as useful new protecting groups for primary amines. Studies along these lines are currently underway.

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Photochemistry of (η^5-indenyl)$_2$Fe$_2$(CO)$_4$ in the Presence of 2e$^-$ Donor Ligands: Reversible Formation of the Radicals (indenyl)Fe(CO)$_2$L

Yee-Min Wuu, Chaofeng Zou, and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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We report the photochemical reaction and the reverse thermal process represented by eq 1 for L = CO, PPh$_3$, and PPh$_2$H. The

$$(\eta^5\text{-indenyl})_2Fe_2(CO)_4 + 2L \underset{\text{alkane, 298 K}}{\overset{h\nu\ (\lambda > 500\ \text{nm})}{\rightleftharpoons}} 2(\text{indenyl})Fe(CO)_2L \tag{1}$$

indenyl ligand can bind in either an η^5 or η^3 fashion,[1-3] and the facile, reversible "ring slippage", $\eta^5 \rightleftharpoons \eta^3$ binding, has been invoked to account for the greater substitution lability of η^5-indenyl complexes compared to η^5-C_5H_5 complexes.[1-4] Ring slippage in a variety of η^5-C_5H_5 complexes and their derivatives has been invoked to account for a number of interesting chemical transformations.[4] Recent work[5] from this laboratory implicating reactions of CO and PPh$_3$ with photogenerated (C_5R_5)Fe(CO)$_2$ (R = H, Me) stimulated us to investigate the photochemistry of (η^5-indenyl)$_2$Fe$_2$(CO)$_4$ with the hope of stabilizing the product from thermal reaction of CO and PPh$_3$ with photogenerated (indenyl)Fe(CO)$_2$ radicals. It should be noted that (η^3-C_3H_5)Fe(CO)$_2$L radicals are known[6] and have been characterized by EPR and IR spectroscopy. The existence of (η^3-C_3H_5)Fe(CO)$_2$L[6] and the facile $\eta^5 \rightarrow \eta^3$ ring slippage of the indenyl ligand[1,4] is consistent with the notion that (η^3-indenyl)Fe(CO)$_2$L might be detectable. We note the recent isolation and X-ray crystal structural characterization of [(η^3-indenyl)Fe(CO)$_3$]$^-$ from reactions of CO with [(η^5-indenyl)Fe(CO)$_2$]$^-$.[7]

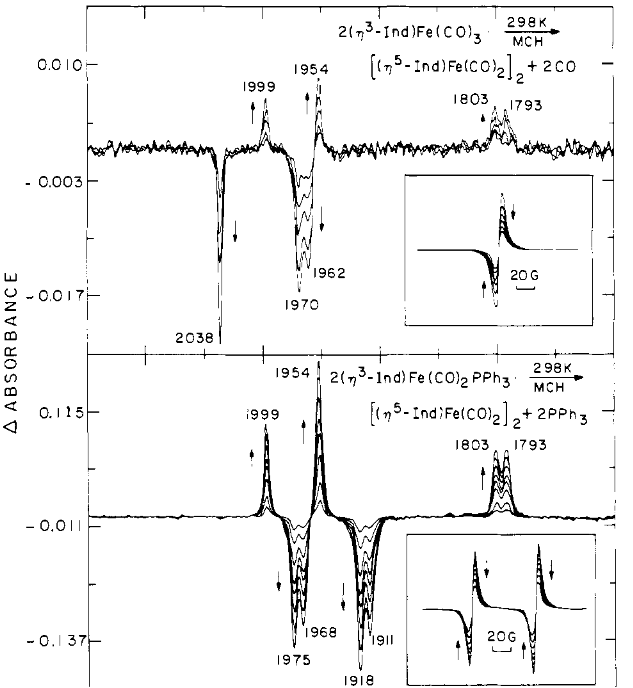

Figure 1. IR and EPR (independently prepared sample) spectral changes accompanying reaction of (indenyl)Fe(CO)$_2$L to form (η^5-indenyl)$_2$Fe$_2$(CO)$_4$ (1999, 1954, 1803, 1793 cm^{-1}) in deoxygenated methylcyclohexane at 298 K. Data for L = CO (top, cell path = 0.1 mm) are for a CO-saturated solution, and the times scale of the IR spectral changes is ~2 min. Data for L = PPh$_3$ (bottom, cell path = 1.0 mm) are for a solution containing 0.05 M PPh$_3$, and the time scale of the IR spectral changes is ~10 min. The (indenyl)Fe(CO)$_2$L radicals were formed by $\lambda > 500$ nm irradiation of (η^5-indenyl)$_2$Fe$_2$(CO)$_4$, and the final IR spectra shown in both cases represent >99% consumption of the photogenerated radical. The IR data are for initial (indenyl)Fe(CO)$_2$L concentration of 0.35 and 0.40 mM for L = CO and PPh$_3$, respectively.

Irradiation of (η^5-indenyl)$_2$Fe$_2$(CO)$_4$[8] yields chemistry consistent with that for (η^5-C_5R_5)$_2$Fe$_2$(CO)$_4$:[9] both CO loss and Fe–Fe homolysis products can be detected, depending on conditions. Fe–Fe homolysis products result from photoexcitation of (η^5-indenyl)$_2$Fe$_2$(CO)$_4$ in fluid solution at 298 K, eq 2 and 3. The

$$(\eta^5\text{-indenyl})_2Fe_2(CO)_4 \xrightarrow[\text{CCl}_4,\ 298\ \text{K}]{h\nu\ (\lambda > 500\ \text{nm})} 2(\eta^5\text{-indenyl})Fe(CO)_2Cl \quad \nu_{CO} = 2049,\ 2004\ \text{cm}^{-1} \tag{2}$$

$$(\eta^5\text{-indenyl})_2Fe_2(CO)_4 + Mn_2(CO)_{10} \xrightarrow[298\ \text{K}]{h\nu} 2(\eta^5\text{-indenyl})Fe(CO)_2Mn(CO)_5 \quad \nu_{CO} = 2080,\ 2013,\ 1991,\ 1975,\ 1941\ \text{cm}^{-1} \tag{3}$$

photochemistry in the presence of CCl$_4$ is consistent with the

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intermediacy of (indenyl)Fe$(CO)_2$ which abstracts Cl from CCl_4. Analogous photochemistry occurs for $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$.[9] The photochemical cross-coulping process in eq 3 provides further evidence supporting the photogeneration of the radical (indenyl)Fe$(CO)_2$ from $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$. Low-temperature (~77 K) irradiation of $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ in a rigid matrix results in relatively slow (compared to $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$) CO loss from only the trans isomer (~20% conversion in ~1 h), according to eq 4, as found for $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$.[9b,d] The two IR peaks for

$$\underset{\text{(trans isomer)}}{(\eta^5\text{-indenyl})_2Fe_2(CO)_4} \xrightarrow[\text{alkane, 77 K}]{h\nu,\ \text{near-UV}} (\eta^5\text{-indenyl})_2Fe_2(\mu\text{-}CO)_3 + CO \quad (4)$$

$$\nu_{CO} = 1810,\ 1826\ \text{cm}^{-1}$$

the CO loss product(s) suggest the presence of two isomers (presumably due to different orientations of the η^5-indenyl rings) or due to the less than D_{3h} symmetry of any of the CO loss products. A new finding is that the CO loss is not effected upon long wavelength (λ > 500 nm) excitation; near-UV is qualitatively more efficient in effecting CO loss at low temperature. In all respects the photochemistry of $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ closely parallels that found for the related $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ (R = H, Me).[9]

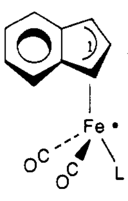
Results above indicate that long wavelength (λ > 500 nm) excitation of $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ results mainly in formation of (indenyl)Fe$(CO)_2$ in fluid solution. In the absence of added ligands irradiation of $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ in hydrocarbon solutions results in slow decomposition. However, when the irradiation is carried out in hydrocarbon solvents containing L (L = CO, PPh_3, PPh_2H) IR and EPR data show that the (indenyl)Fe$(CO)_2$ radical can be trapped, eq 5. The resulting adducts back react thermally at 298 K to regenerate the starting $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$, eq 6. Most work has been done for L = CO

$$(\text{indenyl})Fe(CO)_2 \xrightarrow[\text{alkane, 298 K}]{L} (\text{indenyl})\ Fe(CO)_2L \quad (5)$$

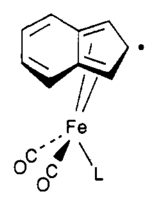
$$2(\text{indenyl})Fe(CO)_2L \xrightarrow[\text{alkane, 298 K}]{\Delta} (\eta^5\text{-indenyl})_2Fe_2(CO)_4 + 2L \quad (6)$$

or PPh_3, and Figure 1 shows IR and EPR data relating to the radicals. The IR spectra in the CO region are remarkably similar to those reported for $(\eta^3\text{-}C_3H_5)Fe(CO)_2L$ (ν_{CO} L = CO: 2045, 1969, 1963 cm^{-1}; L = PPh_3: 1956, 1893 cm^{-1}).[6] The splitting of the features for L = PPh_3 is likely due to the presence of endo and exo isomers as known for species such as $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$[10,11] and suggested for $(\eta^3\text{-}C_3H_5)Fe(CO)_2PPh_3$.[6c] The EPR ($g$ = 2.0103) for L = CO shows no splitting and, in particular, no hyperfine splitting from H's in the indenyl ligand. For L = PPh_3 the EPR (g = 2.0054) shows splitting due to coupling with ^{31}P (A = 68 G), and when L = PPh_2H is used, there is no additional splitting associated with the H bonded to the P. When L = ^{13}CO is used, there is splitting attributed to coupling with ^{13}CO and evidence for multiple substitution to form (indenyl)Fe$(CO)_n(^{13}CO)_{3-n}$ (n = 0, 1, 2) with n depending on the reaction time.[12] The (indenyl)Fe$(CO)_2$L radicals back react to regenerate $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ with a rate that is proportional to the square of the concentration of the radical. In the case of L = PPh_3 it has been demonstrated that reaction of (indenyl)Fe$(CO)_2$L to regenerate $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ is suppressed by added L, consistent with loss of L as the first step followed by coupling of (indenyl)Fe$(CO)_2$ radicals. We do not observe any IR bands assignable to the unknown $(\eta^3\text{-indenyl})_2Fe_2(CO)_6$ from reaction of (indenyl)Fe$(CO)_3$ that would be an analogue of $(\eta^3\text{-}C_3H_5)_2Fe_2(CO)_6$.[6d]

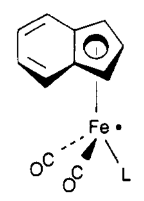
We proposed formulation of the photogenerated radicals from $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ in the presence of L as 17e$^-$ species having an η^3-indenyl ligand I. EPR shows the odd e$^-$ to be Fe-localized,



I



II



III

ruling out II, a C-centered radical with a (η^4-1,3-diene) ligand to make the Fe center electron precise. Formulation of the radicals as 19e$^-$ species III with an η^5-indenyl ligand is not likely based on the IR spectral data in the CO region which are nearly the same as reported for the 17e$^-$ $(\eta^3\text{-}C_3H_5)Fe(CO)_2L$ species.[6] The structure I proposed for the radicals from irradiation of $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ in the presence of CO is the same as found by crystallography for the electron precise $[(\eta^3\text{-indenyl})Fe(CO)_3]^-$.[7] The spectroscopic data for (indenyl)Fe$(CO)_2$L radicals, however, do not unambiguously rule out III, and further structural characterization of the radicals is under way.

A species analogous to II has been suggested[5] to account for the formation of $(\eta^4\text{-}C_5R_5R')Fe(CO)_2L$ from irradiation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ in the presence of L, e.g., for R = Me, R' = benzyl. Our new results establishing the formation of Fe-centered radicals from irradiation of $(\eta^5\text{-indenyl})_2Fe_2(CO)_4$ suggest that it is possible that the photochemistry of $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ in the presence of L proceeds via the intermediacy of a Fe-centered radical $(C_5R_5)Fe(CO)_2L$. Work is in progress to characterize the reactivity of (indenyl)Fe$(CO)_2$L radicals toward R'.

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[11] In benzene solution, the two isomers of (indenyl)Fe$(CO)_2PPh_3$ have overlapping CO absorption near 1968 and 1909 cm^{-1}, similar to $(\eta^3\text{-}C_3H_5)Fe(CO)_2PPh_3$ which has absorptions at 1956 and 1893 cm^{-1}.

[12] The (indenyl)Fe$(^{13}CO)_3$ has features at 1991, 1926, and 1918 cm^{-1}.

The Effect of Hydrophobic–Lipophilic Interactions on Chemical Reactivity. 8. Large-Ring Intramolecular Excimer Formation Brought About by Hydrophobic Forces

Xi-Kui Jiang,* Yong-Zheng Hui, and Zeng-Xiang Fei

Shanghai Institute of Organic Chemistry
Academia Sinica, 345 Lingling Lu, Shanghai, China

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It has been demonstrated recently by kinetic methods that we may deliberately make use of hydrophobic–lipophilic interactions to force the two ends of 13-, 16-, and 17-carbon-chain esters to meet and interact.[1] The same result has also served as the first direct evidence for self-coiling or hairpin looping of monomeric organic molecules and may lead to synthetic applications.[2] Therefore, a demonstration of this hydrophobicity-enforced chain folding by some physical method would be most desirable. This has now been achieved by using fluorescence spectrometry.

Many elegant works have been done on intramolecular excimers or exciplexes.[3-12] Furthermore, it has been recently established

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