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CHCH_2CH_3)[FeC_5H_5]$

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Summary: Photolysis of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CH_2CH_2CH_3)$ *(2) in an unsuccessful effort to cleave the μ-alkylidene ligand led to expulsion of CO and* H_2 *and to formation of* $[C_5H_5Fe(CO)](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CHCH_2CH_3)[FeC_5H_5]$ *(3). The contrast between the facile photochemical cleavage reactions of the μ-alkenylidene complex* $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_2CH_3)$ *(1) and the slow photochemical dehydrogenation of μ-alkylidene complex 2 is discussed.*

Introduction

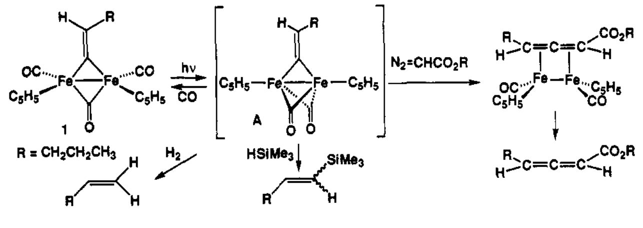
We have developed a number of new carbon–carbon bond forming reactions based on the high stability of both neutral and cationic $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CR)$ systems.[1] To take advantage of these new carbon–carbon bond forming reactions in organic synthesis, we have sought efficient methods for the cleavage of the bridging organic ligand from the diiron framework.[2,3] Modest success along these lines was achieved when diiron μ-alkenylidene complexes such as $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_2CH_3)$ (1) were photolyzed in the presence of trapping agents (Scheme 1).[3] The use of H_2 or trialkylsilanes as the trapping agent produced alkenes or vinylsilanes. When a diazo compound was used as a trap, diiron μ-allene complexes were produced which were subsequently cleaved to free allenes.

Here we report that attempts to extend this photolytic cleavage method to a diiron μ-alkylidene complex led instead to photolytic dehydrogenation of the μ-alkylidene ligand.

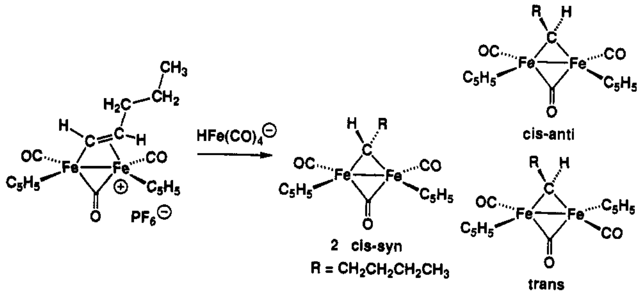
Results

Synthesis of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CH_2CH_2CH_3)$ (2). Diiron μ-alkylidene complexes are readily synthesized by hydride addition to either cationic μ-alkylidyne or μ-alkenylidene complexes.[1b,e,4] Since the latter reaction proceeds more cleanly, the μ-pentylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CH_2CH_2CH_3)$ (2) was prepared in 50% yield by addition of $NEt_4{}^+HFe(CO)_4{}^-$ to $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_2CH_2CH_3)^+PF_6{}^-$ (Scheme 2).[1b] In the ^1H NMR spectrum of 2, the proton on the bridging alkylidyne carbon gives rise to a triplet (δ 11.45, J = 8.2 Hz, 1H) at characteristically high frequency.[1b,d4] Recrystallized 2 is a fibrous, cherry-red solid that is thermally stable to over 100 °C and is moderately air-stable.

Scheme 1



Scheme 2



Only a single stereoisomer of 2 was obtained although three isomers are possible: cis-syn, cis-anti, and trans. In the cis-syn isomer the alkyl group of the bridging ligand is syn to the cis terminal CO ligands. In the IR spectrum of 2, the intensity pattern of the terminal CO stretches consisting of a strong band for the symmetric combination at 1973 cm^{-1} and a medium band for the asymmetric combination at 1935 cm^{-1} established the cis relationship of the terminal carbonyls. For a trans isomer, the higher energy symmetric stretch would be weaker in intensity than the lower energy asymmetric stretch. The presence of a single cyclopentadienyl resonance in both the ^1H and ^{13}C NMR spectra of 2 supports the assignment as a cis carbonyl isomer. The trans isomer has inequivalent cyclopentadienyl groups. While the stereochemistry of 2 cannot be rigorously assigned as either cis-syn or cis-anti, 2 is depicted as the less sterically crowded cis-syn stereoisomer.

Attempted Photolytic Cleavage of the μ-Alkylidene Ligand of 2. In analogy with the photoinduced cleavage of μ-alkenylidene ligands from diiron complexes, solutions of μ-pentylidene complex 2 were photolyzed in the presence of $HSi(CH_3)_3$, $HSi(CH_2CH_3)_3$, H_2, and $N_2CHCO_2CH_2CH_3$. For example, when a solution of 2 (0.022 mmol, 0.055 M) and $HSi(CH_3)_3$ (0.023 mmol) in acetone-d_6 in a sealed NMR tube was photolyzed with a Hanovia medium-pressure mercury vapor lamp for 4 h, ^1H NMR analysis showed

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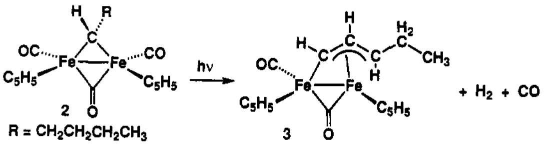
Scheme 3



little change. Under similar conditions, complete reaction of (μ-alkenylidene)diiron complexes had been observed.[3] At longer photolysis times, conversion of 2 to a new diiron complex $[C_5H_5Fe(CO)](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CHCH_2CH_3)[FeC_5H_5]$ (3) was observed.

Synthesis and Characterization of $[C_5H_5Fe(CO)](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CHCH_2CH_3)[FeC_5H_5]$ (3). A preparative-scale photolysis of 2 (150 mg, 0.38 mmol) was carried out in Et_2O under N_2 purge using a Hanovia medium-pressure mercury vapor lamp. After 1 h, the ^1H NMR spectrum indicated complete conversion of 2 to 3 and $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ (4) (Scheme 3). A 44% yield of 20:1 mixture of 3:4 was isolated by filtration and evaporation of solvent. Pure 3 from was obtained by column chromatography.

$[C_5H_5Fe(CO)](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CHCH_2CH_3)[FeC_5H_5]$ (3) was characterized by spectroscopy. The highest mass peak in the electron impact HRMS was at *m/e* 366.0017, consistent with the formula $C_{17}H_{18}Fe_2O_2$ and loss of CO and H_2 in the conversion of 2 to 3. In the IR spectrum, the presence of a single terminal CO stretch at 1943 cm^{-1} and of a bridging carbonyl band at 1768 cm^{-1} are consistent with the assigned structure of 3. The ^{13}C NMR spectrum confirmed the presence of a terminal (δ 216.4) and bridging (δ 269.8) CO. The presence of inequivalent cyclopentadienyl ligands was established both by ^1H NMR (δ 4.25 and 3.99) and ^{13}C NMR spectroscopy (δ 86.6 and 82.8). The presence of the μ-$CHCH{=}CHCH_2CH_3$ group was clearly evident from the ^1H NMR spectrum. The proton on the bridging carbon gave rise to a characteristically high-frequency resonance at δ 11.65 (J = 6.2 Hz) coupled to a single vinyl hydrogen at δ 4.38 (dd, J = 8.7, 6.2 Hz). This vinyl hydrogen is also coupled to a quartet at δ −0.32; the low frequency of this resonance is diagnostic for the γ proton of a μ-η^1,η^3-$CRCR{=}C\mathit{H}R$ ligand.[1d,5] The diastereotopic protons of the ethyl group gave rise to multiplets at δ 1.30 and 1.13, and the methyl group appeared as a triplet at δ 0.99. The ^{13}C NMR spectrum confirmed the presence of the five carbon bridging ligand (δ 172.9, 84.8, 67.9, 29.8, 14.7).

The pattern of resonances for the μ-$CHCH{=}CHR$ ligand of 3 (δ 11.65, 4.38, −0.32) is similar to the patterns reported by Knox[5] for $[C_5H_5Fe(CO)](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}C\mathit{H}C\mathit{H}{=}C\mathit{H}Me)[FeC_5H_5]$ (δ 11.86, 4.61, −0.48) and by Casey[1d] for $[C_5H_5Fe(CO)](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}C\mathit{H}CMe{=}C\mathit{H}Me)[FeC_5H_5]$ (δ 11.73, -, −1.07) and for $[C_5H_5Fe(CO)]$ $(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}C\mathit{H}CEt{=}C\mathit{H}H)[FeC_5H_5]$ (δ 11.75, -, −1.46).

CO and H_2 Formed in the Photochemical Conversion of 2 to 3. A sealed NMR tube containing a 0.04 M toluene solution of 2 (0.067 mmol) was photolyzed in a Rayonet photoreactor (maximum emission at 366 nm) for 3 days, until all of 2 was consumed. The noncondensable gases (0.023 mmol) were transferred into a Toepler pump system and oxidized to CO_2 and H_2O by passage through a closed loop containing CuO at 300 °C. The amount of CO oxidized to CO_2 (0.012 mmol, 18% yield from 2) was determined by measuring the gasses which passed through a trap at −80 °C. The amount of H_2 oxidized to H_2O (0.007 mmol, 10% yield from 2) was determined by measuring the gasses which evolved from the trap upon warming.

In a second experiment, H_2 formed in the photolytic conversion of 2 to 3 was detected by gas chromatography. ^1H NMR analysis of the photolysis of a sealed tube containing a benzene-d_6 solution of 2 (0.05 M) and 4,4′-dimethylbiphenyl (0.05 M, internal NMR integration standard) for 1 week showed 86% consumption of 2 (δ 3.32) and formation of 3 (δ 3.99, 48% yield) and 4 (δ 4.21, 15% yield). $[C_5H_5(CO)Fe]_4$, which was occasionally observed as a side product from the photolysis of 2, was not seen in this case. The NMR tube was broken under vacuum into a closed apparatus. Analysis of this gas mixture by gas chromatography using a thermal conductivity detector showed the presence of H_2 (~1:1, H_2:3).

CO Inhibition of the Dehydrogenation of 2. Since photoinduced loss of CO has been shown to be the dominant first step in the photochemistry of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ (4)[6] and since the photoinduced cleavage reactions of diiron μ-alkenylidene complexes are inhibited by added CO,[3] the effect of CO on the photochemical dehydrogenation of 1 was investigated. Two aliquots of a solution of 2 (0.05 M) and 4,4′-dimethylbiphenyl (as an internal NMR integration standard) in benzene-d_6 were sealed in NMR tubes under vacuum, and a third aliquot was sealed under 0.87 atm of CO. The tubes were photolyzed side by side in a Rayonet photoreactor, and the progress of the photolysis was followed by NMR spectroscopy for 1 week. After 3 days, ^1H NMR spectroscopy showed about 36% consumption of 2 in the samples sealed under vacuum, compared with 23% consumption in the sample sealed under CO; that is, the rate of consumption of 2 was about 1.5 times slower under CO. Lower yields of 3 were seen in the photolysis of 2 under CO. After 3 days, the amount of 3 formed in the tubes sealed under vacuum was three times greater than in the tube sealed under CO. In the samples sealed under vacuum, the rate of disappearance of 2 slowed somewhat as the reaction progressed, possibly due to inhibition of the photolysis by CO formed in the reaction. In the sample sealed under CO, all resonances became significantly broadened as the photolysis progressed.

Photoinduced Exchange of ^{13}CO with 2. A 0.003 M solution of 2 in Et_2O was photolyzed under ^{13}CO (90% ^{13}C). Aliquots were withdrawn after 10, 20, 30, and 120 min and were analyzed by ^{13}C NMR spectroscopy. After 10 min, integration of the CO resonances (δ 271 and 213) relative to the cyclopentadienyl resonance (δ 87) indicated that about 0.40 molecules of ^{13}CO had been incorporated per molecule of 2; the ratio of terminal:bridging ^{13}CO was 4.6:1. As the photolysis progressed, the amount of ^{13}CO incorporated increased rapidly and the ratio of terminal: bridging ^{13}CO approached the statistical 2:1 ratio. After 30 min, 1.24 ^{13}CO's per molecule of 2 had been incorporated, and the ratio of terminal:bridging ^{13}CO was 2.8:1.

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No evidence for formation of 3 was seen in the ^{13}C NMR spectrum even after 120 min of photolysis.

Discussion

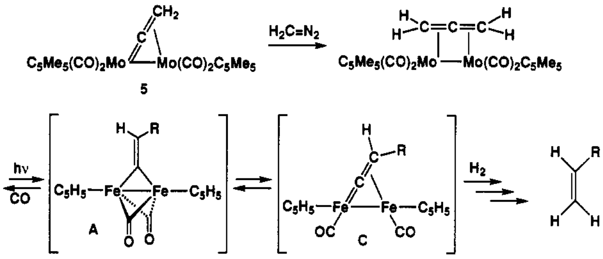
The unusual dehydrogenation of the side chain of the μ-pentylidene complex 2 to the μ-η^1,η^3-pentylidene complex 3 is clearly highly endothermic considering that alkane dehydrogenation (25–35 kcal mol^{-1} endothermic) and CO dissociation from iron (50 kcal mol^{-1} endothermic) are only partially compensated for by coordination of the new alkene to iron (20–30 kcal mol^{-1} exothermic). The role of light in driving the reaction is the generation of a reactive CO-loss intermediate.

The photochemically driven dehydrogenation of alkanes to alkenes catalyzed by transition metal complexes has been reported previously. Crabtree observed that the photoinduced dehydrogenation of cycloalkanes was catalyzed by $[IrH_2(PPh_3)_2(alkene)_2]^+$ complexes.[7] The photochemical conversion of hexane to hexene catalyzed by $RhCl(CO)(PMe_3)_2$ has been studied by the groups of Tanaka,[8] Saito,[9] and Goldman.[10] The thermal disproportionation of 1,3-cyclohexadiene to benzene and cyclohexene catalyzed by *cis*-$[PtCl_2(SnCl_3)_2]^{2+}$ was observed by Shinoda.[11]

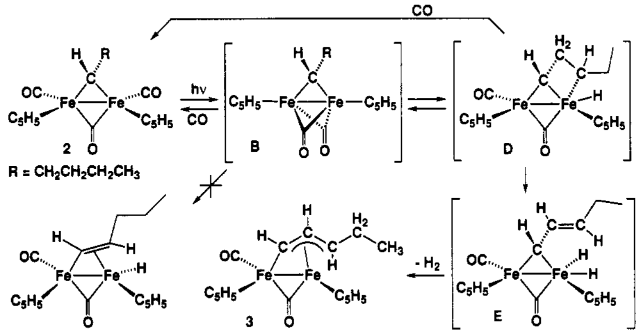
Contrasting Behavior of μ-Alkylidene and μ-Alkenylidene Complexes. Why does μ-alkenylidene complex 1 undergo photochemical cleavage with H_2 (and $HSiR_3$ and $N_2{=}CHCO_2R$) so readily while μ-alkylidene complex 2 does not? Why is side chain dehydrogenation seen only for μ-alkylidene complex 2 and not for μ-alkenylidene complex 1? These are the key questions that need to be addressed.

The photolysis of both 1 and 2 leads to CO loss and the probable formation of triply bridged intermediates. The related triply bridged diiron compound $[C_5H_5Fe]_2(\mu\text{-}CO)_3$ had been directly observed in the low-temperature photolysis of $[Cp(CO)Fe]_2(\mu\text{-}CO)_2$,[6c,d] and $[C_5Me_5Fe]_2(\mu\text{-}CO)_3$ was isolated from the photolysis of $[C_5Me_5(CO)Fe]_2(\mu\text{-}CO)_2$.[12] Bursten reported that photolysis of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ leads to loss of CO and proposed that the triply bridged species $[C_5H_5Fe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ is formed.[13] Our studies of the photochemical incorporation of ^{13}CO into 1 provided evidence for a triply bridged intermediate **A**.[3] At low conversion, ^{13}CO entered only the terminal position of 1, but at longer times ^{13}CO also appeared at the bridging position. The rate of incorporation of ^{13}CO into the bridging position was quantitatively accounted for by a model involving loss of CO to produce a triply bridged intermediate **A** followed by introduction of ^{13}CO into a terminal position. Similarly, the photolysis of 2 in the presence of ^{13}CO led to initial incorporation of ^{13}CO at a terminal position followed by introduction of ^{13}CO into a bridging position at longer photolysis times, consistent with formation of a triply bridged intermediate **B**. Qualitatively, the times for photoinduced ^{13}CO incorporation into both 1 and 2 were similar.

Scheme 4



Scheme 5



While both 1 and 2 undergo photoinduced loss of CO to generate a reactive intermediate, the similarity of their reactivity patterns stops there. The photoinduced cleavage of the μ-alkenylidene ligand of 1 with H_2, $HSiR_3$, or N_2CHCO_2R occurred within minutes. In contrast, no cleavage of the μ-alkylidene ligand of 2 was seen even after photolysis for days under similar conditions; a much slower dehydrogenation of the side chain to give 3 was observed instead. Clearly, the same type of triply bridged intermediate cannot be invoked to explain the differing chemistry of the two types of compounds. We will advance two possible explanations: one involves an intermediate of enhanced reactivity for the μ-alkenylidene complex 1; the other invokes an intermediate of diminished reactivity for the μ-alkylidene complex 2.

The first hypothesis is that neither of the triply bridged intermediates **A** or **B** is reactive toward addition of H_2 and other reagents, but the triply bridged μ-alkenylidene intermediate **A** is in equilibrium with a side-on μ-alkenylidene intermediate **C** which avidly adds reagents such as H_2 and diazo compounds (Scheme 4). Knox has isolated the side-on coordinated (μ-alkenylidene)dimolybdenum complex $[C_5Me_5(CO)_2Mo]_2(\mu\text{-}\eta^1,\eta^2\text{-}C{=}C{=}CH_2)$ (5) and studied its facile thermal reactions with diazo compounds to produce allene complexes.[14]

A second somewhat more complicated hypothesis is that the triply bridged μ-alkenylidene intermediate **A** is reactive toward H_2 and other reagents but the triply bridged μ-alkylidene intermediate **B** readily inserts into a γ-CH bond of the μ-pentylidene side chain to form the metallacyclobutane intermediate **D** (Schemes 5 and 6). If the coordinatively saturated intermediate **D** is unreactive toward H_2 but is capable of reacting with CO to re-form

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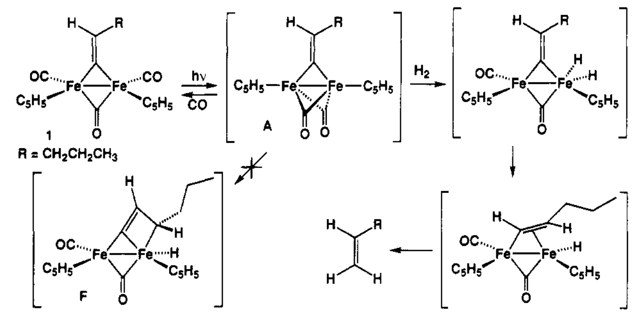
Scheme 6



2, then **D** would effectively protect **2** against reaction with H_2 and other reagents. Intermediate **D** can also account for the dehydrogenation of the side chain: β-hydride elimination of the metallacycle could produce the iron dihydride intermediate **E** which could subsequently reductively eliminate H_2 and coordinate the newly formed carbon–carbon double bond.

Examination of structures of complexes related to **2** and **3** helps to explain why only the μ-alkylidene ligand of **3** undergoes intramolecular CH insertion leading to dehydrogenation. The relatively narrow Fe–C–C (123°) and μ-C–C–C (112°) angles in μ-alkylidene complexes[15] allow the γ-carbon to approach to within 3.2 Å of iron; in contrast, the substantially wider Fe—C=C (140°) and μ-C=C—C (123°) angles in μ-alkenylidene complexes[16] keep the γ-carbon of **2** 3.6 Å away from iron. In addition, if the μ-alkenylidene complex **1** underwent an intramolecular insertion into a γ-CH bond, it would generate a very strained metallacyclobutene intermediate **F**.

At present, we are incapable of distinguishing between these two mechanistic hypotheses that adequately account for the differing reactivity patterns of **1** and **3**.

Experimental Section

General Methods. ¹H NMR spectra were obtained on a Bruker WP200 spectrometer. ¹³C NMR were obtained on a Bruker AM500 spectrometer (125.76 MHz). Infrared spectra were obtained on a Mattson Polaris spectrometer. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Solutions were manipulated in an inert-atmosphere glovebox or by standard Schlenk and high-vacuum techniques. Diethyl ether, THF, hexane, benzene, and benzene-d_6 were distilled immediately prior to use from purple solutions of sodium and benzophenone. CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2. Acetone-d_6 was dried over B_2O_3. For large-scale photolyses, freshly opened cans of anhydrous diethyl ether were employed directly.

Photolyses were performed either with a 450-W Hanovia medium-pressure vapor lamp or in a Rayonet photoreactor equipped with 15 RPR-3500A lamps, which provide 24 W in a broad region centered at 366 nm. NMR tubes were inverted during photolysis because insoluble material deposited on the tube walls during photolysis otherwise led to spectral broadening. Spectra were obtained after shaking and centrifuging solids to the top of the NMR tube.

$[C_5H_5Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CH_2CH_2CH_3)$ (2). A solution of $NEt_4{}^+HFe(CO)_4{}^-$ (5.3 mmol, 0.11 M) in THF at −78 °C was transferred via cannula into a stirred solution of $[C_5H_5Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_2CH_2CH_3)^+PF_6{}^-$ [1b] (4.4 mmol, 0.09 M) at −78 °C. After 30 min, the solution was warmed to room temperature and THF was removed on a rotary evaporator. The resulting viscous purple paste was extracted with diethyl ether (100 mL), the solution was filtered and evaporated to dryness, and the solid was sublimed (90 °C, $<10^{-3}$ mmHg) to give 1.06 g of red solid (90–95% **2**; 5–10% **4** by ¹H NMR analysis; 61% yield of **2**). Recrystallization from hexane at 0 °C gave pure **2**, mp 120–1 °C. ¹H NMR (C_6D_6): δ 11.45 (t, *J* = 8.2 Hz, μ-CH), 4.17 (s, 10H, C_5H_5), 3.36 (q, *J* = 8.2 Hz, $CHCH_2$), 1.91 (m, $CHCH_2CH_2$), 1.65 (sextet, *J* = 7.5 Hz, CH_2CH_3), 1.13 (t, *J* = 7.4 Hz, CH_3). ¹³C NMR (C_6D_6): δ 271.7 (μ-CO), 213.4 (CO), 178.9 (μ-CH), 87.1 (C_5H_5), 57.3 (μ-$CHCH_2$), 39.4 (CH_2Et), 23.5 (CH_2CH_3), 14.7 (CH_3). IR (CH_2Cl_2): 1973 cm⁻¹ (s), 1935 cm⁻¹ (m), 1776 cm⁻¹ (s). UV-vis (CH_2Cl_2): λ (log ε) 222 (4.38), 278 (3.95), 336 (3.81), 504 (2.92) nm. HRMS-FAB (obtained on a VG AutoSpec at VG Instruments, Inc., in Danvers, MA): calcd for $C_{18}H_{20}Fe_2O_3$, *m/e* 396.0111; found, *m/e* 396.0109. Anal. Calcd for $C_{18}H_{20}Fe_2O_3$: C, 54.59; H, 5.09. Found: C, 54.01; H, 5.09.

$[C_5H_5(CO)Fe](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CHCH_2CH_3)[FeC_5H_5]$ (3). A solution of **2** (150 mg, 0.38 mmol) in 500 mL of anhydrous diethyl ether was photolyzed for 1 h with a 450-W medium-pressure Hanovia mercury vapor lamp in a large immersion well under a continuous nitrogen purge. The resulting green solution was concentrated to 50 mL, filtered to remove a brown solid, and evaporated to dryness to give **3** (70.2 mg, 6% $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ (**4**) impurity, 44% yield), as a green solid. Column chromatography (alumina, 4:1 hexane:ether) provided pure **3** (17 mg, 12%), mp 165 °C dec. ¹H NMR (benzene-d_6): δ 11.65 (d, *J* = 6.2 Hz, μ-CH), 4.39 (dd, *J* = 8.7, 6.2 Hz, μ-CHC*H*), 4.25 (s, C_5H_5), 3.99 (s, C_5H_5), 1.30, 1.13 (complex multiplets, C*HH*CH_3), 0.99 (t, *J* = 7 Hz, CH_3), −0.32 (q, *J* = 8.7 Hz, μ-CHCHC*H*). ¹³C NMR (CD_2Cl_2): δ 269.8 (μ-CO), 216.4 (CO), 172.9 (μ-CH), 86.6 (C_5H_5), 84.8 (μ-CH*C*H), 82.8 (C_5H_5), 67.9 (*C*HCH_2), 29.8 (CH_2), 16.5 (CH_3). IR (CH_2Cl_2): 1943 (s), 1768 (m) cm⁻¹. HRMS-El (Kratos MS-80): calcd for $C_{17}H_{18}Fe_2O_2$, *m/e* 366.0007; found, *m/e* 366.0017.

GC Detection of H_2 from Photolysis of 2. A benzene-d_6 solution of **2** (10 mg, 0.025 mmol, 0.05 M) and 4,4′-dimethylbiphenyl (0.05 M, internal NMR integration standard) was photolyzed in a sealed NMR tube in a Rayonet photoreactor. After 181 h, ¹H NMR integration indicated 14% remaining **2** (δ 3.32), 41% formation of **3** (δ 3.99, 48% yield from **2**), and 13% **4** (δ 4.21, 15% yield from **2**). $[C_5H_5Fe(CO)]_4$, which was occasionally observed as a side product, was not observed.

The NMR tube was broken under vacuum into a 7.3-mL closed apparatus topped with a septum. N_2 was added to atmospheric pressure, and a 100-μL sample of the gas mixture was injected on a thermal conductivity gas chromatograph (25 °C, 5-Å molecular sieve column, N_2 carrier gas). A single peak for H_2 (retention time 15 s) was seen. Comparison with standard mixtures of H_2 and N_2 indicated that the mixture contained 3% H_2 (0.01 mmol, ~1:1 H_2:**3**).

Toepler Pump Assay of H_2 and CO from Photolysis of 2. A solution of **2** (26.5 mg, 67 μmol) in 15 mL of toluene was photolyzed for 68 h in a sealed vessel in a Rayonet photoreactor. The flask was attached to a Toepler pump system, the solution was frozen in liquid N_2, and the noncondensible gasses (23 μmol) were transferred to the Toepler system using three freeze–pump–thaw cycles. The gasses were then circulated on the Toepler pump system through a loop containing solid CuO at 300 °C to oxidize CO to CO_2 and H_2 to H_2O. The gas mixture was then circulated through a liquid nitrogen cooled trap. No measurable amount of gas was left in circulation. The trap was warmed to −80 °C, and the amount of CO_2 (12 μmol, 18% yield of CO from **2**) was measured in the Toepler system and removed by an external vacuum pump. The trap was warmed to room temperature, and the amount of H_2O vapor (7 μmol, 10% of H_2 from **2**) was measured in the Toepler system.

Solvent was evaporated from the original photolysis solution to give 39.3 mg of a solid. ¹H NMR analysis (benzene-d_6) showed a 55:35:10 ratio of **3** (δ 3.99 and 4.25):**4** (δ 4.22):$[C_5H_5Fe(CO)]_4$ (δ 4.63) and no **2**.

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Photolysis of 2 with ^{13}CO. A solution of 2 (60 mg, 0.15 mmol, 0.003 M) in Et_2O under ^{13}CO (90% ^{13}C, 750 mmHg, 4.0 mmol) in a water-cooled quartz flask equipped with a septum was photolyzed in a Rayonet photoreactor. Aliquots were withdrawn after 10, 20, 30 and 120 min and evaporated to dryness, and the solids were dissolved in benzene-d_6 containing $Cr(acac)_3$ (0.05 M as a shiftless relaxation reagent) immediately prior to ^{13}C NMR analysis. A 5-s relaxation delay was employed in the NMR experiment to ensure accurate integration of ^{13}C signals. The extent of ^{13}CO incorporation was measured by comparison of the ^{13}C NMR integrations for the bridging and terminal CO groups (δ 271 and 213) with those of the Cp group (δ 87).

Effect of Added CO on Photolysis of 2. A solution of 2 (0.05 M) and 4,4′-dimethylbiphenyl (internal NMR integration standard) in benzene-d_6 was divided into three NMR tubes. Two of the tubes were sealed under vacuum, and one of the tubes was sealed under CO (660 mmHg). Tubes were inverted and photolyzed in a Rayonet photoreactor. The extent of reaction as a function of time was followed by ^{1}H NMR integration of the μ-CHR resonance of 2 at δ 3.32, of the cyclopentadienyl resonance of 3 at δ 3.99, and of the δ 2.15 methyl peak of the internal standard.

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