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The Phenyl Rotational Barrier in 1,1′-Diphenyluranocene

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Line-shape analysis of the ^{1}H NMR spectrum of 1,1′-diphenyluranocene as a function of temperature gives the activation parameters $\Delta H^\ddagger = 4.4 \pm 0.3$ kcal mol^{-1} and $\Delta S^\ddagger = -4.7 \pm 1.3$ eu for the rotation of the phenyl group about the bond to the eight-membered ring.

Paramagnetic organometallic U(IV) (5f^2) compounds have served as useful probes in the observation of a variety of nuclear magnetic resonance properties and processes.[1-3] The large isotropic shifts can result in greater amplification of chemical shift differences and increase the time resolution of the ^{1}H NMR experiment, according to the approximate solutions of the modified Bloch equations[4] (eq 1 and 2). Such increase in time resolution permits ob-

$$1/\tau = (\pi\Delta\nu)^2/4[1/T_2^{\text{exch}} - 1/T_2^{0}] \qquad (1)$$

$$1/\tau = \pi\Delta\nu/2^{0.5} \qquad (2)$$

servation by ^{1}H NMR of dynamic processes with free energies of activation lower than the 7–8 kcal mol^{-1} typically required for observation in diamagnetic complexes. As part of our study of substituted bis(π-[8]annulene)uranium(IV) (uranocene) complexes, we have used this probe to determine the rotational barrier of the phenyl ring about the C–C bond to the [8]annulene ring in 1,1′-diphenyluranocene, **1**. This compound was prepared in the usual way by the addition of phenylcyclooctatetraene dianion to a solution of UCl_4 in THF under argon. The recovered solid was extracted with toluene and crystallized from THF/hexane to give dark green, air-sensitive crystals.

At 30 °C, the ^{1}H NMR spectrum of **1** in toluene-d_8 contains seven peaks: three phenyl proton resonances, δ −13.66 (ortho, 2 H), 0.87 (meta, 2 H), 0.96 (para, 1 H), and four [8]annulene ring proton resonances, δ −33.90, −35.73, −35.98, −36.71 (H5). These values differ slightly from those reported earlier,[1] probably because of temperature differences with the older 180-MHz spectrometer. The ortho- and meta-phenyl proton chemical shifts are average shift positions for the endo and exo proton environments (Figure 1) since the phenyl ring is not coplanar with the [8]annulene ring but rotates rapidly about the C–C bond at 30 °C. As the sample is cooled to −40 °C, the ortho proton resonance begins to broaden until it collapses into the base line at −100 °C. This phenomenon is undoubtedly a dynamic NMR effect of the slowing of the phenyl rotation rate to the NMR time scale. In particular, it is not a general solvent viscosity effect because the other peaks are not affected and remain relatively sharp. Unfortunately, **1** is poorly soluble in solvents at the temperatures required for observation of the slow-exchange limit (below −125 °C) and the required $\Delta\delta$ values for the two separate states (endo and exo ortho protons) could not be obtained directly. It is possible, however, to estimate the chemical shifts of these proton positions from the ^{1}H NMR data of 1,1′-di-*o*-tolyluranocene, **2**.

1,1′-Di-*o*-tolyluranocene was obtained by a preparation similar to the synthesis of diphenyluranocene. Addition of *o*-tolyllithium to cyclooctatetraene resulted in a 30% isolated yield of *o*-tolylcyclooctatetraene. This product was treated with potassium metal to give the dianion, which was added to a solution of UCl_4 in THF under argon. Extraction with hexane, followed by recrystallization from a hexane–THF mixture, resulted in a dark green, air-sensitive solid. The ^{1}H NMR of **2** is similar to diphenyluranocene with regard to the pattern and location of the [8]annulene ring resonances. The tolyl ring resonances show that this ring, unlike the unsubstituted phenyl ring, does not rotate at these temperatures and is essentially frozen in a single type of conformation, that in which the methyl group is exo to the uranium. The methyl resonance is far downfield (δ 17.01 at 30 °C) in the expected direction for a dipolar shift. The magic angle in uranocene passes close to the uranocene ring hydrogens; groups above this angle have positive dipolar shifts and those below have negative shifts.[1] For comparison, the mesityl ring of 1,1′-dimesityluranocene is also not free to rotate and the two ortho-methyl chemical shifts occur at δ 24.2 (exo) and −46.2 (endo) at 30 °C.[5]

The presence of a single proton resonance far upfield (δ −46.8 at 30 °C) indicates that the single ortho proton of **2** is close to the uranium metal (endo). Similarly, the two meta protons can be assigned unambiguously: δ 7.3 (30 °C, extrapolated from results at lower temperature because at this temperature the peak is too close to the ring protons of the solvent toluene-d_8), exo, and δ −4.0, endo. The contact shift contributions to the aryl protons in aryluranocenes appear to be small. For example, the meta and para chemical shifts in **1** are quite similar. Contact shift contributions to these positions would be expected to be significantly different if either were large. Similarly, the average shift for the two meta protons in **2** is quite close to the para proton, δ 1.61. A significant comparison is to phenylcyclooctatetraene radical anion. The spin density in the phenyl ring that gives rise to the contact shifts in the uranocene is expected to be roughly comparable to the relative spin density in the radical anion as measured by electron spin resonance hyperfine coupling.[6] Such hyperfine coupling constants are extremely small, 0–0.01 G for the phenyl protons compared to 3.68 and 2.38 G for the cyclooctatetraene protons in the radical anion, in part because of the twisting of the two rings with respect to each other that reduces conjugation.[7] Thus,

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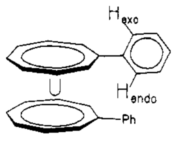

Figure 1. 1,1′-Diphenyluranocene, 1, showing defination of exo and endo.

delocalization of spin density to the phenyl rings in 1 should be comparably small. In a further comparison, note that the contact shift contributions to the benzo ring of dibenzouranocene, which is undoubtedly more conjugated to the uranocene system than the aryluranocenes, are also relatively small.[6]

The resonances for di-*o*-tolyluranocene remain sharp from −100 to 80 °C and follow normal $1/T$ dependence, indicating that the compound is restricted to this single conformation throughout this temperature range. A large conformational change leading to significant chemical shift differences in one or more protons would cause deviations from simple $1/T$ behavior.[1] The similarity of the chemical shifts of the para proton on both aryl rings (δ 0.96 for 1 and δ 1.61 for 2) and of the average meta protons of both rings (δ 0.87 for 1 and 1.64 for 2) suggests that 1 and 2 have similar aryl conformations, except that the aryl ring in diphenyluranocene has a lower barrier to rotation. This similarily also means that the methyl substituent in 2 has only a small effect on the chemical shifts of the other ring protons. Thus, it is a reasonable approximation to assign the chemical shift of the ortho (endo) proton of 2 to the endo ortho proton of diphenyluranocene in the slow-exchange limit. The chemical shifts of the exo proton can then be readily extracted from the average shift position for both ortho protons in 1 and the endo ortho proton in 2.

These shift values could be extrapolated from a plot of the chemical shift vs. T^{-1} to the estimated coalescence temperature to determine the corresponding free energy of activation using the Eyring equation and eq 2. A more dependable method for determining thermodynamic parameters is by computer-simulated line-shape analysis of the broadened exchange peaks to determine the mean nuclei lifetimes, τ, over a series of temperatures. Values for τ were determined by inputting frequency values for nonexchanging peaks, along with natural line widths, and best fitting the computer-generated curve for a specific τ value to the actual NMR peak. Converting τ values to exchange rate constants and plotting against inverse temperature yields values for the activation enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$. The $\Delta G^{\ddagger}$ value calculated from the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values is not sensitive to errors in judging the coalescence temperature and is expected to be more reliable.

Experimental Section

1,1′-Diphenyluranocene, 1. Phenylcyclooctatetraene was prepared by using the method of DeKock.[8] The ligand was converted to the dianion by addition of 0.41 g (10.5 mmol) of potassium to 0.89 g (4.9 mmol) of phenylcyclooctatetraene in 125 mL of anhydrous THF under argon. The solution was stirred for 5 h and cannulated into a solution of 0.96 g (2.5 mmol) of UCl_4 in 100 mL of dry, degassed THF. After the solution was stirred for an additional 30 min, the flask was connected to a vacuum line and the solvent was pumped off. Extraction with 100 mL of toluene, followed by removal of solvent, left a dirty green amorphous solid. Dark green, air-sensitive crystals of 1,1′-diphenyluranocene resulted after recrystallization in hot hexane; yield 0.90 g (60%). ^1H NMR data are given above and in ref 1.

Anal. Calcd for $C_{28}H_{24}U$: C, 56.19; H, 4.04. Found: C, 55.96; H, 4.14.

1,1′-Di-*o*-tolylcyclooctatetraene. A 250-mL, three-neck flask equipped with condenser, dropping funnel, and mechanical stirrer was flame-dried and purged with argon. To this was added 2.0 g (290 mmol) of clean, finely cut lithium wire (1% sodium) and 100 mL of dry ether. Next, 20 g (120 mmol) of *o*-bromotoluene was slowly dropped in, after which the solution was refluxed for 2 h. The excess lithium was physically removed, and 20.5 g of freshly distilled cyclooctatetraene (BASF) (197 mmol) was added. The mechanically stirred solution was slowly warmed to 100 °C, during which time the ether was allowed to evaporate. The yellow mixture was stirred for 2 h and was then cooled to 0 °C, whereupon 100 mL of ether was added to dissolve the mixture. Air was bubbled through for 1 h, and the reaction was quenched by adding 100 mL of water and 100 mL of hexane. The layers were separated, and the organic phase was washed successively with 100 mL of water followed by 60 mL of saturated NaCl. The yellow solution was dried over calcium carbonate and evaporated to a yellow oil, bp 95–98 °C (0.5 mm). This material was further purified by filtration through a silica column eluted with hexane. ^1H NMR (90 MHz, $CDCl_3$): δ 6.95 (m, 4 H), 5.7 (m, 7 H), 2.3 (s, 3 H). ^{13}C NMR (25 MHz): 144.4, 141.9, 135.2, 132.9, 132.4, 131.7, 130.4, 129.9, 129.2, 128.8, 127.5, 127.0, 126.0, 125.5, 20.1 ppm.

Anal. calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.51; H, 7.42.

1,1′-Di-*o*-tolyluranocene, 2. In an argon-filled glovebox 1.75 g (9.1 mmol) of *o*-tolylcyclooctatetraene dissolved in 135 mL of THF (tetrahydrofuran) was treated with 0.7 g (18.2 mmol) clean potassium. The mixture was stirred for 8 h, whereupon all of the potassium had disappeared leaving a brown solution. To this was added 1.7 g (5 mmol) of uranium tetrachloride dissolved in 100 mL of THF. The solution turned green and was stirred for 3 h. The THF was removed by vacuum transfer and the residue subjected to high vacuum overnight. The green residue was then loaded into a Soxhlet extractor and extracted with 100 mL of hexane for 10 h. The hexane was removed, leaving 1.1 g (39% yield) of a green solid. A small amount of this material was recrystallized from a hexane–THF mixture. ^1H NMR (200 MHz, toluene-d_8, −45 °C, given as δ, 10^{-3} slope vs. $1/T$, intercept): 23.17 (s, 3 H), 5.52, −1.12; 6.55 (s, 1 H), −0.68, 9.55; −0.97 (s, 1 H), −2.40, 9.55; −9.21 (s, 1 H), −4.81, 11.88; −47.6 (s, 2 H), −13.31, 10.81; −48.0 (s, 2 H), −12.57 (s, 2 H), 7.07; −52.9 (s, 2 H), −13.13, 4.98; −55.6 (s, 1 H), −13.33, 3.25; −71.4 (br s, 1 H), −22.49, 27.40. Visible spectrum: λ_{max} 623, 650, 668. Mass spectrum; m/z (relative intensity) 626 (M^+, 94.32), 433 (16.58), 432 (100.00), 164 (90.80), 179 (88.50).

Anal.[9] Calcd for $C_{30}H_{28}U$: C, 57.51; H, 4.50. Found: 57.46; H, 4.70.

1,1′-Bis(*p*-(dimethylamino)phenyl)uranocene, 3.[10] To 3.9 g (0.1 mol) of dispersed potassium in 100 mL of THF was added 11.15 g (0.05 mol) of (*p*-(dimethylamino)phenyl)cyclooctatetraene.[11] The solution was stirred until all of the potassium had reacted (5 h). To this solution at −20 °C was added 9.5 g (0.025 mol) of anhydrous UCl_4 dissolved in 50 mL of THF. The mixture turned dark green immediately and was allowed to warm slowly to room temperature. The THF was removed by vacuum transfer after the mixture was stirred for 2 h. The green residue was extracted with cyclohexane, yielding 15.4 g (90%) of the desired product. ^1H NMR (180 MHz, C_4D_4O, 30 °C): δ −37.13 (s, 1 H), −36.46 (s, 2 H), −36.15 (s, 2 H), −34.29 (s, 2 H), −14.10 (d, 2 H, J = 7.6 Hz), 0.13 (d, 2 H, J = 7.6 Hz), −0.04 (s, 6 H).

NMR Spectra. The ^1H NMR spectra were run on the UC Berkeley FT-NMR 200-MHz spectometer. The system employs a superconducting magnet, a deuterium lock system, and Nicolet software. Temperature was monitored by a Doric Trendicator 410A. Line-shape analyses were performed by using an exchange program written for the 1180 Nicolet system as part of the NTCFT software package.[12] All measurements were carried out in ap-

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Table I. Resonance Frequency Data (200 MHz) for Phenyluranocene

I, °C	endo proton (Hz)[a]	ortho protons (Hz)[b]	exo proton (Hz)[c]
-45	-14 409	-4700	+5009
-50	-14 840	-4901	+5038
-55	-15 308	-5068	+5160
-60	-15 756	-5274	+5208
-65	-16 285	-5472	+5341
-70	-17 000	-5689	+5422
-75	-17 420	-5915	+5590
-80	-17 983	-6175	+5633

[a] Experimentally determined from the resonance frequency of the endo ortho proton of di-*o*-tolyluranocene, 2. [b] Experimentally determined from the average resonance frequency of the endo and exo ortho protons of diphenyluranocene, *1*. [c] Extrapolated from the given experimental data.

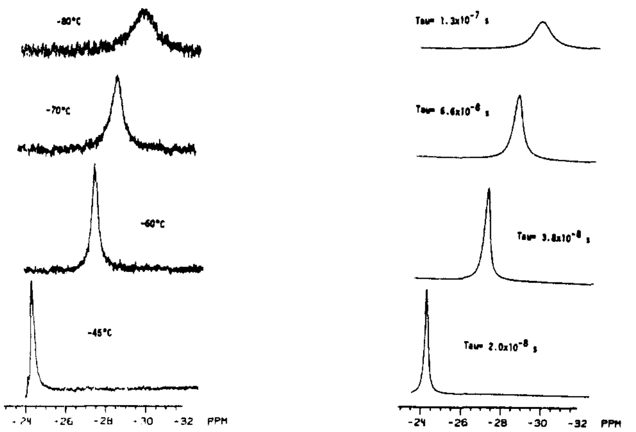

Figure 2. Line-shape analysis for ortho-proton coalescence in 1,1′-diphenyluranocene.

proximately 10^{-3} M solutions of toluene-d_8 and THF-d_8. Older work[1] was done with the Berkeley 180-MHz spectrometer.

Chemical shifts for 1,1′-diphenyluranocene and 1,1′-di-*o*-tolyluranocene were determined at 5-deg intervals from −45 to −80 °C as well as at some other temperatures. The line width of the ortho peak at room temperature (fast exchange limit) and of the para-phenyl peak down to −85 °C (no exchange) was found to be 20 Hz. Thus, the natural line width of the ortho peak was taken to be 20 Hz.

Errors in ΔH^* and ΔS^* were calculated by the program Acteng[12] (k, ±10%, T, ±0.5 °C). Calculation of ΔG^* for the phenyl rotational barrier was made by using the ΔH^* and ΔS^* values from the line-shape analysis ($\Delta G_c^* = \Delta H^* - T_c\Delta S^* = 5.1$ kcal/mol) and also by extrapolating $\Delta\nu$ values to the estimated coalescence temperature (from chemical shift vs. T^{-1} plots, $\Delta\nu = 31\,530$ Hz) and then substituting into the formulas $k = 2^{-0.5}\pi\Delta\nu$ and $-\Delta G^* = RT \ln (kh/\kappa k_BT)$, where $\kappa = 1$ ($\Delta G^* = 5.2$ kcal/mol).

Results and Discussion

The resonance frequency data for the endo proton of di-*o*-tolyluranocene and the ortho protons (average shift position of exo and endo) of 1 are given in Table I. Also included in this table are the calculated frequencies for the exo proton in the absence of exchange. All of the protons exhibit approximate Curie–Weiss behavior throughout the temperature range studied. Simulation of the broadened fast-exchange peak of the ortho protons in 1 (Figure 2) provides the mean nuclei lifetimes τ given in Table II for the temperature range −45 to −80 °C.

An Eyring plot of the rate constants (Figure 3) results in the following activation parameters for this temperature range: $\Delta H^* = 4.4 \pm 0.3$ kcal mol^{-1}; $\Delta S^* = -4.7 \pm 1.3$ e.u.; $E_a = 4.8 \pm 0.3$ kcal mol^{-1}; $A = (1.1 \pm 0.7) \times 10^{11}$ s^{-1}.

Table II. Results of Computer Simulation To Determine the Mean Lifetime for Rapidly Exchanging Nuclei in 1

T, °C	$10^8\tau$, s	$10^{-5}k$, s^{-1}
-45	2.0	250
-50	2.4	210
-55	2.8	180
-60	3.8	130
-65	5.1	98
-70	6.6	76
-75	9.6	52
-80	13	38

Table III. Mean Nuclei Lifetime for Exchanging Ortho Protons in 3

T, °C	$10^8\tau$, s	T, °C	$10^8\tau$, s
-45	2.1	-65	5.0
-55	2.8	-70	6.6

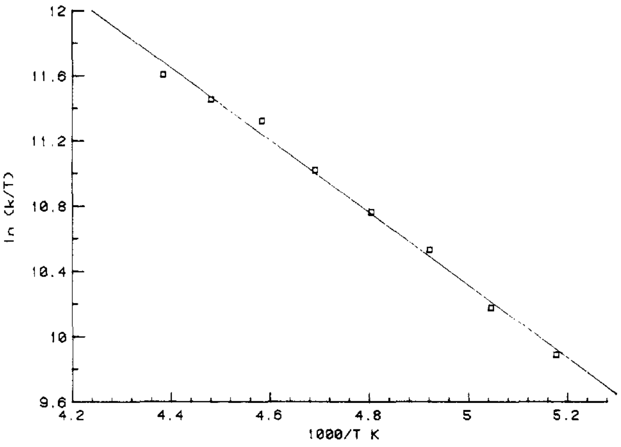

Figure 3. Eyring plot to determine thermochemical activation parameters for the phenyl ring rotational barrier in 1.

The free energy of activation can be determined by approximating the coalescence temperature to be 20–30 °C below the point at which the peak collapses into the base line, a method used by Marks in estimating the coalescence temperature for exchanging bridging and terminal hydrides in $(C_5H_5)_3UBH_4$.[2] Thus, with $T = (150 \pm 10)$ K, $\Delta G^* = 5.1 \pm 0.5$ kcal mol^{-1} for rotation of the phenyl ring about the [8]annulene ring plane. As a comparison, calculation of the rotational barrier by extrapolating $\Delta\nu$ to the coalescence temperature results in a ΔG^* of 5.2 kcal mol^{-1}, in excellent agreement with the value derived from line-shape analysis.

Additional substituents on the phenyl ring, such as *p*-dimethylamino, appear to have little effect on the rotational barrier. Mean nuclei lifetimes resulting from line-shape analysis of the ortho peak of 1,1′-bis(*p*-(dimethylamino)phenyl)uranocene, 3, are given in Table III. The results are virtually identical with those reported in Table II for 1. The dynamic behavior of 3 appears to mimic that of the parent complex 1. Di-*o*-tolyluranocene was used as the model compound for 3 as well as for 1, since the small difference in the chemical shifts of the compounds' protons suggests they are structurally similar (1, δ −13.66; 3, δ −14.10; ortho protons, 30 °C).

When line-shape analysis was performed on the spectra of 1 and 3 in solutions of THF-d_8, the rate constants duplicated the values determined in solutions of toluene-d_8. Thus, this change in solvent has no apparent effect on the rate of peak broadening. A small broadening effect observed for the meta proton peak at low temperatures is undoubtedly due to the same rotational phenomenon. The

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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 ($\Delta\nu$ = 20 000–35 000 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.

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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

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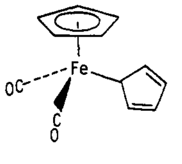
Irradiation of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) (I), (η^5-C_5H_5)Fe(CO)$_2$(η^1-indenyl) (II), or (η^5-indenyl)Fe(CO)$_2$(η^1-indenyl) (III) with near-UV light at 298 K leads to the loss of CO and formation of the sandwich complexes Fe(η^5-C_5H_5)$_2$, Fe(η^5-C_5H_5)(η^5-indenyl), or Fe(η^5-indenyl)$_2$, 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.



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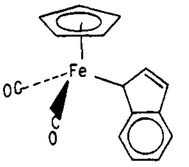

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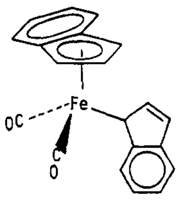

III

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

$$\eta^5\text{-}C_5R'_5)\text{Fe(CO)}_2\text{R} \xrightarrow{h\nu} (\eta^5\text{-}C_5R'_5)\text{Fe(CO)R} + \text{CO} \quad (1)$$

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

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 photochem-

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

ical conversion can be effected at sufficiently low tem-

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