larger distance from uranium and the resulting smaller difference in endo and exo chemical shifts compared to ortho results in a much lower coalescence temperature.

Measuring a dynamic process with such a small barrier by ^{1}H NMR spectroscopy as in the present example is unusual but is made possible by the unique structure and paramagnetism of uranocene that results in widely different magnetic environments for the endo and exo protons ($\Delta\nu$ = 20000–35000 Hz at 200 MHz). The barrier is substantially larger than the analogous rotation of a phenyl group in unsubstituted biphenyl. Various determinations of this quantity have been summarized recently.[14] Recent semiempirical and ab initio computations give rotation barriers in biphenyl of 1–2 kcal mol^{-1}. Experimental determinations include an estimate of 1.7 kcal mol^{-1} based on the retention volume of biphenyl on graphitized carbon black[15] and a recent electron diffraction value of 1.4 kcal mol^{-1}.[16] Undoubtedly, the higher barrier in diphenyluranocene results from the wider C–C–C bond angle in the [8]annulene ring compared to benzene.

Acknowledgment. This research was supported by the Director, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

---

[14] Haefelinger, G.; Regelmann, C. *J. Comput. Chem.* **1985**, *6*, 368.

[15] Poshkus, P. P.; Grumadas, A. J. *J. Chromatogr.* **1980**, *191*(1), 169.

[16] Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Samdal, S. *THEOCHEM.*, in press Cited in ref 12.

Photochemical Conversion of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) and Related Complexes to Ferrocene and Related Derivatives: Reactivity of the Monocarbonyl Intermediate

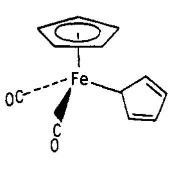
James A. Belmont and Mark S. Wrighton*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

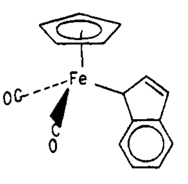
Received September 18, 1985

Irradiation of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) (I), (η^5-C_5H_5)Fe(CO)$_2$(η^1-indenyl) (II), or (η^5-indenyl)Fe(CO)$_2$(η^1-indenyl) (III) with near-UV light at 298 K leads to the loss of CO and formation of the sandwich complexes Fe(η^5-C_5H_5)$_2$, Fe(η^5-C_5H_5)(η^5-indenyl), or Fe(η^5-indenyl)$_2$, respectively. Low-temperature irradiation allows the observation of monocarbonyl intermediates which are thermally and photochemically sensitive. The chemistry is complicated by the fact that both the dicarbonyl starting materials and monocarbonyl intermediates can exist as two isomers, as deduced from IR spectral studies. The less thermodynamically stable of the monocarbonyl isomers typically thermally isomerizes to the more stable isomer. Only determination of the thermal rate of conversion of the more thermodynamically stable monocarbonyl isomer to the sandwich complex has been made quantitatively. The Arrhenius activation energy for the formation of Fe(η^5-C_5H_5)$_2$ from its monocarbonyl precursor is about 58 kJ/mol, while the formation of the Fe(η^5-indenyl)$_2$ from its monocarbonyl precursor occurs with an activation energy of 91 kJ/mol.

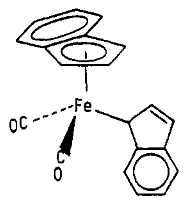
We wish to report on the generation of η^3-cyclopentadienyl intermediates from the near-UV irradiation of η^1-cyclopentadienyl complexes and the subsequent thermal conversion of the η^3-cyclopentadienyl species to η^5-cyclopentadienyl species. The complexes investigated are I–III. The cornerstone complex investigated is (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) (I)[1] which can be regarded as a member of the class of complexes (η^5-$C_5R'_5$)Fe(CO)$_2$R known[2-4] to be photosensitive with respect to CO loss (eq 1). Light-induced homolysis of the Fe–R bond (eq 2) is



I



II



III

$$\eta^5\text{-}C_5R'_5)Fe(CO)_2R \xrightarrow{h\nu} (\eta^5\text{-}C_5R'_5)Fe(CO)R + CO \quad (1)$$

$$(\eta^5\text{-}C_5R'_5)Fe(CO)_2R \xrightarrow{h\nu} (\eta^5\text{-}C_5R'_5)Fe(CO)_2 + R\cdot \quad (2)$$

a much less competitive excited-state decay route in most cases.[2] Of particular relevance to the work reported here is the fact that for R = η^1-allyl[3] or η^1-$CH_2C_6H_5$,[2b] loss of CO according to eq 1 yields the η^3-allyl or η^3-$CH_2C_6H_5$ complexes, respectively, with high chemical and quantum efficiency. Indeed, there is a good deal of work concerning light-induced extrusion of CO followed by hapticity changes in hydrocarbon ligands that has been reported.[5] We thus began our study with the expectation that near-UV irradiation would give an efficient conversion of an η^1-cyclopentadienyl complex to an η^3-cyclopentadienyl complex according to eq 3. Fortunately, the photochemical conversion can be effected at sufficiently low tem-

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

---

[1] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

[2] (a) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602. (b) Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

[3] Fish, R. W.; Giering, W. P.; Marten, D.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *105*, 101.

[4] Faller, J. W.; Johnson, B. V.; Dryja, T. P. *J. Organomet. Chem.* **1974**, *65*, 395.

[5] Hitam, R. B.; Mahmoud, K. A.; Rest, A. J. *Coord. Chem. Rev.* **1984**, *55*, 1; *J. Organomet. Chem.* **1985**, *291*, 321.

0276-7333/86/2305-1421$01.50/0 © 1986 American Chemical Society

peratures that the η^3-C_5H_5 species is inert, and warmup can be shown to yield η^3- to η^5-C_5H_5 conversion concomitant with loss of CO (eq 4).

$$(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5) \xrightarrow{\Delta} Fe(\eta^5\text{-}C_5H_5)_2 + CO \quad (4)$$

The work described here shows that the η^3- to η^5-conversion of a cyclopentadienyl group concomitant with CO loss is a process that can involve substantial activation energy, even when the ultimate product is one which is associated with considerable thermodynamic stability. Despite a great deal of interest in η^3-cyclopentadienyl complexes,[6] including crystallographically characterized complexes,[7,8] there is little direct information concerning the thermal parameters associated with extrusion of a 2e donor ligand concomitant with the η^3- to η^5-cyclopentadienyl conversion. Ring slippage of η^5-bonded systems to give η^3-bonded intermediates has been proposed as important in the mechanism of CO substitution of various η^5-indenyl–metal carbonyl complexes.[9] Also, such η^5- to η^3-cyclopentadienyl ring slippage has been proposed as important in the photochemical reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$[10] and $(\eta^5\text{-}C_5R'_5)M(CO)_2$ (M = Co, Ir),[11,12] including the oxidative addition of alkanes.[11] Also, irradiation of $Mo(CO)_6$ in the presence of C_5H_6 yields η^5-C_5H_5 products presumably via intermediates which undergo an η^3- to η^5-C_5H_5 conversion.[13] We now report results on the photochemical conversion typified by eq 3 and the subsequent thermal process represented by eq 4. Additionally, results for the η^1-indenyl (η^1-C_9H_7) species II and III are included providing information relating to the rate of η^3- to η^5-C_9H_7 conversion compared to η^3- to η^5-cyclopentadienyl conversion.

Experimental Section

Instruments and Equipment. UV–vis absorption spectra were recorded on a Cary 17 UV–vis–near-IR absorption spectrophotometer. IR spectra were recorded by using either a Nicolet 7199 or 60SX Fourier transform spectrometer. ^1H NMR were recorded by using a Bruker 250 MHz Fourier transform spectrometer.

Low-temperature IR spectra were recorded for deoxygenated alkane solutions of the complexes held in a cell with CaF_2 windows. The cell was mounted in a Specac Model P/N 21 000 Dewar assembly or in a CTI Cryogenics/Spectrim Model 21 variable-temperature sample holder. Irradiations and associated equipment are as described previously for other $(\eta^5\text{-}C_5R'_5)Fe(CO)_2R$ complexes.[2]

Chemicals. All solvents were reagent or spectroscopic grade and distilled or dried before use. Hexane and toluene were distilled from CaH_2 under N_2. Tetrahydrofuran (THF) and methylcyclohexane (MCH) were distilled from Na under Ar. Spectroscopic grade 3-methylpentane was dried by passing through activated alumina (Woelm neutral activity 1). Alumina for chromatography was MCB activated alumina. All reactions and manipulations of organometallic complexes were carried out in a Vacuum Atmospheres drybox or a conventional Schlenk line under Ar. $Fe(\eta^5\text{-}C_5H_5)_2$ (Aldrich) and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ (Strem) were used as received. Indene (Aldrich) was distilled prior to use. $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$,[14] $Fe(\eta^5\text{-}C_9H_7)_2$,[14] $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$,[15] and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$[1] were prepared by the literature procedures. $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_9H_7)$[16] was prepared[17] by treating a CH_2Cl_2 solution (50 mL) of $(C_5H_5)Fe(CO)_2{}^+BF_4{}^-$[17] (870 mg) with indene (750 mg) at ambient temperature and subsequently with Et_3N (333 mg) at 273 K. After chromatography (Al_2O_3, hexanes and then hexanes/THF (9/1)) the yellow product was crystallized from hexanes at low temperature. $(\eta^5\text{-}C_9H_7)_2Fe_2(CO)_4$[18] was prepared by cautiously treating a suspension of 10.9 g of $Fe(CO)_4I_2$[19] in 150 mL of Et_2O at 273 K with a 25 mL of Et_2O solution of 25 mM LiC_9H_7. CO is evolved rapidly. After being stirred and allowed to warm to room temperature for 1 h, the reaction mixture was passed through a short Al_2O_3 column, eluting with Et_2O to remove black material. After chromatography (Al_2O_3, toluene/hexanes (1/1) and then toluene/THF (5/1)) 1.17 g of $(\eta^5\text{-}C_9H_7)_2Fe_2(CO)_4$ was obtained. $(\eta^5\text{-}C_9H_7)Fe(CO)_2I$[20] was obtained by treating $(\eta^5\text{-}C_9H_7)_2Fe_2(CO)_4$ with I_2 as described for the analogous η^5-C_5H_5 species.[15]

$(\eta^5\text{-}C_9H_7)Fe(CO)_2(\eta^1\text{-}C_9H_7)$ was prepared by treating a suspension of 0.79 g of $(\eta^5\text{-}C_9H_7)Fe(CO)_2I$ in 50 mL of Et_2O with 10 mL of 0.24 M LiC_9H_7 in Et_2O. After being stirred for 5 h, the reaction mixture was passed through a short Al_2O_3 column eluting with THF. The solvent was removed under vacuum, and the residue was chromatographed (Al_2O_3, hexanes/THF (19/1 to 5/1)). The product was further purfied by a second chromatography (Al_2O_3, 200 mL of hexanes and then hexane/THF (19/1)). The product was crystallized from hexanes at low temperature. Elemental analysis (Schwartzkopf) was satisfactory. Anal. Calcd (Found): C 70.20 (70.06); H 4.12 (4.19). IR and ^1H NMR data for $(\eta^5\text{-}C_9H_7)Fe(CO)_2(\eta^1\text{-}C_9H_7)$ and other relevant complexes are given in Tables I and II.

Results

Photochemistry of I, II, and III in Alkane Solution. Near-UV irradiation of complexes I–III at 298 K in deoxygenated alkane solution results in rapid conversion to the corresponding metallocenes according to eq 5–7. By

$$\underset{\text{I}}{(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)} \xrightarrow{h\nu} Fe(\eta^5\text{-}C_5H_5)_2 + 2CO \quad (5)$$

$$\underset{\text{II}}{(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_9H_7)} \xrightarrow{h\nu} Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7) + 2CO \quad (6)$$

$$\underset{\text{III}}{(\eta^5\text{-}C_9H_7)Fe(CO)_2(\eta^1\text{-}C_9H_7)} \xrightarrow{h\nu} Fe(\eta^5\text{-}C_9H_7)_2 + 2CO \quad (7)$$

^1H NMR the chemical yield of the metallocene is greater than 90%, and the quantum yield for disappearance of the starting material at 366 nm exceeds 0.1. Table II gives ^1H NMR data for all starting materials and metallocene products. When monitored by IR, the bulk of the metal carbonyl absorption declines upon irradiation of I–III and only small product peaks are observed. For all three

---

[6] Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929 and references therein.

[7] Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329.

[8] Nesmeyanov, A. N.; Ustynyuk, N. A.; Makarova, L. G.; Andrianov, V. G.; Struchkov, Y. T.; Malyugina, S. G. *J. Organomet. Chem.* **1978**, *159*, 189.

[9] Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740 and references therein.

[10] (a) Fettes, D. J.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2311. (b) Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1365. Note that these workers have proposed that $(\eta^3\text{-}C_5H_5)Fe(CO)_3Me$ results upon irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ in a CO matrix. However, it is likely that this product is actually $(\eta^4\text{-}C_5H_5Me)Fe(CO)_3$; see ref 2b.

[11] Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624.

[12] Crichton, O.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc.*, Dalton *Trans.* **1980**, 167.

[13] Mills, III, W. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 5830.

[14] (a) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 796. (b) Fritz, H. P.; Kreiter, G. G. *J. Organomet. Chem.* **1965**, *4*, 198.

[15] King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110.

[16] Cotton, F. A.; Musco, A.; Yagupsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 6136.

[17] $(C_5H_5)Fe(CO)_2{}^+BF_4{}^-$ was synthesized by the procedure given in: Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

[18] McArdle, P. A.; Manning, A. R. *J. Chem. Soc. A* **1969**, 1498.

[19] Hieber, W.; Bader, G. *Chem. Ber.* **1928**, *61*, 1717.

[20] Abel, E. W.; Morehouse, S. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1706.

Table I. IR and UV Spectral Data for Relevant Complexes[a]

complex	T, K	absorption bands (ϵ or rel OD) IR, cm^{-1}	UV, nm
(η^5-C_5H_5)Fe(CO)$_2$-(η^1-C_5H_5) (two isomers)	298	2016 (6400)	315 (10000)
		2022 (2700)	
		1968 (6100)	
		1975 (3700)	
	169	2016 (1.00)	
		1966 (0.99)	
		2022 (0.29)	
		1973 (0.40)	
	83	2013 (1.00)	
		2018 (sh)	
		1963 (0.96)	
		1969 (sh)	
(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$	298	2006 (3000)	
		1962 (6400)	
		1794 (6200)	
(η^5-C_5H_5)Fe-(CO)(η^3-C_5H_5) (two isomers)	167	1933, 1964	
	83	1931, 1953	
(η^5-C_5H_5)Fe(CO)$_2$-(η^1-C_9H_7)	298	2013 (9200)	345 (7400)
		1964 (8100)	279 (sh)
	195	2012 (1.00)	
		1962 (0.86)	
	83	2010 (1.00)	
		1959 (0.80)	
(η^5-C_9H_7)$_2$Fe$_2$-(CO)$_4$[b]	298	2000 (0.67)	
		1953 (1.0)	
		1803 (0.42)	
		1794 (0.44)	
(η^5-C_5H_5)Fe-(CO)(η^3-C_9H_7)	298	1976	
	195	1936, 1976 (two isomers)	
	90	1934	
(η^5-C_9H_7)Fe(CO)$_2$-(η^1-C_9H_7)	298	2009 (9200)	371 (9800)
		1961 (8600)	285 (sh)
	195	2008 (1.00)	
		1959 (0.93)	
	90	2007 (1.00)	
		1957 (0.95)	
(η^5-C_9H_7)Fe-(CO)(η^3-C_9H_7)	288	1968	
	195	1967	
	109	1937	
(η^5-C_5H_5)Fe-(CO)(η^3-allyl)[c]	298	1940 (endo isomer)	
		1962 (exo isomer)	

[a] All data are for alkane, methylcyclohexane, or 3-methylpentane solutions. IR maxima have an error of about about 2 cm^{-1}. UV maxima have an error of about 3 nm. [b] IR data from ref 18, heptane solvent. [c] IR data from ref 3, petroleum ether or heptane solvent.

complexes small yields of products from the homolysis of the Fe—η^1-C_5H_5 or Fe—η^1-C_9H_7 bond are found. The metal carbonyl products from this low efficiency photoreaction are (η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$ or (η^5-C_9H_7)$_2$Fe$_2$(CO)$_4$ from I and II or III, respectively. Table I gives the essential metal carbonyl absorptions for the starting materials and products. With the assumption that the metallocenes are formed by primary photochemical loss of CO followed by thermal reaction of the monocarbonyl product, the qualitative aspects of the photochemistry of I–III are consistent with the general photochemical behavior of other (η^5-$C_5R'_5$)Fe(CO)$_2$R complexes.[2-5]

Low-temperature studies confirm that I–III are photosensitive with respect to loss of CO to give monocarbonyl products which are thermally labile and lead to the formation of the metallocenes. Figure 1 shows IR spectral changes showing the light-induced loss of CO from I and II at 77 K. The appearance of an absorption at 2132 cm^{-1}, due to uncomplexed CO,[21] is unambiguous evidence that light-induced loss of CO occurs. Note that I has four, not two, IR absorptions in the CO stretching region due to the

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

complex	chem shift, ppm vs. Si(CH$_3$)$_4$
(η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5)	4.85 (br, 5 H), 4.28 (s, 5 H)
Fe(η^5-C_5H_5)$_2$	4.05 (s)
(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$	4.61 (s)
(η^5-C_5H_5)Fe(CO)$_2$(η^1-C_9H_7)	7.50 (dd, 1 H), 7.29 (dd, 1 H), 7.00 (m, 2 H), 6.66 (dd, 1 H), 6.51 (d, 1 H), 4.00 (s, 5 H), 3.87 (d, 1 H)
Fe(η^5-C_5H_5)(η^5-C_9H_7)	7.42 (dd, 2 H), 6.80 (dd, 2 H), 4.80 (d, 2 H), 3.93 (t, 1 H), 3.66 (s, 5 H)
(η^5-C_9H_7)Fe(CO)$_2$(η^1-C_9H_7)	7.60 (m, 1 H), 7.29 (m, 3 H), 7.03 (m, 4 H), 6.63 (dd, 1 H), 6.55 (d, 1 H), 5.10 (s, 1 H), 4.76 (s, 1 H), 4.45 (d, 1 H), 3.88 (t, 1 H)
Fe(η^5-C_9H_7)$_2$	6.79 (m, 8 H), 4.47 (d, 4 H), 3.92 (t, 2 H)
(η^5-C_9H_7)$_2$Fe$_2$(CO)$_4$	7.21 (m, 4 H), 7.03 (m, 4 H), 5.04 (br s, 4 H), 4.82 (br s, 2 H)[b]

[a] All data are for cyclohexane-d_{12} solutions at 298 K. Integrations and peak multiplicities are given in parentheses. [b] The abbreviation "br s" indicates broad singlet.

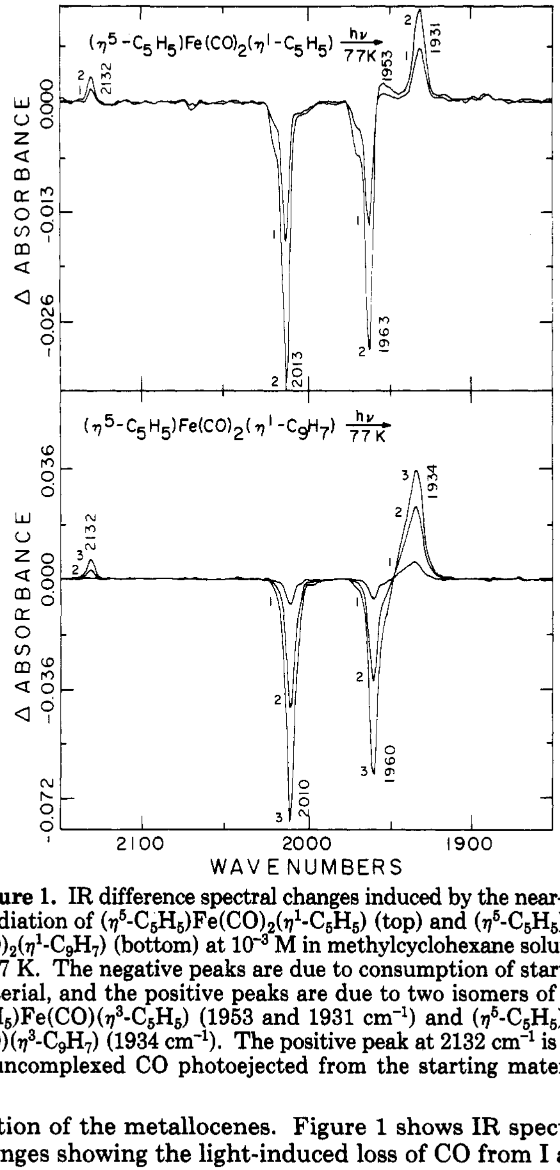


Figure 1. IR difference spectral changes induced by the near-UV irradiation of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) (top) and (η^5-C_5H_5)Fe-(CO)$_2$(η^1-C_9H_7) (bottom) at 10^{-3} M in methylcyclohexane solution at 77 K. The negative peaks are due to consumption of starting material, and the positive peaks are due to two isomers of (η^5-C_5H_5)Fe(CO)(η^3-C_5H_5) (1953 and 1931 cm^{-1}) and (η^5-C_5H_5)Fe-(CO)(η^3-C_9H_7) (1934 cm^{-1}). The positive peak at 2132 cm^{-1} is due to uncomplexed CO photoejected from the starting material.

---

(21) Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* **1985**, *24*, 0000.

fact that I exists as two isomers in solution.[22] As the solutions are cooled the four bands persist, but at the lowest temperature studied, about 77 K, the relative importance of the isomer absorbing at higher frequencies is much less than the 30–50% at 298 K. As the data in Figure 1 (top) show, both isomers are photosensitive. The principal absorptions at 2013 and 1963 cm^{-1} decline as do the weaker absorptions appearing as shoulders at 2018 and 1969 cm^{-1}. A comparison of the absorbance due to appearance of uncomplexed CO and the negative absorbance due to consumption of the starting complex I or II allows the conclusion that approximately (within 15%) one CO is produced per starting molecule consumed. This fact rules out significant net photochemistry stemming from homolysis of the Fe–η^1-C_5H_5 or Fe–η^1-C_9H_7 bond.

The metal carbonyl products from photolysis of the two isomers of I at 77 K are logically the two isomeric monocarbonyls analogous to the two isomers of (η^5-C_5H_5)Fe(CO)(η^3-allyl) formed from the irradiation of (η^5-C_5H_5)Fe$(CO)_2$(η^1-allyl).[3] The two isomeric monocarbonyl photoproducts arising from I absorb at 1931 cm^{-1} (isomer A) and 1953 cm^{-1} (isomer B), with isomer A being far more significant at 77 K (eq 8). At higher temperatures, where

$$\underset{\text{I}}{(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\eta^1\text{-C}_5\text{H}_5)} \xrightarrow{h\nu} \underset{\substack{\text{isomer A: 1931 cm}^{-1}\text{ at 77 K}\\ \text{isomer B: 1953 cm}^{-1}\text{ at 77 K}}}{(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\eta^3\text{-C}_5\text{H}_5)} + \text{CO} \quad (8)$$

the higher energy absorbing isomer of I is more important, isomer B becomes a more significant primary photoproduct. For example, short irradiation of I at about 170 K followed by immediate acquisition of the IR spectrum shows the ratio of absorption for isomer A (1933 cm^{-1}) to isomer B (1964 cm^{-1}) is about 3:1. The absolute positions of the absorptions for isomers A and B are in good agreement with the absorptions previously reported for the two isomers formed from irradiation of (η^5-C_5H_5)Fe$(CO)_2$(η^1-allyl).[3] Note there are small shifts of the absorptions at different temperatures (Table I). The shift in the absorption of isomer B from 1953 cm^{-1} at 77 K to 1964 cm^{-1} at 170 K seems somewhat larger than in the other cases, but it should be noted that the starting material absorption spectrum overlaps with that of the product (Figure 1), and it is difficult to assign the low-temperature absorption position for isomer B. The interesting correlation appears to be that one isomer of I, the one absorbing at higher frequencies, gives rise to a particular isomer of the monocarbonyl, the one designated as B and absorbing at higher energy. The ratio of the two isomers of (η^5-C_5H_5)Fe(CO)(η^3-allyl) complexes produced photochemically from the η^1-allyl precursor complex was also suggested to depend on the conformation of the precursor complex.[3] Unfortunately, the monocarbonyl products from I are themselves photosensitive, and all irradiations of I ultimately give Fe$(\eta^5$-$C_5H_5)_2$ according to eq 5. This is unfortunate, because it is impossible to accumulate sufficent concentrations of the monocarbonyl species to obtain NMR data that would substantially add to the characterization. As will be developed below, the monocarbonyl species are thermally labile with respect to formation of Fe$(\eta^5$-$C_5H_5)_2$ at temperatures where high sensitivity NMR could, in principle, be acquired for thermally inert substances.

Irradiation of II (Figure 1 (bottom)) results in formation of only one isomer of a monocarbonyl species at 77 K. The 1934 cm^{-1} absorption assigned to the photoproduct is presumably the analogue of isomer A produced from compound I. At 195 K irradiation of II gives two products, one absorbing at 1936 cm^{-1} (the species formed at 77 K) and one absorbing at 1976 cm^{-1}. The higher frequency absorption is assigned to a second isomer of the monocarbonyl product (η^5-C_5H_5)Fe(CO)(η^3-C_9H_7) (eq 9).

$$\underset{\text{II}}{(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\eta^1\text{-C}_9\text{H}_7)} \xrightarrow{h\nu} \underset{\substack{\text{isomer A}'\text{: 1936 cm}^{-1}\text{ at 195 K}\\ \text{isomer B}'\text{: 1976 cm}^{-1}\text{ at 195 K}}}{(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\eta^3\text{-C}_9\text{H}_7)} + \text{CO} \quad (9)$$

However, unlike I, compound II only shows two IR bands in the CO stretching region of the IR (at all temperatures investigated), and there is consequently no evidence for ground-state population of more than one isomer. Thus, the correlation between product isomer and starting isomer in the case of I may be fortuitous, though it is possible that photoexcitation of II leads to its isomerization concomitant with CO loss. As for the monocarbonyl products from I, the monocarbonyls from II are photosensitive with respect to further loss of CO, and the monocarbonyls cannot be accumulated in sufficient quantity to be investigated by NMR. The ultimate photoproduct from II at any temperature investigated, between 77 and 298 K, is given by eq 6.

The low-temperature photochemistry of III is somewhat different than that of I and II. Figure 2 shows the IR spectral changes as a function of irradiation time for III irradiated at 77 K. There is undoubtedly light-induced loss of CO as evidenced by the feature at 2132 cm^{-1} due to uncomplexed CO. The primary photoproducts, however, are very photosensitive with respect to further CO loss, based on the relative optical density changes associated with appearance of CO, disappearance of III, and appearance of the metal carbonyl products at 2015, 1962, and 1935 cm^{-1}. The ultimate photochemistry of III, even at the lowest temperature accessible (25 K) is given by eq 7. The absorption feature at 1935 cm^{-1} is associated with one isomer of (η^5-C_9H_7)Fe(CO)(η^3-C_9H_7) and part of the absorption at 1962 cm^{-1} is attributable to the other isomer (eq 10). The assignment of the 1962 cm^{-1} feature to isomer B″ (eq 10) is substantiated by the fact that irradiation of III at 195 K gives only one photoproduct, absorbing at 1967 cm^{-1}, that is assigned to isomer B″. The small difference in absorption maxima at 77 K and at 195 K is attributable to the change in the nature of the medium from a rigid matrix to a fluid solution. The photoproduct with absorption at 2015 cm^{-1} is difficult to identify. At least a portion of the 1962 cm^{-1} absorption is associated with the species absorbing at 2015 cm^{-1}, because irradiation at 25 K leads to disappearance of III, but there is no appearance of CO at the early irradiation times (less than 5% conversion). Under these conditions there is no 1935 cm^{-1}

$$\underset{\text{III}}{(\eta^5\text{-C}_9\text{H}_7)\text{Fe(CO)}_2(\eta^1\text{-C}_9\text{H}_7)} \rightarrow \underset{\substack{\text{isomer A}''\text{: 1935 cm}^{-1}\text{ at 77 K}\\ \text{isomer B}''\text{: 1967 cm}^{-1}\text{ at 195 K}}}{(\eta^5\text{-C}_9\text{H}_7)\text{Fe(CO)}(\eta^3\text{-C}_9\text{H}_7)} + \text{CO} \quad (10)$$

---

[22] (η^5-C_5H_5)Fe$(CO)_2$(η^1-C_5H_5) has been crystallographically characterized and shows only one conformer in the solid, presumably the dominant species at low temperature in rigid matrices: Bennett, M. J.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S. J.; Morehouse, S. M. *J. Am. Chem. Soc.* **1966**, *88*, 4371. However, the IR has been previously reported to show four bands in the CO region attributed to the presence of two conformers in solution: Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 7523.

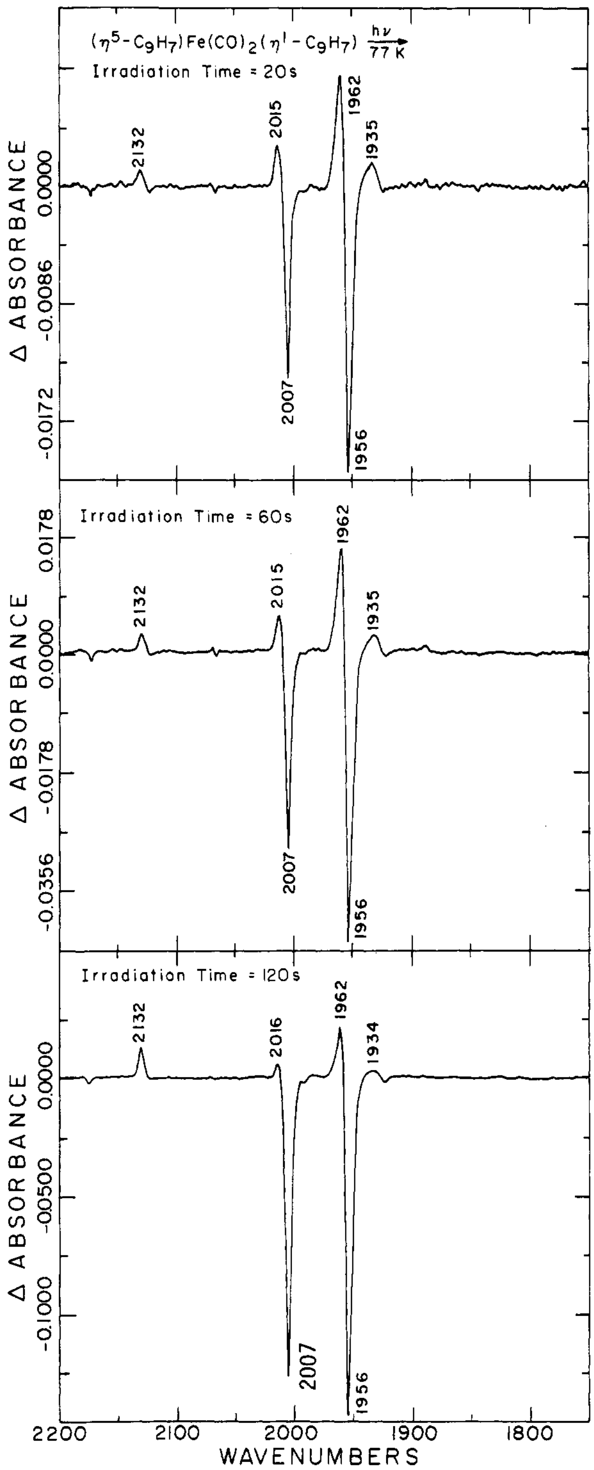


Figure 2. IR difference spectral changes as a function of near-UV irradiation time of 10^{-3} M $(\eta^5\text{-}C_9H_7)Fe(CO)_2(\eta^1\text{-}C_9H_7)$ in methylcyclohexane at 77 K. The feature at 1935 cm^{-1} is assigned to the CO-loss product $(\eta^5\text{-}C_9H_7)Fe(CO)(\eta^3\text{-}C_9H_7)$ and the feature at 2132 cm^{-1} is due to the uncomplexed CO photoejected from the starting material. The features at 2015 and 1962 cm^{-1} are assigned to an isomer of the starting material. The negative peaks are associated with consumption of starting material.

absorbing product, and the 2015 and 1962 cm^{-1} absorptions are in an approximately 1:1 ratio. Since no CO is produced when the product absorbing at 2015 and 1962 cm^{-1} is produced, the product must be a dicarbonyl. Irradiation of III in an alkane matrix at 77 K does not produce an EPR signal. The results suggest that the 2015 and 1962 cm^{-1} absorbing species is an isomer of III, and there are at least two realistic possibilities as products. One possibility is that the dicarbonyl product is another conformer of III analogous to the conformers of I that are observable at all temperatures in the starting material. The other possibility is that the product is a ring-slippage type product: $(\eta^3\text{-}C_9H_7)_2Fe(CO)_2$. Ring slippage of $\eta^5\text{-}C_5R_5$ has been invoked to explain some photochemical reactions at low temperatures.[10-12] Both possibilities for the nature of the isomer from III should have two IR absorptions in the CO stretching region. However, it is not possible to unambiguously establish the product identity with the data available. Warming samples containing the photogenerated 2015 and 1962 cm^{-1} species leads to the regeneration of III, and we shall assume that productive chemistry results only when CO is extruded to form the isomer(s) of $(\eta^5\text{-}C_9H_7)Fe(CO)(\eta^3\text{-}C_9H_7)$ (eq 10). It is attractive to consider the isomer from III to be a conformer, since this would allow a consistent correlation to be made between the conformation of the starting dicarbonyls and the isomer of the monocarbonyl formed. However, additional evidence, including results from studies of ^{13}CO-enriched complexes, is required to substantiate this conclusion.

To summarize the photochemistry of I–III, CO loss is an important primary photoprocess and ultimately leads to the metallocenes according to eq 5–7. The monocarbonyls from I to III can exist as two isomers and can be detected by IR in low-temperature media. The monocarbonyls are photosensitive with respect to CO loss at low temperature, and the metallocenes can be formed cleanly at 77 K. The monocarbonyls are also thermally reactive and give the metallocenes with quantitatively measureable rates, as will be developed in the section below.

Thermal Reactivity of the Photogenerated Monocarbonyls from I to III. The monocarbonyl species produced from irradiation of I–III are thermally reactive and yield formation of the metallocenes, in competition with regeneration of I–III via reaction with CO available in the solution from the primary photochemical conversion (eq 8–10). Detailed measurements have been made for the thermal reactions of isomer A and B of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5)$ and isomer B′ of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_9H_7)$. The quantitative measurements have been made by monitoring the IR spectral changes, at various temperatures, following photogeneration of the monocarbonyl species. All of the monocarbonyls can react with CO to regenerate the dicarbonyl starting materials, and this process is especially important for the monocarbonyls from II and III. For the experiments developed below the regeneration of the dicarbonyl accounts for less than 10% of the monocarbonyl that reacts. Thus, the rate of monocarbonyl disappearance can be regarded as a good approximation to the rate of formation of the metallocenes.

For the monocarbonyl photogenerated from I, $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5)$, IR spectral changes at 166 K in alkane solution are shown in Figure 3. In the top portion of the figure the IR spectral changes show that isomer A reacts to form some of isomer B, based on the growth of the absorption at 1964 cm^{-1}. It is also likely that some $Fe(\eta^5\text{-}C_5H_5)_2$ is formed, because the growth in absorbance at 1964 cm^{-1} is not equal to the loss in absorbance at 1933 cm^{-1} due to reaction of isomer A. Since isomers A and B are very similar, the extinction coefficients for the lone IR bands should be nearly equal. With this assumption, we conclude that isomer A undergoes reaction to form both isomer B and $Fe(\eta^5\text{-}C_5H_5)_2$ in an approximately 1:3 ratio at 166 K. In this case there is no regeneration of the dicarbonyl I. Equations 11 and 12 thus represent the

$$(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5) \xrightarrow{\Delta} Fe(\eta^5\text{-}C_5H_5)_2 + CO \quad (11)$$
isomer A or B

$$\underset{\text{isomer A}}{(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5)} \xrightarrow{\Delta} \underset{\text{isomer B}}{(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5)} \quad (12)$$

thermal chemistry of isomer A at 166 K. The rate constant for disappearance of isomer A is sufficiently large that no loss of isomer B occurs on the time scale where essentially complete consumption of isomer A is found. Note the large difference in the time axis of the top (disappearance of isomer A) and bottom (disappearance of isomer B) portions of Figure 3. Isomer B gives $Fe(\eta^5\text{-}C_5H_5)_2$ (eq 11) with a relatively small rate constant compared to reaction of isomer A (Figure 3 (bottom)). Figure 4 shows the Arrhenius plot for the conversion of isomer B to $Fe(\eta^5\text{-}C_5H_5)_2$; the activation parameters for the conversion are included in the figure. The activations parameters in Figure 4 are for 298 K.

Quantitative data for the conversion of isomer B′ of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_9H_7)$ to the metallocene (eq 13) have

$$\underset{\text{isomer B}'}{(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_9H_7)} \xrightarrow{\Delta} Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7) + CO \quad (13)$$

been obtained. The rate constants as a function of temperature are summarized by the data presentation in the bottom portion of Figure 4. In this case, temperatures close to room temperature are most convenient for the quantitative measurements. The activation parameters show that the conversion represented by eq 13 requires substantially greater activation energy than the analogous conversion for the η^3-bonded C_5H_5 system represented by eq 11. While quantitative data have not been acquired, the conversion of isomer B″ of $(\eta^5\text{-}C_9H_7)Fe(CO)(\eta^3\text{-}C_9H_7)$ gives the metallocene with rate constants and activation parameters that are similar to those for the chemistry represented by eq 13. The conversion of isomer B′ of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_9H_7)$ or isomer B″ of $(\eta^5\text{-}C_9H_7)Fe(CO)(\eta^3\text{-}C_9H_7)$ to the respective metallocenes is only competitive with back reaction with CO to reform the starting dicarbonyls. However, the reaction with CO occurs very slowly at the latter stages of the reaction and allows quantitative (approximately first-order decay) data to be obtained as a function of temperature near room temperature.

Discussion

Results concerning the photochemistry of I–III show that complexes I–III are unexceptional complexes of the $(\eta^5\text{-}C_5R'_5)Fe(CO)_2R$ class:[2-4] CO loss dominates the photochemistry in solution and homolysis of the Fe–R is a relatively minor primary event. Compound III shows the interesting additional reaction of isomerization to give a product that could not be unambiguously identified by IR. The fact that CO loss can be detected at 77 K from I to III is consistent with the ability of the η^1-bonded ligand to "trap" the presumed 16e intermediate produced by the photoejection of the CO. While a recent report describes the formation and IR detection of a 16e species from photoejection of CO from $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ at 12 K in polyvinyl chloride,[23] in the experiences of this laboratory it has not been generally possible to observe the 16e photoproduct $(\eta^5\text{-}C_5R'_5)Fe(CO)R$ from photoextrusion of CO from $(\eta^5\text{-}C_5R'_5)Fe(CO)_2R$ in rigid alkane media at temperatures as low as 40 K.[2,24] Even the $(\eta^5\text{-}C_5H_5)Fe(CO)Me$ is apparently not detectable in a CH_4 matrix at 12 K, suggesting that the polyvinyl chloride matrix has sites that tend to trap the 16e species.[23] In fact, detection of the photochemical formation of the monocarbonyl products at 77 K generally requires R to be capable of saturating the Fe center, e.g., R = η^1-$CH_2C_6H_5$, or the irradiation must be carried out in a donor matrix such as 1-pentene or 2-methyltetrahydrofuran. The 1951 cm^{-1} absorption for the monocarbonyl species obtained from irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ at 12 K in polyvinyl chloride is, in fact, seemingly too high in comparison with the Ru analogue and the starting material absorptions to be an unsaturated fragment;[23] perhaps there are sites in the polyvinyl chloride that serve to trap the monocarbnyl and lead to oxidative addition product(s). With respect to results under discussion here, the η^1- to η^3-conversion of C_5H_5 or C_9H_7 is apparently very fast and allows the detection of the monocarbonyl products at low temperature in an alkane matrix.

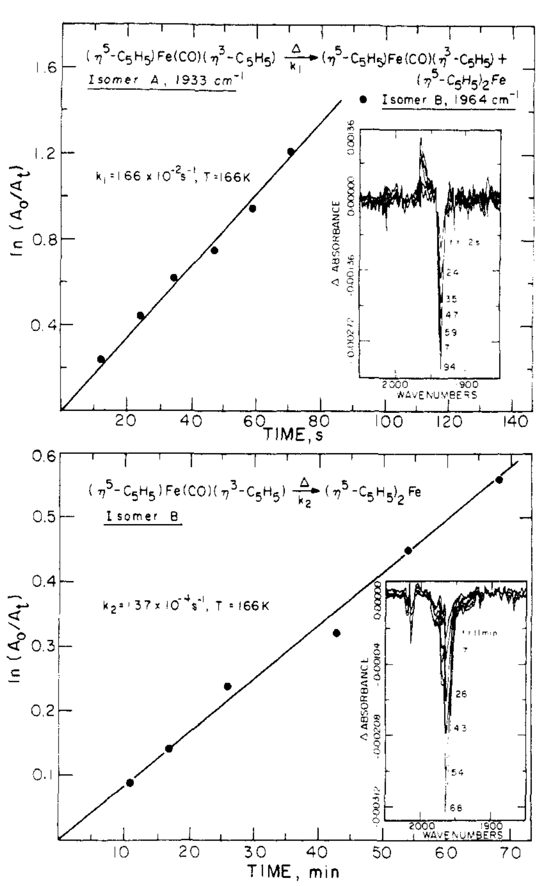


Figure 3. IR difference spectral changes accompanying the thermal reaction of isomers A (inset, top) and B (inset, bottom) of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5)$ at 166 K in alkane solution. Isomer A goes to isomer B and to $Fe(\eta^5\text{-}C_5H_5)_2$ with the rate constant indicated, and isomer B goes to $Fe(\eta^5\text{-}C_5H_5)_2$ with the (much smaller) rate constant indicated. The straight line plots show the disappearance of isomers A and B to both be first order. Note the difference in time scales on the horizontal axes for the reaction of isomers A (top) and B (bottom).

The monocarbonyl products from I to III are regarded as complexes of η^3-bonded ligands in part because the monocarbonyls with η^1-bonded ligands would not be expected to be observable in alkane matrices, as developed

---

[23] Hooker, R. H.; Rest, A. J.; Whitwell, I. *J. Organomet. Chem.* **1984**, *266*, C27.

[24] (a) Blaha, J. P. Ph. D. Thesis, MIT, 1985. (b) Randolph, C. L. Ph. D. Thesis, MIT, 1985. (c) Blaha, J. P.; Dewan, J. C.; Wrighton, M. S. *Organometallics* **1986**, *5*, 899. (d) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

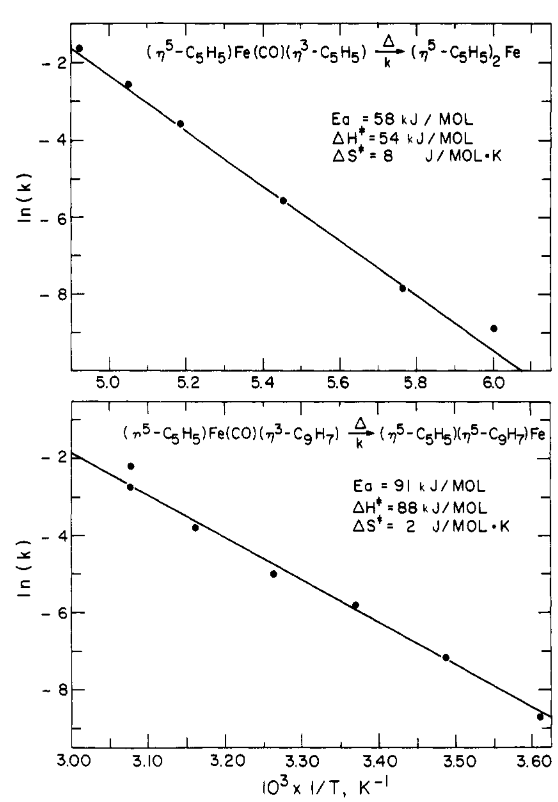
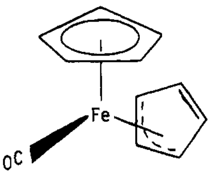
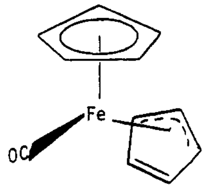


Figure 4. Arrhenius plots and activation parameters at 298 K for the thermal reactions indicated. The data in the top portion of the figure are for isomer B of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5)$. The data in the bottom portion of the figure are for the B′ isomer of $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_9H_7)$. Data are for thermal reactions of photogenerated intermediates carried out in alkane solution.

above. But in addition, the monocarbonyls have IR spectra in the CO region that are in good accord with previously characterized complexes of η^3-allyl ligands.[3] The fact that the monocarbonyls exist as two isomers also accords well with the established structures for the $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-allyl})$.[3] By analogy to the results[3] for the η^3-allyl we assign isomer A and B to be the endo and exo species shown as Ia and Ib.



Ia
isomer A (endo)



Ib
isomer B (exo)

The complexes with η^3-bonded ligands from irradiation of I–III are thermally and photochemically labile. The photochemical sensitivity is revealed in the low-temperature matrices where complete loss of metal carbonyl absorption can be observed. Thermal back reaction of the monocarbonyl and CO can occur upon warming matrices containing these photogenerated species, especially for the η^3-indenyl species. Work in this group has shown that $(\eta^5\text{-}C_5R'_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5)$ is labile with respect to uptake of a 2e donor ligand, presumably via capture of the 16e $(\eta^5\text{-}C_5R'_5)Fe(CO)(\eta^1\text{-}CH_2C_6H_5)$ that is formed thermally from the $\eta^3\text{-}CH_2C_6H_5$ complex.[2b] It is possible that the conversion of the isomers of the monocarbonyls from I to III also occurs via η^3- to η^1- to η^3-bonded ligands as proposed earlier in accounting for isomerizations of the allyl complexes.[3] Interestingly, and consistent with the η^3-allyl complexes, it is the exo isomers of the monocarbonyls from I to III that are more stable than the endo isomers, as steric considerations would suggest.

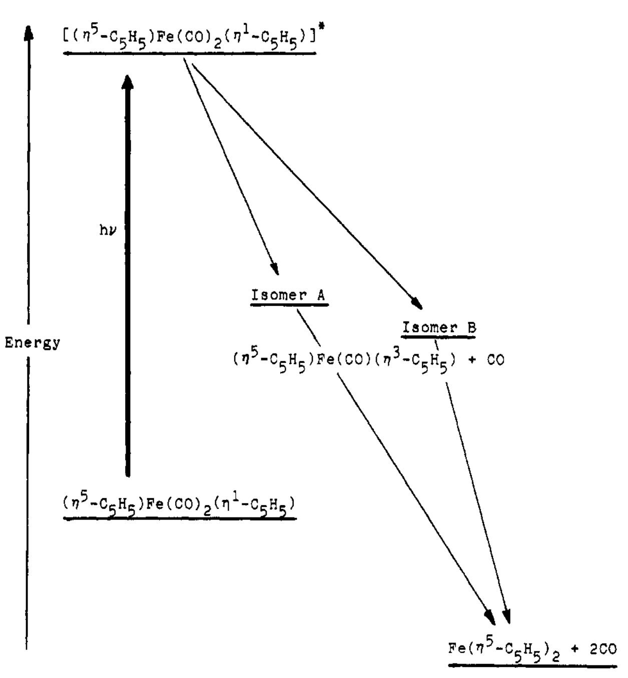


Figure 5. Sketch of the qualitative energetic relationships between the species involved in the photochemistry of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$.

The most interesting thermal chemistry of the monocarbonyl photoproducts from I to III is the conversion to the corresponding metallocenes. Figure 5 shows the qualitative energy relationships for the various species involved in the system derived from compound I. The results show that the activation energies for the conversion of the monocarbonyls to the metallocenes are substantial. Moreover, the activation energy for the η^3-indenyl system is significantly larger than for the η^3-cyclopentadienyl system. The latter finding provides quantitative support for the expectation that the η^3-indenyl system would be more stable than a corresponding η^3-cyclopentadienyl system. Additionally, the results show that a firmly bound ligand like CO can be driven from the coordination sphere of a metal complex in the conversion of an η^3-complex to a η^5-complex, though the activation energy is fairly large. This is regarded as the "fast" step in ligand substitution reactions of $(\eta^5\text{-indenyl})Mn(CO)_3$.[9] Since we have used low-temperature photochemical methods to generate the monocarbonyls from I to III, it is possible to monitor what would ordinarily be regarded as a fast step (non-rate-determining step) in a reaction sequence.

We hope to be able to extend the studies presented here, in order to establish the factors that will control the ability of an η^3-bonded ligand to drive a 2e donor ligand from the coordination sphere of a complex. While it does appear that the η^3-indenyl system is more inert than the η^3-cyclopentadienyl system and a plausible rationale can be advanced to explain this,[9] there is not a clear reason why there are $\eta^3\text{-}C_5H_5$ and $\eta^3\text{-}C_9H_7$ complexes (most notably $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_5H_5)$ and $(\eta^5\text{-}C_9H_7)W(CO)_2(\eta^3\text{-}C_9H_7)$) that are suficiently inert that they can be crystallographically characterized.[7,8] It is clear that the bond dissociation energy of the M–CO bond should be as large as possible in order to prevent CO loss, but purely dissociative loss of CO prior to the η^3- to η^5-conversion is presumably not the pathway for the conversion of the monocarbonyls from I to III to the metallocenes because the Fe–CO bond is presumably thermally inert to dissociation in such systems. In fact, the large difference in the activation energy for the

η^3-indenyl vs. η^3-cyclopentadienyl (Figure 4) strongly supports the contention that the dissociative loss of CO does not precede the η^3- to η^5-conversion. The bond dissociation energies for metal carbonyls varies widely,[25] but the $(\eta^5\text{-}C_5R'_5)Fe(CO)_2R$ complexes are typically robust complexes with respect to dissoctive loss of CO. Loss of one CO to form substituted complexes typically increases the back-bonding to the remaining CO, thereby increasing the metal–CO multiple-bond character and increasing the bond strength. Thus, it is very likely that a concerted η^3- to η^5-conversion/CO loss is the pathway by which the metallocenes are thermally formed from the monocarbonyls produced photochemically from I–III.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. I, 12247-96-0; II, 33568-92-2; III, 101377-15-5; $Fe(\eta^5\text{-}C_5H_5)_2$, 102-54-5; $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$, 54845-16-8; $Fe(\eta^5\text{-}C_9H_7)_2$, 1272-49-7; $(C_5H_5)Fe(CO)_2{}^+BF_4{}^-$, 93757-32-5; $(\eta^5\text{-}C_9H_7)_2Fe_2(CO)_4$, 36632-68-5; $Fe(CO)_4I_2$, 14878-30-9; LiC_9H_7, 20669-47-0; $(\eta^5\text{-}C_9H_7)Fe(CO)_2I$, 36561-93-0; indene, 95-13-6.

---

[25] Darensbourg, D. J. *Adv. Organomet. Chem.* **1982,** *21,* 113.

Electroreductive Alkylation of Iron Porphyrins. Iron(III), Iron(II), and Iron(I) Alkyl Complexes from the Reaction of Doubly Reduced Iron(II) Porphyrins with Alkyl Halides

Doris Lexa, Jean-Michel Savéant,* and Dan Li Wang

Laboratoire d'Electrochimie de l'Université Paris 7, Unité de Recherche Associée au CNRS No. 438 "Electrochimie Moléculaire", 75251 Paris Cedex 05, France

Received November 5, 1985

Electrochemical investigation of the reduction of four iron porphyrins (octaethylporphyrin, tetraphenylporphyrin, and two amide-linked basket-handle porphyrins) in the presence of alkyl halides shows that not only the singly reduced iron(II) complex, formally an iron(I) complex, undergoes alkylation at the iron atom but also this is the case for the doubly reduced iron(II) complex. No ring alkylation, as possible with a radical anion or a dianion structure, is observed. At low concentrations of alkyl halide, the one-electron reduction product of the iron(II) alkyl complex, formally an iron(I) alkyl complex, could be transiently observed. When the concentration is raised, catalytic reduction of the alkyl halide by the $Fe^{II}R^-/Fe^{I}R^{2-}$ couple occurs. It is found that the presence of the amide-linked chains exerts a pronounced influence on the electrochemical and chemical reactivity of the alkyl complexes, stabilizing the negatively charged species. Implications concerning the alkylation mechanism and the chemical catalysis of the electrochemical reduction of alkyl halides by metal complexes are discussed.

Three main ways of access to σ-alkyl–iron porphyrins have been demonstrated thus far: reaction of iron(III) porphyrins with a source of carbanions, usually a Grignard reagent[1] combination of an alkyl radical with an iron(II) porphyrin,[2] and reaction of iron(I) porphyrins with a source of carbocations, typically an alkyl halide.[3] In all three cases a (formal) $^+Fe^{III}R^-$ complex is first obtained. In the third case, however, owing to the fact that iron(I) is generated electrochemically, an $Fe^{II}R^-$ complex is actually obtained since the standard potential of the $Fe(II)/Fe(I)^-$ couple is negative with respect to that of the $^+Fe^{III}R/Fe^{II}R^-$ couple.[3] Electrochemically generated cobalt(I) in porphyrins or in vitamin B_{12} also reacts with alkyl halides yielding $Co^{III}R$ complexes.[4] In contrast with what happens with iron, however, the $Co^{III}R$ complex is electrochemically stable at the potential where Co(I) is generated. The $Co^{II}R^-$ complex can be obtained by reduction of $Co^{III}R$ at a more negative potential.

There has been thus far no report of the possibility of alkylating doubly reduced iron(II) porphyrins, formally iron("0") complexes, by alkyl halides. We discuss hereafter this problem starting from electrochemically generated iron("0") and using, for identification, the characteristics of the $Fe^{III}R$ and $Fe^{II}R^-$ complexes previously gathered by electrochemical generation of these species from Fe(I).[3]

The nature of singly and doubly reduced porphyrins, formally iron(I) and iron("0") complexes, has been the object of active investigation and discussion in recent years. Regarding the singly reduced complexes, there is strong evidence, based on ESR,[5] UV–vis,[5b,c,6,7] NMR,[6] and reso-

---

[1] (a) Clarke, D. A.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Chem. Commun.* **1966,** 208. (b) Clarke, D. A.; Dolphin, D.; Grigg, R.; Johnson, A. W.; Pinnock, H. *J. Chem. Soc. C* **1968,** 881. (c) Cocolios, P.; Laviron, E.; Guilard, R. *J. Organomet. Chem.* **1982,** *228,* C39. (d) Cocolios, P.; Lagrange, G.; Guilard, R. *J. Organomet. Chem.* **1983,** *253,* 65.

[2] (a) Brault, D.; Bizet, C.; Morlière, P.; Rougée, M.; Land, E. J.; Santus, R.; Swallow, A. J. *J. Am. Chem. Soc.* **1980,** *102,* 1015. (b) Brault, D.; Neta, P. *J. Am. Chem. Soc.* **1981,** *103,* 2705.

[3] Lexa, D.; Mispelter, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1981,** *103,* 6806.

[4] (a) Hill, H. A. O.; Pratt, J. M.; Riordan, M. P.; Williams, F. R.; Williams, R. P. J. *J. Chem. Soc. A* **1971,** 1859. (b) Lexa, D.; Savéant, J. M.; Soufflet, J. P. *J. Electroanal. Chem.* **1979,** *100,* 159. (c) Lexa, D.; Savéant, J. M.; Soufflet, J. P. In *Vitamin B12;* Zagalak, B., Friedrich, W., Eds.; de Gruyter: Berlin **1979;** p 213. (d) Lexa, D.; Savéant, J. M. *Acc. Chem. Res.* **1983,** *16,* 235.

[5] (a) Cohen, I. A.; Ostfeld, D.; Lichtenstein, B. *J. Am. Chem. Soc.* **1972,** *94,* 4522. (b) Lexa, D.; Momenteau, M.; Mispelter, M. *Biochim. Biophys. Acta* **1974,** *338,* 151. (c) Kadish, K. M.; Larson, G.; Lexa, D.; Momenteau, M. *J. Am. Chem. Soc.* **1975,** *97,* 282. (d) Srivatsa, G. S.; Sawyer, D. T.; Boldt, N. J.; Bocian, D. F. *Inorg. Chem.* **1985,** *24,* 2123. (e) Kadish, K. M.; Boisselier-Cocolios, B.; Simonet, B.; Chang, D.; Ledon, H.; Cocolios, P. *Inorg. Chem.* **1984,** *24,* 2148. (f) The Fe(I) complex is believed not to bind axial ligands at room temperature[5d] whereas coordination with THF,[5b] and more recently with pyridine and 1-methylimidazole,[5d] has been detected at 77 K.

[6] Hickman, D. L.; Shirazi, A.; Goff., H. M. *Inorg. Chem.* **1985,** *24,* 563.

[7] (a) Reed, C. A. *Adv. Chem. Ser.* **1982,** *No. 201,* 333. (b) Mashiko, T.; Reed, C. A.; Haller, K. J.; Scheidt, W. R. *Inorg. Chem.* 1984, *23,* 3192.

0276-7333/86/2305-1428$01.50/0