

# Low-Temperature Photochemistry of $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ (R = H, Me): Substitution by P-Donor Ligands and Kinetics of Thermal Fe-Mn Bond Homolysis

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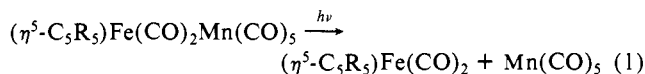
**Abstract:** Low-temperature irradiation of  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  (R = H, Me) results in loss of CO as the only detectable photoprocess ( $\Phi_{\text{app}}$  for CO =  $10^{-3}$  at 313 nm, and  $\Phi_{313}/\Phi_{366} = 20$  at 93 K) and yields a coordinatively unsaturated dinuclear photoproduct,  $(\eta^5\text{-C}_5\text{R}_5)\text{FeMn}(\text{CO})_6$ . It should be appreciated that CO loss and Mn-Fe bond cleavage are competitive processes with CO loss far more dominant at low temperature in a rigid glass. Warming of a glass containing  $(\eta^5\text{-C}_5\text{R}_5)\text{FeMn}(\text{CO})_6$  in the presence of  $\text{PR}_3$  (R = Ph, OPh) results in formation of  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PR}_3$ . The substitution product could be generated by an independent route from irradiation of a room temperature solution of  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}(\text{CO})_4\text{PR}_3]_2$ . Spectroscopic evidence, including IR, UV-vis, NMR, and MS, supports the conclusion that substitution of CO by  $\text{PR}_3$  in  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  occurs exclusively on the Mn atom. It was further determined that  $\Phi_{\text{diss}}$  for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  at room temperature in the presence of  $\text{P}(\text{OPh})_3$  in  $\text{CCl}_4$  is  $0.89 \pm 0.08$  and  $0.89 \pm 0.1$  at 313 and 366 nm, respectively, and  $\Phi_{\text{app}}$  for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$  is  $0.26 \pm 0.03$  and  $0.29 \pm 0.04$  at 313 and 366 nm, respectively, in the same solution. The products  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  are labile with respect to Fe-Mn bond cleavage and a kinetic analysis yielded activation parameters for this thermal reaction:  $\Delta H^\ddagger = 106 \pm 6$  and  $84.3 \pm 4$  kJ mol $^{-1}$  for R = H, Me, respectively, and  $\Delta S^\ddagger = 41.5 \pm 40$  and  $-21.4 \pm 23$  J mol $^{-1}$  K $^{-1}$  for R = H and Me, respectively.

In this article we report on the photochemical loss of CO from the heterodinuclear molecules,  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  (R = H, Me). While it is true that CO loss has been found to be a primary photoprocess for homodinuclear compounds, such as  $\text{Mn}_2(\text{CO})_{10}^1$  and  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$  (R = H, Me),<sup>2</sup> this information does not facilitate a prediction as to whether, for the heterodinuclear compounds  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , photochemically promoted CO loss can be selective for Fe or Mn or whether such selectivity could be controlled by altering the excitation wavelength. Further, it is known that both  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$  and  $\text{XMn}(\text{CO})_5$  complexes<sup>3a</sup> undergo efficient photostitution, yet such data do not allow conclusions regarding photochemical ejection of CO from the Fe-Mn complexes. The photochemical reactivity patterns of heterodinuclear complexes have been explored in only a few cases,<sup>3-5</sup> and the use of photochemistry as a tool in studying such systems should at least provide much needed synthetic and mechanistic information.

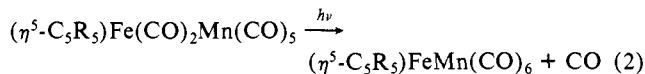
Interest in the chemistry of heterodinuclear compounds stems from the desire for development of reactivity patterns which could exploit the cooperativity between metal centers in a single molecule. It is control over reactivity at one metal center or the other that will aid in the optimization of catalytic or stoichiometric chemical transformations with multinuclear metal-metal bonded transition-metal complexes. A large body of information is available on the synthesis and characterization of mixed-metal compounds,<sup>6</sup> but few studies have demonstrated that site selectivity can be achieved in thermal substitution reactions. A recently published study of  $(\text{CO})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$  has shown that thermal substitution of CO by  $\text{PPh}_3$  occurs only on the Ru atom.<sup>7</sup> In another report it was found that the mixed-metal cluster,  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , undergoes substitution of CO by a variety of P-donor ligands only on the Ru atom.<sup>8</sup> The elucidation of site-selectivity can be further complicated if reaction at a particular metal center is accompanied by disruption of the metal-metal interaction or geometric isomerization as was discovered to be the case for the reaction of  $\text{PPh}_3$  with  $(\text{CO})_4\text{Fe}(\mu\text{-AsMe}_2)\text{Mn}(\text{CO})_5$ .<sup>9</sup>

We now report the results of an investigation of the photostitution properties of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ . Basically, Fe-Mn homolysis and CO loss are competitive excited-state processes. Previous investigation<sup>4</sup> of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  and similar compounds has in-

dicated that efficient photochemical homolytic cleavage of the Fe-Mn bond occurs in room temperature alkane solution, eq 1.



The resulting metal-centered radicals can be subsequently trapped with alkyl halides leading to production of the mononuclear metal carbonyl halides. Our present findings indicate that the near-UV irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  at low temperature in alkane glasses leads to loss of CO as the only observed primary photoprocess, eq 2. The photogenerated intermediates can be



spectroscopically characterized at low temperature, and their reactivity toward  $\text{PPh}_3$ ,  $\text{P}(\text{OPh})_3$ , and  $\text{CCl}_4$  has been examined. The principal finding is that substitution by the P-donor ligands occurs exclusively on the Mn atom to give  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{L}$  complexes. Unfortunately, it is not possible to prepare complexes  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  that are enriched

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Table I. Spectroscopic Data for Relevant Compounds

compound <sup>a</sup>	IR ( $\nu_{CO}$ ), ( $\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup> ) <sup>b</sup>	UV-vis ( $\epsilon \times 10^{-4}$ L mol <sup>-1</sup> cm <sup>-1</sup> ) <sup>c</sup>
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Fe(CO) <sub>2</sub> Mn(CO) <sub>5</sub>	2080 (3600), 2013 (1700), 1990 (14000), 1984 (sh), 1974 (5600), 1944 (950)	385 (4.0), 490 (0.5)
( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )Fe(CO) <sub>2</sub> Mn(CO) <sub>5</sub>	2071 (10000), 2002 (6200), 1981 (19000), 1966 (9300)	407 (3.5), 536 (1.0)
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Fe(CO) <sub>2</sub> Mn(CO) <sub>4</sub> PPh <sub>3</sub>	2037 (3000), 1964 (21000), 1951 (7300), 1929 (6000)	415 (3.1), 525 (0.5)
( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )Fe(CO) <sub>2</sub> Mn(CO) <sub>4</sub> PPh <sub>3</sub>	2022 (2800), 1960 (17000), 1953 (8000), 1927 (5200)	420 (2.0), 580 (0.4)
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Fe(CO) <sub>2</sub> Mn(CO) <sub>4</sub> P(OPh) <sub>3</sub>	2047 (4000), 1978 (17000), 1967 (14000), 1947 (5800)	404 (3.0), 494 (0.8)
[( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Fe(CO) <sub>2</sub> ] <sub>2</sub>	1995 (3500), 1954 (2000), 1785 (4000)	410 (0.9), 520 (0.1)
[( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )Fe(CO) <sub>2</sub> ] <sub>2</sub>	1922 (3600), 1755 (2500)	420 (0.5), 533 (0.2)
[Mn(CO) <sub>5</sub> ] <sub>2</sub>	2047 (5600), 2012 (24000), 1980 (2200)	340 (3.5), 400 (0.6)
[Mn(CO) <sub>4</sub> PPh <sub>3</sub> ] <sub>2</sub>	1953 (14000)	375 (3.0), 440 (0.6)
[Mn(CO) <sub>4</sub> P(OPh) <sub>3</sub> ] <sub>2</sub>	1974 (15000)	370 (3.0), 410 (sh)
ClMn(CO) <sub>4</sub> PPh <sub>3</sub>	2095 (2410), 2030 (3060), 2010 (4230), 1958 (3510)	
ClMn(CO) <sub>4</sub> P(OPh) <sub>3</sub>	2102 (2380), 2036 (3100), 2015 (4240), 1964 (3400)	
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Fe(CO) <sub>2</sub> Cl	2055 (3060), 2011 (3020)	
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Fe(CO)P(OPh) <sub>3</sub> (Cl)	1989 (4900)	

<sup>a</sup>All data were recorded in toluene solution at 298 K. <sup>b</sup>Band positions in cm<sup>-1</sup>. <sup>c</sup>Band positions in nm.

in <sup>13</sup>CO at Fe or Mn to establish the origin of ejected CO at low temperature. P-donor ligand substitution products of ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> are thermally labile with respect to Fe–Mn bond homolysis, and a kinetic investigation of the thermal reaction of these compounds has led to a determination of activation parameters for Fe–Mn bond homolysis.

### Experimental Section

**Instrumentation.** Infrared spectra were obtained on a Nicolet Model 60SX or 7199 Fourier transform IR spectrometer. UV-visible spectra were recorded by using a Cary-17 spectrophotometer or a Hewlett-Packard 8451A diode array spectrometer. <sup>13</sup>C NMR spectra were recorded on a Bruker WM270 FTNMR spectrometer equipped with a B-VT 1000 variable-temperature unit. Chemical shifts were referenced to the ipso carbon of toluene-*d*<sub>8</sub>, occurring at 137.5 ppm.

Low-temperature measurements were performed with use of a Precision Cell, Inc. Model P/N 21000 variable-temperature cell with CaF<sub>2</sub> inner and outer windows, using N<sub>2</sub> as the coolant. The temperature of the alkane glass was monitored with a copper–constantan thermocouple in contact with the inner window of the cell.

Kinetic measurements were performed on the HP 8451A spectrometer fitted with a custom-built cell holder with a flow-through jacket. The temperature of the cell was controlled with a Forma Scientific, Inc. Model 2095 constant-temperature bath. The temperature of the sample was monitored continuously through the kinetic run with a gold–chromel thermocouple placed directly in contact with the reaction solution. Temperatures for the kinetic measurements are accurate to  $\pm 1$  °C.

**Irradiations.** The 313-nm irradiations were carried out with use of a Bausch and Lomb SP250 high-pressure Hg lamp filtered by a 10-cm H<sub>2</sub>O filter with Pyrex windows followed by a 1-cm cell containing a K<sub>2</sub>CrO<sub>4</sub>/K<sub>2</sub>CO<sub>3</sub> solution to give  $313 \pm 20$  nm. Near-UV irradiations for kinetic runs were performed with use of a GE Blacklite. Quantum yields were measured by using ferrioxalate actinometry to measure the light intensity for each sample.

**Materials.** Methylcyclohexane (MCH) was purchased olefin free ("Photorex" grade, J. T. Baker) and distilled from sodium under argon prior to use. Hexane and toluene were distilled from CaH<sub>2</sub> under argon prior to use. Mn<sub>2</sub>(CO)<sub>10</sub> and [( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> (R = H, Me) were obtained commercially (Strem Chemicals, Inc.) and were used without further purification for the synthesis of the mixed Fe–Mn compounds. PPh<sub>3</sub> was recrystallized from ethanol before use. CCl<sub>4</sub> was distilled from P<sub>2</sub>O<sub>5</sub> and stored under argon before use. All subsequently described chemical manipulations were carried out under inert atmosphere in an argon-filled glovebox.

**Preparation of ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> (R = H, Me).** The Fe–Mn species were prepared by photolysis of a mixture of Mn<sub>2</sub>(CO)<sub>10</sub> and [( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> in hydrocarbon solvent.<sup>4b,11</sup> Purification was by chromatography on Al<sub>2</sub>O<sub>3</sub> eluting with hexane. The Fe–Mn species elute after Mn<sub>2</sub>(CO)<sub>10</sub>.

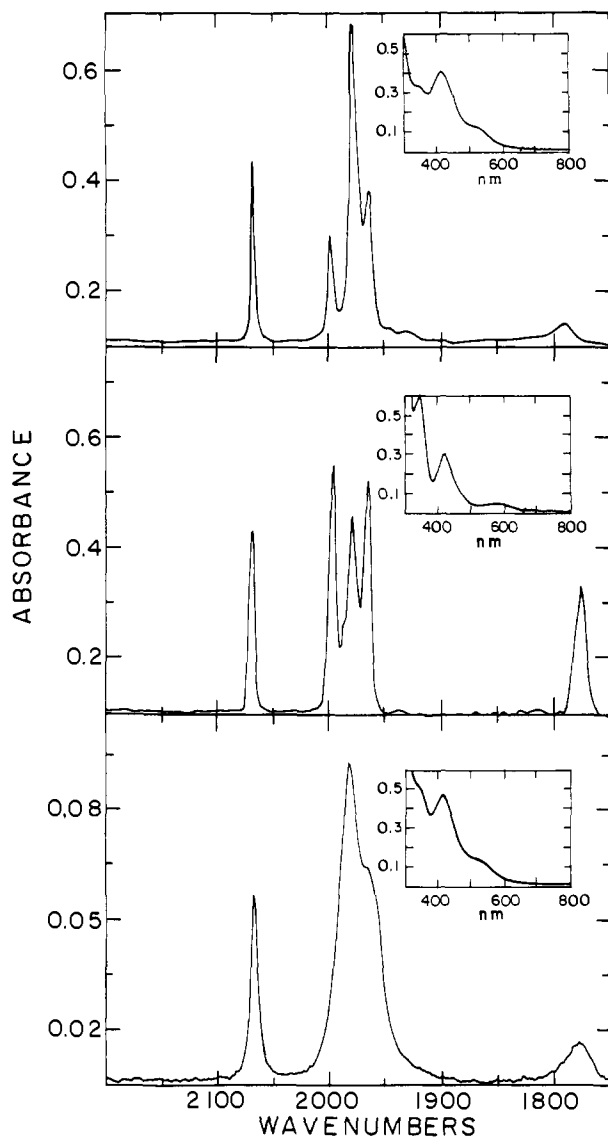
**Preparation of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>4</sub>P(OPh)<sub>3</sub>.** [Mn(CO)<sub>4</sub>L]<sub>2</sub> (L = PPh<sub>3</sub>, P(OPh)<sub>3</sub>) was prepared according to published procedures.<sup>4b,10,11</sup> A 200-mL round-bottom flask was charged with 100 mL of dry, deoxygenated toluene, 0.08 g of [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub>, and 0.20 g of [Mn(CO)<sub>4</sub>P(OPh)<sub>3</sub>]<sub>2</sub>. The solution was stirred under argon and irradiated with a 550-W Hanovia medium-pressure Hg arc with the output filtered for  $\lambda > 366$  nm. The reaction was monitored by IR spectroscopy to follow the growth of absorption at 2047 cm<sup>-1</sup>. The irradiation was discontinued after about an hour, when the relative amount of the product did not increase above 30% conversion. The

solvent was subsequently removed by vacuum. The residue was taken up in the minimum amount of toluene and chromatographed in the dark on grade 1 alumina with 6:1 hexane–toluene. The product was an orange band, eluting second after the residual [Mn(CO)<sub>4</sub>P(OPh)<sub>3</sub>]<sub>2</sub>. The chromatographic fraction was reduced in volume by suction and precipitated with pentane. The powder was collected by suction filtration, washed with pentane, and dried under vacuum in the dark over night. Yield: 0.02 g, 16%. IR in toluene solution: 2047 (4000), 1978 (28000), 1967 (12000), 1947 (5500) cm<sup>-1</sup> (absorptivities in M<sup>-1</sup> cm<sup>-1</sup>). UV-vis: 404 (25000), 494 (5000) nm (absorptivities in M<sup>-1</sup> cm<sup>-1</sup>). <sup>1</sup>H NMR  $\delta$  7.31 (d, 6 H, *J* = 7.9 Hz), 7.02 (t, 6 H, *J* = 7.5 Hz), 6.86 (t, 3 H, *J* = 7.4 Hz), 4.12 (s, 5 H) (benzene-*d*<sub>6</sub>). <sup>13</sup>C NMR  $\delta$  83.6 (s) 222.7 (s) (toluene-*d*<sub>8</sub>). <sup>31</sup>P NMR  $\delta$  170.6 (broad) (toluene-*d*<sub>8</sub>, referenced externally to P(OMe)<sub>3</sub>). Exact mass determined by FAB/MS: calculated for C<sub>29</sub>H<sub>20</sub>O<sub>9</sub>PMnFe 653.9575, determined 653.9600, error 2.5 mmu, 38 ppm.

**<sup>13</sup>CO-Enriched Compounds.** Enriched dinuclear metal compounds were prepared by irradiating the compound under an atmosphere of <sup>13</sup>CO and separating the product by chromatography. The heterodinuclear compounds were enriched in <sup>13</sup>CO by preparing the compounds from a photochemical cross-coupling reaction (*vide supra*) under an atmosphere of <sup>13</sup>CO. For ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> the resulting level of <sup>13</sup>CO enrichment was sufficient that the IR band at 2080 cm<sup>-1</sup> decreased in absorptivity by 80%. An attempt was made to prepare ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> which was selectively enriched on Fe by the reaction of <sup>13</sup>CO-enriched ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Na with Mn(CO)<sub>5</sub>Br in THF at room temperature. Filtering of the NaBr and chromatography in the dark yielded 8% of the product whose <sup>13</sup>C NMR spectrum was indistinguishable from the ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> obtained from photochemical cross-coupling synthesis under a <sup>13</sup>CO atmosphere.

### Results and Discussion

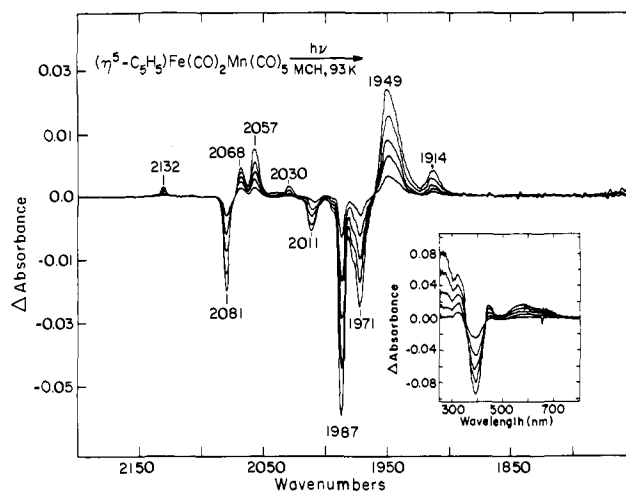
**IR and UV-vis Spectral Features of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub>.** Spectroscopic data for relevant compounds are presented in Table I. There are a few facts concerning the IR and UV-vis absorptions for ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> and ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> that deserve attention. The solution IR spectrum of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> remains qualitatively unchanged throughout the temperature range 298–93 K. However, cooling an alkane solution of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> is accompanied by significant changes in the IR and UV-vis spectra (Figure 1). In alkane solution, ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> has a very weak IR band at 1796 cm<sup>-1</sup>, which increases in absorptivity by about a factor of 5 as the solution is cooled to 93 K, taking into account an expected increase in intensity by a factor of about 1.3 due to solvent contraction. This change is accompanied by a decrease in the absorptivity of the band at 1981 cm<sup>-1</sup> and an increase in the bands at 2071, 2002, and 1966 cm<sup>-1</sup>. The optical spectrum of each of the dinuclear compounds in Table I is characterized by two prominent bands. ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub> exhibits an intense absorption at 385 nm and a weaker band at 490 nm, which are assigned as the  $\sigma\sigma^*$  and a  $d\pi\sigma^*$  transition, respectively.<sup>12</sup> The two prominent absorptions for ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>-



**Figure 1.** (Top)  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in MCH solution ( $7 \times 10^{-4}$  M) at 298 K. Inset shows UV-vis of the same sample. (Middle)  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in MCH solution, same sample as above, after cooling to 93 K. Inset shows UV-vis of the same sample. (Bottom)  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in acetonitrile solution ( $9.5 \times 10^{-4}$  M) at 298 K. Inset shows UV-vis of the same sample. All spectra were obtained with use of a 0.02 cm path length cell.

$\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  do not shift in energy appreciably upon cooling but increase in absorptivity by approximately 10% due to solvent contraction. However, the lower energy  $d\pi\sigma^*$  absorption maximum for  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  changes from 536 nm at 298 K to 576 nm at 93 K in MCH glass (insets of Figure 1). In contrast, the  $\sigma\sigma^*$  absorption in  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  does not shift in energy but decreases in absorptivity at low temperature. The decrease in the bands at 407 and 536 nm is concomitant with an increase in the band at 350 nm.

The IR and UV-vis spectra of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  do not show appreciable solvent polarity dependence. In room temperature  $\text{CH}_3\text{CN}$  solution the absorptivities of the IR bands are much less and the line widths are much greater than in MCH, but the qualitative aspects of the spectra remain unchanged (Figure 1). We attribute the temperature dependence of the IR and UV-vis spectra to the formation of a structural isomer of



**Figure 2.** FTIR difference spectra accompanying 313-nm irradiation of  $5 \times 10^{-4}$  M  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in MCH glass at 93 K. Inset shows corresponding UV-vis changes. Irradiation times are 5, 10, 15, 20, and 25 min.

$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in which significant bridging of at least one of the carbonyls occurs. Further evidence for this assignment is provided by the observation that the resonance at 1.25 ppm in the  $^1\text{H}$  NMR spectrum of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in MCH- $d_{14}$  broadens significantly upon cooling from 298 to 250 K, and two broad resonances can be distinguished but not completely resolved at 1.25 and 1.24 ppm at 250 K. The IR and UV-vis spectra of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  may be compared with those for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$ .<sup>13</sup> That a temperature-dependent equilibrium between bridged and nonbridged forms causes a shortening of the Ru-Ru bond is manifested by the shift of the  $\sigma\sigma^*$  absorption to higher energy by  $7000\text{ cm}^{-1}$ , with little effect on the  $d\pi\sigma^*$  transition. Evidently, for the bridged form of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , the  $d\pi\sigma^*$  state shifts to lower energy compared to the unbridged form, and this is attributed to a change in geometry around the metal centers. The absorption at 350 nm in the low-temperature UV-vis spectrum of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  is attributed to the  $\sigma\sigma^*$  absorption of the bridged form.

On the basis of the spectroscopic evidence it is concluded that, at low temperature, a CO-bridged structural isomer of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  represents a significant component of a mixture that is photosensitive with respect to CO loss, as discussed below. From the changes in the relative intensities of the IR bands as the temperature is decreased, it is evident that both isomers have an absorption at  $2071\text{ cm}^{-1}$ , and the absorptions at  $1770$  and  $2002\text{ cm}^{-1}$  are due to the bridged form only. The absorption at  $1981\text{ cm}^{-1}$  is probably due only to the unbridged form, whereas the shoulder which appears at  $1989\text{ cm}^{-1}$  is due only to the bridged form. Interestingly,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  shows no evidence for a CO-bridged structure under any conditions.

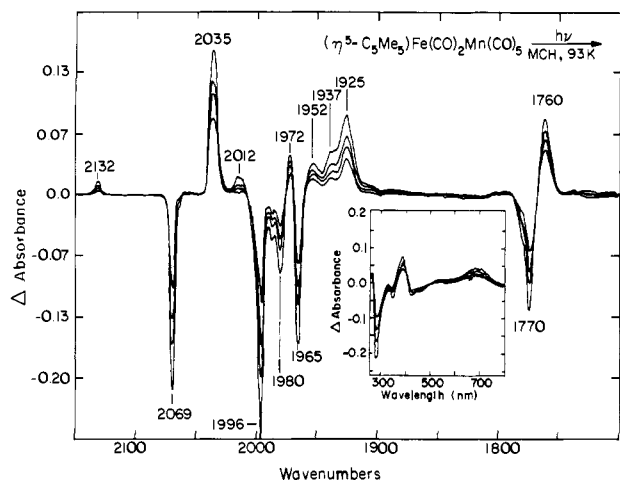
**Low-Temperature Photochemistry of  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ .** The IR and UV-vis spectral changes observed upon 313-nm irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in rigid methylcyclohexane glass at 93 K are presented in Figure 2. The IR difference spectra at low conversion (<25%) show disappearance of the features at  $2081$ ,  $2011$ ,  $1987$ , and  $1971\text{ cm}^{-1}$  due to the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  and concomitant appearance of a feature at  $2132\text{ cm}^{-1}$  due to uncomplexed CO in the glass. Previous work<sup>14</sup> in our laboratories has provided us with the information necessary to measure the relative amounts of metal complex consumed and uncomplexed CO formed in the glass. The ratio of absorbance change for the bands at  $2081$  and  $2132\text{ cm}^{-1}$  remains constant at low conversion, and, from the relative molar

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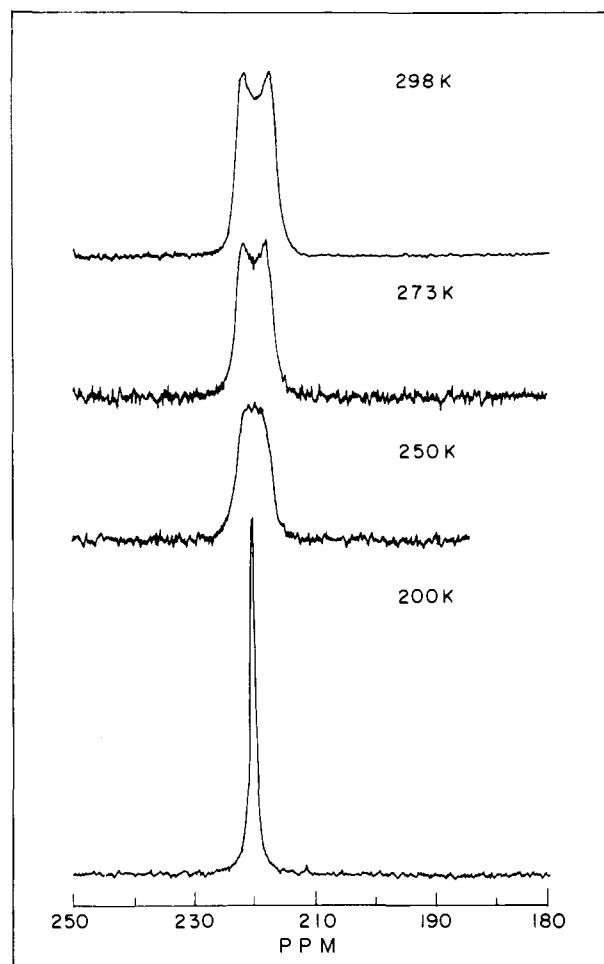
**Figure 3.** FTIR difference spectra accompanying 313-nm irradiation of  $3 \times 10^{-4}$  M  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in MCH glass at 93 K. Inset shows corresponding UV-vis changes. Irradiation times are 15, 20, 24, and 30 min.

absorptivities of these bands, it is clear that they represent a 1:1 molar ratio. We therefore conclude that near-UV irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in rigid MCH at 93 K results in extrusion of CO as the only detectable primary photoprocess at low conversion. We assign the bands at 2068, 2057, 2030, 1949, and 1914  $\text{cm}^{-1}$  to the dinuclear photoproduct, which contains six carbonyls as formulated in eq 2. The absence of any absorptions between 1900 and 1500  $\text{cm}^{-1}$  in the photoproduct suggests a lack of bridging carbonyls in the photoproduct. The relative quantum efficiencies for CO loss from  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in an MCH glass with 313- and 366-nm irradiation were measured, and it was found that  $\Phi_{313}/\Phi_{366} \sim 20$ . The absolute efficiency of CO photoextrusion in the glass under 313-nm irradiation is low,  $\sim 10^{-3}$ .

The optical changes (inset of Figure 2) clearly show the appearance of a weak low-energy absorption and a more intense absorption at higher energy concomitant with disappearance of the  $\sigma\sigma^*$  absorption due to the starting complex at 390 nm. The presence of two isosbestic points in the optical region also reflects the constant ratio of reactant consumed to photoproduct produced in the glass.

The photochemistry of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , under the same conditions as those described for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , results in spectral changes as shown in Figure 3. The key similarities between the results for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  are that (1) a 1:1 molar ratio of metal complex consumed to uncomplexed CO formed is observed at low conversion and (2) other UV-vis and IR absorptions appear which may be attributed to the formation of a dimeric photoproduct containing six carbonyls as indicated in eq 2. In the case of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , the bridging form of the starting heterodinuclear compound has an absorption at 1770  $\text{cm}^{-1}$  at 93 K. Upon irradiation the disappearance of the absorption at 1770  $\text{cm}^{-1}$  is accompanied by the appearance of a band at 1760  $\text{cm}^{-1}$ . This indicates that a bridging carbonyl is a structural feature of the photoproduct.

An important question that arises is whether the CO that is photoejected from the heterodinuclear complexes was originally bonded to Fe or Mn, or to both. For a stereorigid molecule, the answer could be most easily provided via preparation of a molecule in which the ligands on only one of the metal centers are enriched with  $^{13}\text{C}$ . The feasibility of such an experiment is suggested from a report concerning the CO exchange mechanism in the molecule  $(\text{CO})_5\text{ReMn}(\text{CO})_5$ .<sup>15</sup> To evaluate this possibility, the  $^{13}\text{C}$  NMR spectrum of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , approximately 80% enriched in  $^{13}\text{C}$ , was measured as a function of temperature (Figure 4). At room temperature, the broad feature



**Figure 4.** Temperature-dependent  $^{13}\text{C}$  NMR (67.3 MHz) for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  from 298 to 200 K in toluene- $d_8$  solution. Cyclopentadienyl  $^{13}\text{C}$  resonance (not shown) was observed at 83.3 ppm at all temperatures.

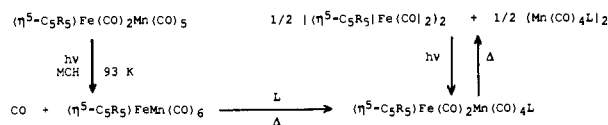
centered at 220 ppm is the only  $^{13}\text{C}$  resonance that is observed in the region 350–150 ppm. The  $^{13}\text{C}$  resonance due to the cyclopentadienyl ring, observed at 83.3 ppm, maintains a constant line width of about 12 Hz over the temperature range 298–200 K. The  $^{13}\text{C}$  resonance, however, sharpens progressively as the temperature is lowered and eventually becomes a singlet at 200 K with a line width of about 20 Hz. The unfortunate conclusion to be drawn is that CO site exchange in  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  is rapid on the NMR time scale, at least at 200 K, and this suggests that a selective labeling experiment is impossible for this compound. Interestingly, the broadening of the NMR line width at higher temperatures is not due to fluxional behavior of the molecule, rather it is likely due to  $^{55}\text{Mn}$ - $^{13}\text{C}$  spin-spin coupling, which varies due to the temperature-dependent spin-lattice relaxation of the quadrupolar  $^{55}\text{Mn}$  nucleus. This assignment is based upon detailed study of the  $^{51}\text{V}$ - $^1\text{H}$  spin system<sup>16a,b</sup> and on reports of "thermal decoupling" for R-Mn(CO)<sub>5</sub> (R = alkyl or benzyl).<sup>16c</sup> Further studies will be required to address the issue of site origin of the photoejected CO at low temperature. Nevertheless, an investigation of the reaction of the photogenerated coordinatively unsaturated intermediates,  $(\eta^5\text{-C}_5\text{R}_5)\text{FeMn}(\text{CO})_6$ , with P-donor ligands has led to discovery of regioselectivity in this net substitution reaction, as developed below.

**Reaction of  $(\eta^5\text{-C}_5\text{R}_5)\text{FeMn}(\text{CO})_6$  with  $\text{PR}_3$  (R = Ph, OPh) and  $\text{CCl}_4$ .** The ability to photogenerate CO loss products from  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  at low temperature in an alkane glass has prompted us to in-

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**Scheme I. Photochemical Generation of**  
 $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{L}$  (L =  $\text{PPh}_3$ ,  $\text{P}(\text{OPh})_3$ )



investigate the thermal reaction of these intermediates with the ligands  $\text{PR}_3$  (R = Ph, OPh). In the case of each metal complex, upon warming the MCH glass to 140 K after irradiation, back-reaction with CO occurs and regeneration of starting material is observed. The yield for regeneration of starting material was 90% in the best cases, even for carefully degassed samples. The same yield of starting material regeneration is obtained if  $\text{CCl}_4$  ( $7 \times 10^{-3}$  M) is present upon warming, a result that suggests the lack of importance of mononuclear, metal-centered radicals in the reaction. Metal-centered radicals were expected to react with  $\text{CCl}_4$  to give  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Cl}$  and  $\text{Mn}(\text{CO})_5\text{Cl}$ .<sup>4</sup> If the warm-up of the photogenerated hexacarbonyl is performed with a 10-fold excess of  $\text{PR}_3$  present (typically  $10^{-3}$  M  $\text{PR}_3$ ), annealing results in some substitution by  $\text{PR}_3$ , and this reaction also proceeds with the same chemical yield in the presence of  $5 \times 10^{-3}$  M  $\text{CCl}_4$ .

A series of experiments have been carried out in order to characterize the substitution products derived from warm-up of  $(\eta^5\text{-C}_5\text{R}_5)\text{FeMn}(\text{CO})_6$  in the presence of P-donor ligands. Table I includes the spectroscopic data for the P-donor substitution products generated by the warm-up experiments outlined above. The optical spectra of these products are similar to those of the starting compounds  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , featuring one intense band at an energy higher than a band an order of magnitude less intense. This is consistent with the formulation of these compounds as simple dinuclear substitution products of the starting metal complexes. However, one of the key issues is whether the products feature substitution on Fe, on Mn, or on both.

Further insight is provided by an examination of the 298 K solution photochemistry of a mixture of the corresponding homonuclear dimers,  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}(\text{CO})_4\text{PR}_3]_2$ . The near-UV irradiation of a toluene or MCH solution, equimolar in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$ , results in the formation of a product that is spectroscopically indistinguishable from  $(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6\text{PPh}_3$  prepared by warm-up of photogenerated  $(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6$  in the presence of  $\text{PPh}_3$ . Completely analogous results are obtained with  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]_2$  instead of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ . Thus, the substitution products can be generated by an independent route that is consistent with the P-donor ligand being coordinated to Mn (assuming that the Mn-P bond is inert) rather than Fe, and this chemistry is summarized in Scheme I. The cross-coupling synthesis has been used to prepare and isolate gram quantities of the compound  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$ , as described in the Experimental Section. The FAB/MS spectrum of this compound shows a molecular ion and fragment ions attributed to  $\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ , but no peak due to  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{P}(\text{OPh})_3$ . The <sup>31</sup>P NMR spectrum of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$  in toluene-*d*<sub>8</sub> shows a single broad resonance at 170.6 ppm (referenced to  $\text{P}(\text{OMe})_3$ ); this is compared to the broad resonance observed at 170.5 ppm observed for  $[\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3]_2$ . In contrast, the compound  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OPh})_3$ , prepared by irradiation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  in the presence of  $\text{P}(\text{OPh})_3$ ,<sup>17</sup> exhibits a sharp <sup>31</sup>P resonance at 154.0 ppm. The irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6\text{P}(\text{OPh})_3$  in  $\text{CCl}_4$  gives rise only to  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$  and  $\text{ClMn}(\text{CO})_4\text{P}(\text{OPh})_3$ . Furthermore, the irradiation of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OPh})_3$  and  $\text{Mn}_2(\text{CO})_{10}$  in toluene solution does not give rise to the expected IR bands at 2047 or 1947  $\text{cm}^{-1}$  due to  $(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6\text{P}(\text{OPh})_3$ ; instead, an IR feature at 2093  $\text{cm}^{-1}$  is attributed to the formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{P}$

**Table II. Quantum Efficiencies for Irradiation of**  
 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5^a$

compound	$\lambda_{\text{irrad}}^b$	$\Phi_{\text{diss}}$	$\Phi_{\text{appear}}$
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$	313	$0.89 \pm 0.08$	
	366	$0.89 \pm 0.10$	
$\text{Mn}(\text{CO})_5\text{Cl}$	313		$0.38 \pm 0.01$
	366		$0.39 \pm 0.03$
$\text{Mn}(\text{CO})_4(\text{P}(\text{OPh})_3)\text{Cl}$	313		$0.20 \pm 0.03$
	366		$0.22 \pm 0.03$
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-Mn}(\text{CO})_4\text{P}(\text{OPh})_3$	313		$0.26 \pm 0.03$
	366		$0.29 \pm 0.04$
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$	313		$0.40 \pm 0.09$
	366		$0.37 \pm 0.05$

<sup>a</sup> Irradiations of four independent samples at 10% conversion. Concentrations were  $7.26 \times 10^{-4}$  M  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  and  $5.39 \times 10^{-3}$  M  $\text{P}(\text{OPh})_3$ . Solutions prepared in degassed  $\text{CCl}_4$ . <sup>b</sup> Ferrioxalate actinometry was used to determine the light intensity for each individual sample.

$(\text{OPh})_3\text{Mn}(\text{CO})_5$ , although the Fe-substituted heterodinuclear compound has not been otherwise characterized. Although an X-ray diffraction study has not been performed on  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{P-donor})$ , it is concluded from the chemical and spectroscopic evidence presented that the P-donor is coordinated to Mn and not to Fe in  $(\eta^5\text{-C}_5\text{R}_5)\text{FeMn}(\text{CO})_6(\text{P-donor})$ . A more detailed structural study will be necessary in order to determine if the P-donor is in an axial or equatorial position, but we favor axial coordination that would yield less steric congestion and would be analogous to  $[\text{Mn}(\text{CO})_4\text{L}]_2$  and  $\text{Mn}_2(\text{CO})_{10}$ .

The quantum efficiency for metal-metal bond homolysis has been found to exceed 0.1 for certain homo- and other heterodinuclear systems,<sup>1,3a,4</sup> but no information is available on the efficiency of photochemical CO extrusion for heterodinuclear complexes. It was therefore of interest to quantitatively assess the photosensitivity of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in the presence of  $\text{P}(\text{OPh})_3$ . To investigate this, a  $10^{-4}$  M solution of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in  $\text{CCl}_4$  with  $10^{-3}$  M  $\text{P}(\text{OPh})_3$  was irradiated with 313- and 366-nm light. The reaction of a thermal blank was found to be small (<1% disappearance of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ ) during the time of the photochemical reactions. The results of quantum yield measurements are presented in Table II. It is found that the quantum efficiency at 313 nm for disappearance of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  is 0.89 in the presence of  $\text{P}(\text{OPh})_3$ , and this is accompanied by a rather high value of 0.26 for the quantum efficiency of appearance of the substitution product,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$ . The disappearance of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  is accounted for, within experimental error, by the appearance of  $\text{P}(\text{OPh})_3$ -substituted product,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$ , and by Fe-Mn homolysis products. A possible species,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{P}(\text{OPh})_3(\text{Cl})$ , is not observed by IR, possibly due to the fact that the expected IR band at 1989  $\text{cm}^{-1}$  is obscured. The  $\text{ClMn}(\text{CO})_4\text{P}(\text{OPh})_3$  presumably arises from substitution of CO by  $\text{P}(\text{OPh})_3$  at the radical  $\text{Mn}(\text{CO})_5$  stage;<sup>18</sup> it is a primary product. The fact that no  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  or  $\text{Mn}_2(\text{CO})_{10}$  is observed suggests that all radicals were scavenged by  $\text{CCl}_4$  and the formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$  results from CO extrusion as a primary photoprocess rather than from a radical pathway. It is noteworthy that the 298 K solution quantum yield, 0.26, for CO loss is so large compared to the rigid medium quantum yield,  $\sim 10^{-3}$ . This is likely a consequence of the "cage effect" associated with the rigid medium.

**Kinetics of Thermal Iron-Manganese Bond Homolysis.** An interesting aspect of the electronic structure of the heterodinuclear complexes is revealed from careful consideration of the  $\sigma\sigma^*$  transition energies for the relevant compounds, as presented in Table III. It has been previously demonstrated that, for a variety of heterodinuclear compounds containing an unsupported M-M'

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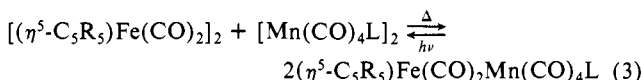
**Table III.** Comparison of  $\sigma\sigma^*$  Transition Energies in Relevant Complexes

compound	band position, <sup>a</sup> $\text{cm}^{-1}$
$\text{Mn}_2(\text{CO})_{10}$	29 400
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$	26 000
$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$	24 600
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$	22 600 <sup>b</sup>
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]_2$	19 400 <sup>b</sup>
$[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$	26 700
$[\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3]_2$	27 000
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$	24 100
$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$	23 800
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$	25 000

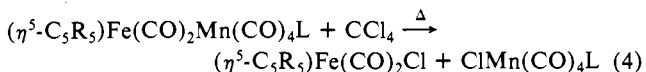
<sup>a</sup>Data recorded in toluene solution at 298 K. <sup>b</sup>Band position calculated from the Fe–Mn dimer and  $\text{Mn}_2(\text{CO})_{10}$  as discussed in text.

bond, the energetic position of the  $\sigma\sigma^*$  transition in M–M' is approximately the average of that observed in M–M and M'–M'.<sup>11</sup> The energetic position for the strongest bands in the compounds  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  (R = H, Me) falls half-way between the  $\sigma\sigma^*$  energies for the corresponding homonuclear dimers, provided that the values for the (unknown) nonbridged forms of the Fe dimers are calculated from the known compounds,  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  and  $\text{Mn}_2(\text{CO})_{10}$ .

The substitution products  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  are unstable relative to the corresponding homonuclear dimers. Attempts to isolate the heterodinuclear PPh<sub>3</sub> substitution products under rigorous light-excluded conditions have resulted only in the near quantitative recovery of  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$  and  $\text{Mn}_2(\text{CO})_{10}$ . Photogeneration of  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  in toluene solution has been monitored in an IR cell following near-UV irradiation of an equimolar mixture of the corresponding homonuclear dimers. When irradiation is discontinued, the heterodinuclear product reacts and, in the absence of oxygen, cleanly regenerates  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$ . This cycle of photogeneration followed by thermal back-reaction, eq 3, can be repeated several times at low conversion without



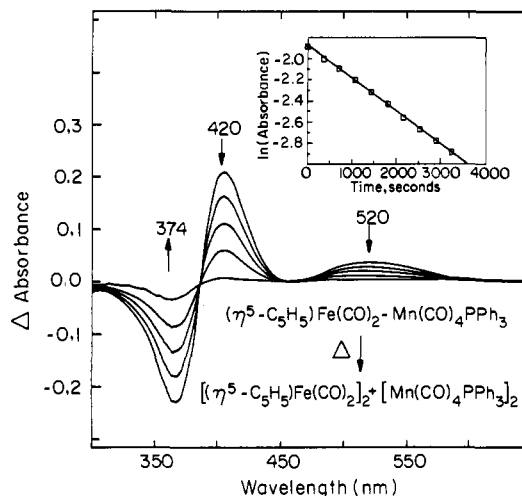
noticeable degradation of the system. If a volume of  $\text{CCl}_4$  equivalent to the initial volume of toluene is added to the reaction mixture immediately after photogenerating the  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  compounds, the near-quantitative formation of the metal carbonyl chlorides,  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Cl}$  and  $\text{ClMn}(\text{CO})_4\text{PPh}_3$ , occurs thermally, eq 4. The ability to follow



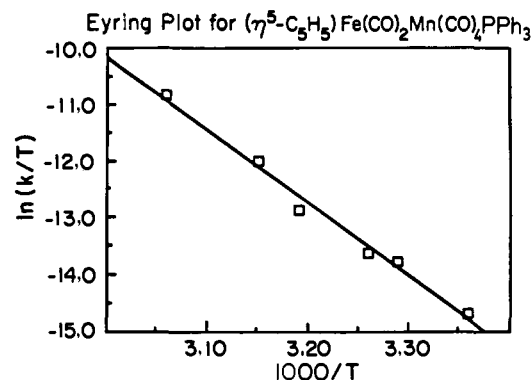
the thermal reaction of the compounds  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  has motivated a kinetic study, thus providing new information about Fe–Mn bond strengths.

Previous studies have provided information on the strengths of metal–metal bonds in other systems, notably including the kinetics of decomposition of a series of substituted manganese carbonyl dimers.<sup>10,19</sup> However, very little quantitative information is available on the relative strengths of metal–metal interactions in heterodinuclear systems. The thermal reaction of  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  to form  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$  has the advantage that all reactants and products are known. Furthermore, light can be used to perturb the system, and the thermal relaxation back to equilibrium can be monitored on a convenient time scale.

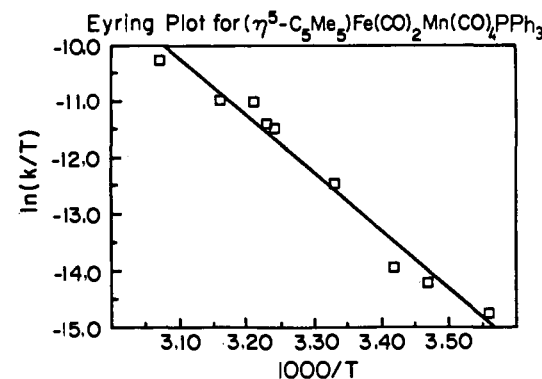
We have chosen to monitor the kinetics of the thermal reaction of the  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  complexes by UV–vis spectroscopy. This offers no technical advantage over other spectroscopic techniques, but it has the aesthetic appeal of being



**Figure 5.** UV–vis difference spectra accompanying thermal Fe–Mn bond homolysis for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  at 316 K in toluene solution. Arrows indicate direction of appearance or disappearance of absorptions. Inset shows plot of  $\ln(A - A_0)$  vs. time for disappearance of the band at 420 nm over a period of 1 h.



**Figure 6.** Temperature dependence of the rate of thermal Fe–Mn bond homolysis for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$ . Values of  $\ln(k_{\text{obsd}}/T)$  were obtained over the temperature range 297–326 K.



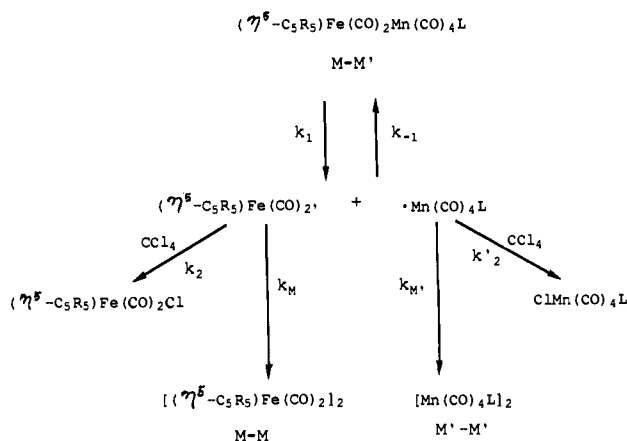
**Figure 7.** Temperature dependence of the rate of thermal Fe–Mn bond homolysis for  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$ . Values of  $\ln(k_{\text{obsd}}/T)$  were obtained over the temperature range 281–326 K.

able to monitor a chromophore that is directly associated with the reaction site. Following near-UV irradiation of a toluene solution of  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$ , the disappearance of the compounds  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  was monitored at 406 or 420 nm for R = H and Me, respectively. Figure 5 illustrates the quality of data that can be obtained under these conditions. In all cases, the functional dependence of [M–M'] was found to be strictly first order according to eq 5, with good linearity in a plot of  $\ln(\text{extent reaction})$  vs. time over 4 half-lives.

$$d[\text{M}-\text{M}']/dt = k_{\text{obsd}}[\text{M}-\text{M}'] \quad (5)$$

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**Scheme II.** Thermal Chemistry of  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  (R = Me, H)



**Table IV.** Activation Parameters for Fe–Mn Bond Homolysis

compound	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$	106 ± 6	41.5 ± 40
$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$	84.3 ± 4	-21.4 ± 23

Application of the Eyring equation to the temperature dependence of the rates,  $k_{\text{obsd}}$ , for reaction of  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  (Figures 6 and 7) shows behavior consistent with transition-state theory.<sup>20</sup> Consideration of the reaction sequence shown in Scheme II is necessary to derive activation parameters for M–M' bond homolysis. The rate of thermal cleavage of each of the homodinuclear compounds under consideration to produce the radicals  $[\text{M}^\bullet]$  and  $[\text{M}'^\bullet]$  was determined to be negligible compared to the time scale of the kinetic measurements for  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  by monitoring the reaction of each of the homonuclear complexes in  $\text{CCl}_4$  to produce the corresponding metal carbonyl halides. Values for the second-order radical coupling rate constants  $k_m$ ,  $k_m'$ , and  $k_{-1}$  can be estimated to be  $\sim 10^9$  l mol<sup>-1</sup> s<sup>-1</sup> on the basis of flash photolysis studies in solution of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]_2$ , and  $\text{Mn}_2(\text{CO})_{10}$ .<sup>21</sup> Assuming that the steady-state approximation for the concentrations  $[\text{M}^\bullet]$  and  $[\text{M}'^\bullet]$  is valid, the rate for homolytic cleavage may be expressed as a product of the forward rate,  $k_1[\text{M}-\text{M}']$ , and a factor which depends on the various different radical coupling rate constants, eq 6. The observed first-order behavior of the system is fully consistent with Scheme II and eq 6. The forward rate constant,  $k_1$ , was measured directly at 303

$$\frac{d[\text{M}-\text{M}']}{dt} = k_1 \left[ \frac{k_{-1}}{k_{-1} + \sqrt{k_m k_m'}} - 1 \right] [\text{M}-\text{M}'] \quad (6)$$

K by first irradiating a  $5 \times 10^{-3}$  M toluene solution of the dimers,  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$ , to produce  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  and then adding an equal volume of  $\text{CCl}_4$  to completely scavenge the radicals,  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2$  and  $\text{Mn}(\text{CO})_4\text{PPh}_3$ , which quantitatively yields the corresponding chlorides, eq 4. We assume  $k_2[\text{CCl}_4]$  and  $k'_2[\text{CCl}_4]$  to be sufficiently large to allow us to ignore back-reaction of radicals. Consistent with this assumption, we find only mononuclear metal carbonyl products. The value of  $k_1$  was determined by monitoring the disappearance of the heterodinuclear compounds by UV-vis, and  $k_1$  is  $4.28 \times 10^{-4}$  and  $1.41 \times 10^{-3}$  s<sup>-1</sup>, for R = H and Me, respectively, at 303 K. The ratio  $k_{\text{obsd}}/k_1$  was found to be 0.74 and 0.80 for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{-}$

$\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$ , respectively. The temperature dependence of  $k_{\text{obsd}}/k_1$  is considered to be negligible over the temperature range investigated. The activation parameters determined from  $k_1$  for reaction according to eq 3 are presented in Table IV;  $\Delta H^\ddagger$  was determined to be  $106 \pm 6$  and  $84.3 \pm 4$  kJ mol<sup>-1</sup>, and the associated  $\Delta S^\ddagger$  was  $41.5 \pm 40$  and  $-21.4 \pm 23$  J mol<sup>-1</sup> K<sup>-1</sup> for R = H and Me, respectively. Reported errors are standard deviations of the slope and intercepts of the Eyring plots.

The results show a significantly lower  $\Delta H^\ddagger$  for  $(\eta^5\text{-C}_5\text{Me}_5)\text{-Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$ , whereas the  $\Delta S^\ddagger$  values for these reactions in toluene are not significantly different within the experimental error. A large, positive  $\Delta S^\ddagger$  would be expected for a reaction that is kinetically dominated by a dissociative step, such as metal–metal bond cleavage. The relatively large experimental errors for the present  $\Delta S^\ddagger$  values preclude conclusions from being drawn concerning the relative amounts of order in the transition states for Fe–Mn bond cleavage in the compounds  $(\eta^5\text{-C}_5\text{R}_5)\text{-Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  (R = H, Me). The relative enthalpy values are consistent with the idea that increased steric congestion around the metal centers enhances the metal–metal bond lability, although, as yet, the relative contributions of steric and electronic factors cannot be separated in this case. Our enthalpies of activation may be compared to results for the Mn–Mn homolysis in the reaction of a series of substituted manganese dimers upon reaction with O<sub>2</sub> or CO.<sup>19b</sup> Present results show the Fe–Mn bond homolysis activation enthalpy for  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  to be about 40 kJ mol<sup>-1</sup> less than was measured for Mn–Mn bond homolysis in  $\text{Mn}_2(\text{CO})_{10}$ .<sup>19b,22</sup> That the determined labilities of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$ ,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$ , and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  correlate qualitatively with the energetic position of the  $\sigma\sigma^*$  transition is consistent with the proposition that the electronic spectra for this class of compounds can be used to predict relative labilities toward thermal metal–metal bond cleavage: a higher energy for the  $\sigma\sigma^*$  transition corresponds to a stronger Fe–Mn bond.

### Summary

The near-UV irradiation of  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  (R = H, Me) in rigid methylcyclohexane at 93 K results in the ejection of CO as the only detectable photochemistry, and this photoreaction is more efficient at 313-nm ( $\Phi = \sim 10^{-3}$ ) than at 366-nm irradiation by a factor of about 20. The resulting photoproduct,  $(\eta^5\text{-C}_5\text{R}_5)\text{FeMn}(\text{CO})_6$ , can be thermally scavenged with L = PPh<sub>3</sub>, P(OPh)<sub>3</sub>, and it was established from a variety of chemical and spectroscopic evidence that substitution occurs only on the Mn atom to give  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{L}$ . Due to the fluxional character of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , a selective <sup>13</sup>C-labeling study was deemed not feasible, and no conclusions can be drawn concerning the site origin of the photoejected CO ligand. The 298 K quantum efficiency for the appearance of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$  from the irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$  in  $\text{CCl}_4$  solution in the presence of P(OPh)<sub>3</sub> was found to be 0.26 and 0.29 at 313 and 366 nm, respectively, and these values indicate relatively efficient net CO loss from  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ . The compounds  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$  (R = H, Me) were found to be thermally labile with respect to Fe–Mn bond homolysis, and the kinetics were studied to determine the activation parameters for the thermal reaction. Results show a significantly lower activation enthalpy for  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4\text{PPh}_3$ ,  $\Delta H^\ddagger = 84.3$  kJ mol<sup>-1</sup>, than that for the R = H analogue,  $\Delta H^\ddagger = 106$  kJ mol<sup>-1</sup>. The present study, in comparison with other work, strengthens the hypothesis that, in compounds containing an unsupported metal–metal bond, the energetic position of the  $\sigma\sigma^*$  transition can be used as a predictor of relative lability.

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Registry No. ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub>, 12088-73-2; ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>5</sub>, 95421-00-4; ( $\eta^5$ -H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>4</sub>P(OPh)<sub>3</sub>, 108563-04-8; [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub>, 12154-95-9; [Mn(CO)<sub>4</sub>P(OPh)<sub>3</sub>]<sub>2</sub>, 15529-62-1; ( $\eta^5$ -H<sub>5</sub>)Fe(CO)<sub>2</sub>Mn(CO)<sub>4</sub>PPh<sub>3</sub>, 108563-05-9; ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-

Fe(CO)<sub>2</sub>Mn(CO)<sub>4</sub>PPh<sub>3</sub>, 108563-06-0; [ $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub>, 35344-11-7; [Mn(CO)<sub>5</sub>]<sub>2</sub>, 10170-69-1; [Mn(CO)<sub>4</sub>PPh<sub>3</sub>]<sub>2</sub>, 10170-70-4; ClMn(CO)<sub>4</sub>PPh<sub>3</sub>, 14841-08-8; ClMn(CO)<sub>4</sub>P(OPh)<sub>3</sub>, 85362-16-9; ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Cl, 12107-04-9; ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)P(OPh)<sub>3</sub>(Cl), 35025-27-5; Mn(CO)<sub>4</sub>P(OPh)<sub>3</sub>Cl, 85362-16-9; ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)FeMn(CO)<sub>6</sub>, 108563-07-1; ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)FeMn(CO)<sub>6</sub>, 108563-08-2; Mn(CO)<sub>5</sub>Cl, 14100-30-2; Mn<sub>2</sub>(CO)<sub>10</sub>, 10170-69-1.

## Reactions of Ditungsten Hexaalkoxides with Alkynylplatinum(II) Complexes: Formation of Heterometallic Dicarbido Complexes in Competition with Products Derived from Alkyne Metathesis

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**Abstract:** In hydrocarbon solutions *trans*-Pt(C≡CH)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (I) and W<sub>2</sub>(O-*t*-Bu)<sub>6</sub> (II) react to give by successive eliminations of *t*-BuOH *trans*-Pt(C≡CH)[C<sub>2</sub>W<sub>2</sub>(O-*t*-Bu)<sub>5</sub>](PMe<sub>2</sub>Ph)<sub>2</sub> (III) and *trans*-Pt[C<sub>2</sub>W<sub>2</sub>(O-*t*-Bu)<sub>5</sub>]<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (IV). Compounds III and IV are shown to contain dicarbido(4-) ligands on the basis of <sup>13</sup>C NMR studies and single-crystal X-ray crystallography. The PtC<sub>2</sub>W<sub>2</sub> units may also be classified as  $\pi$ -coordinated, dimetalla-substituted alkynes,  $\{(\mu\text{-PtC}\equiv\text{CW}_2)\equiv\text{W}_2\}$ . (*t*-BuO)<sub>3</sub>W=CC≡W(O-*t*-Bu)<sub>3</sub> (V) is also formed in the reaction between I with II. Its proposed mechanism of formation includes alkyne metathesis, *trans* to *cis* isomerization about Pt(II), and intramolecular reductive elimination from Pt(II). The complexes (quin)(*t*-BuO)<sub>3</sub>W=CH and Pt(PMe<sub>2</sub>Ph)<sub>4</sub> are formed in the reaction between I and II in the presence of excess quinuclidine and PMe<sub>2</sub>Ph, respectively, supporting the proposed mechanism. I and W<sub>2</sub>(O-*i*-Pr)<sub>6</sub>(py)<sub>2</sub> (II') yield products derived from alkyne metathesis, W<sub>2</sub>(O-*i*-Pr)<sub>6</sub>( $\mu$ -C<sub>2</sub>H<sub>2</sub>)(py)<sub>2</sub>, and dicarbide formation, *trans*-Pt(C≡CH)[C<sub>2</sub>W<sub>2</sub>(O-*i*-Pr)<sub>5</sub>](PMe<sub>2</sub>Ph)<sub>2</sub> (VI) and *cis*-Pt[C<sub>2</sub>W<sub>2</sub>(O-*i*-Pr)<sub>5</sub>](PMe<sub>2</sub>Ph)<sub>2</sub> (VII). VII, a *cis* complex, is unstable toward reductive elimination at ambient temperature, whereas IV, its bulkier *trans* analogue, is thermally stable to at least 75 °C. The reaction between II' and *trans*-Pt(C≡CMe)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (I') yields W<sub>3</sub>( $\mu$ -O-*i*-Pr)<sub>3</sub>(O-*i*-Pr)<sub>6</sub>( $\mu_3$ -CMe) as a product derived from C≡C scission. The Pt-containing products formed in the reactions of both II' with I and II' with I' are unstable toward reductive elimination, and Pt(PMe<sub>2</sub>Ph)<sub>4</sub> is eventually formed. Phosphine exchange in IV is very slow relative to that in III or I because of the steric bulk of the two -C<sub>2</sub>W<sub>2</sub>(O-*t*-Bu)<sub>5</sub> ligands. Carbon monoxide adds across the W=W bonds of IV forming first *trans*-Pt[C<sub>2</sub>W<sub>2</sub>(O-*t*-Bu)<sub>5</sub>][C<sub>2</sub>W<sub>2</sub>( $\mu$ -CO)(O-*t*-Bu)<sub>5</sub>](PMe<sub>2</sub>Ph)<sub>2</sub> (VIII) and then *trans*-Pt[C<sub>2</sub>W<sub>2</sub>( $\mu$ -CO)(O-*t*-Bu)<sub>5</sub>]<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (IX).

We are currently developing the organometallic chemistry of molybdenum and tungsten supported by alkoxide ligands with a view toward modeling the chemistry of the oxides of these elements.<sup>1</sup> Very few carbido clusters supported by alkoxide ligands are presently known,<sup>2</sup> especially when compared to the large variety and vast number of such clusters supported by carbonyl ligands.<sup>3,4</sup> Alkoxy ligands, which are strong  $\pi$ -donors, are clearly very different from the carbonyl ligand, a neutral  $\pi$ -acceptor. Because of this, the physical properties and reactivity of the carbido centers in the two types of clusters may be very different.

The reactions between W<sub>2</sub>(OR)<sub>6</sub>(M≡M) compounds and alkynes have yielded a variety of products including terminal<sup>5-9</sup> and bridging ( $\mu_2$ <sup>10,11</sup> and  $\mu_3$ <sup>12,13</sup>) alkyldiene complexes, alkyne

adducts,<sup>13-15</sup> and  $\mu$ -C<sub>4</sub>R'<sub>4</sub>-containing compounds.<sup>16,17</sup> We anticipated that reactions employing metal-alkynyl complexes would provide an entry into heterometallic carbido chemistry in which the heterometal atom(s) and alkoxide-supported tungsten(s) would be coordinated to either a C<sup>4-</sup> or C<sub>2</sub><sup>x-</sup> unit ( $x = 2, 3, 4, 5, \text{ or } 6$ ). Our initial efforts in this area were concentrated on reactions between *trans*-Pt(C≡CH)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub><sup>18</sup> (I) and W<sub>2</sub>(O-*t*-Bu)<sub>6</sub><sup>19</sup> (II). The choice of reactants was based on the well-defined coordination chemistry of Pt(II) and the wealth of information that can be gleaned from coupling constants involving spin-active nuclei, <sup>195</sup>Pt, <sup>13</sup>C, <sup>31</sup>P, <sup>183</sup>W, and <sup>1</sup>H as shown below. Small

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