Intramolecular Rearrangements on Ultrafast Timescales: Femtosecond Infrared Studies of Ring Slip in (η^1-C$_5$Cl$_5$)Mn(CO)$_5$

Christine K. Payne, Preston T. Snee, Haw Yang,[‡]
Kenneth T. Kotz, Laurel L. Schafer, T. Don Tilley, and
Charles B. Harris*

*Department of Chemistry, University of California
Berkeley, California 94720
Chemical Sciences Division, Ernest Orlando Lawrence
Berkeley National Laboratory, Berkeley, California 94720*

Ring slip has been proposed as a mechanism for a variety of organometallic reactions, taking advantage of the decrease in hapticity, or slip of the ring, to maintain an 18-electron count on the metal center throughout the reaction.[1] Spectroscopic studies of dynamics have provided limited information for two reasons. First, ring slip was originally formulated to describe the decrease in hapticity of a cyclopentadienyl (Cp) ring and the Cp ring is still used as a model for the mechanism.[2] However, previous studies have not focused on the Cp ring, but have instead examined species for which crystal structures of the ring slipped intermediates were more easily obtained.[3,4] Second, the extreme reactivity of the intermediates required a low-temperature matrix environment for their observation, providing only a static picture of the formation of the ring slipped intermediate. Alternatively, conventional room-temperature experiments were unable to detect the fast formation of intermediates.[5]

We were able to address both these issues by examining the photochemistry of (η^1-C$_5$Cl$_5$)Mn(CO)$_5$ on a femtosecond to microsecond timescale in room-temperature alkane solution. Using UV-pump IR-probe spectroscopy we observe the "reverse" ring slip following the photoexcitation of (η^1-C$_5$Cl$_5$)Mn(CO)$_5$. Experimental observations reveal the fast formation of the two-carbonyl-loss product, (η^5-C$_5$Cl$_5$)Mn(CO)$_3$, as well as a two-step mechanism for the formation of the ring slipped intermediate. Density functional calculations suggest that the ring slipped structure, conventionally described as an η^3 species, is instead best described as a 17-electron η^2 species. Additional calculations show that the formation of a 17-electron intermediate may be the general mechanism for many reactions which are characterized as ring slip, a deviation from the standard 18-electron rule of organometallic chemistry.

Details of the femtosecond IR spectrometer have been published elsewhere.[6] The (η^1-C$_5$Cl$_5$)Mn(CO)$_5$ species was synthesized according to published procedure.[7] Spectra recorded on the ultrafast timescale, following the UV excitation of (η^1-C$_5$Cl$_5$)-Mn(CO)$_5$, revealed the bleach of the parent species, **A**, and the formation of four photoproducts, **B**, **C**, **D**, and **E**, shown in Figure
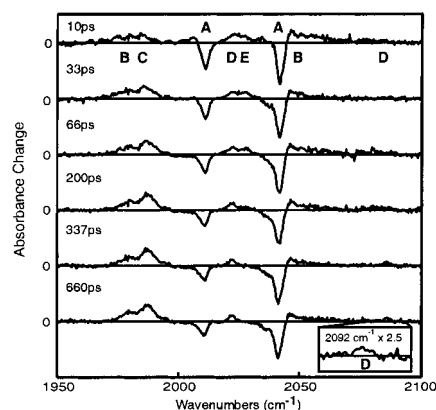

Figure 1. Ultrafast transient difference spectra following 295 nm photolysis of (η^1-C$_5$Cl$_5$)Mn(CO)$_5$ at various time delays.[11]

1. Species **B**, with peaks at 1980 and 2046 cm^{-1}, is assigned as (η^5-C$_5$Cl$_5$)Mn(CO)$_3$ by comparison to the IR peak positions of the isolated species.[7] This is a surprising result, as the appearance of a two-carbonyl-loss product is unusual for a single photon excitation in the solution phase on the ultrafast timescale.[8,9] The radical species Mn(CO)$_5$, **C**, appears at 1990 cm^{-1} as confirmed by earlier experiments.[10] The kinetics of both **B** and **C** show a fast formation of less than 50 ps, corresponding to vibrational relaxation, and then remain constant over 660 ps.

Photoproducts **D** and **E** are more difficult to assign. The correlation of the decay of **E**, at 2024 cm^{-1}, with the recovery of the parent species, **A**, makes it possible to consider **E** to be an electronic excited state of the parent species which reforms ground state (η^1-C$_5$Cl$_5$)Mn(CO)$_5$ on a timescale of approximately 250 ps for 295 nm excitation and 180 ps for 325 nm excitation.[12,13] On the ultrafast timescale there are two peaks corresponding to **D**, 2020 and 2092 cm^{-1}. Previously, peaks appearing at 1963, 2018, and 2093 cm^{-1} had been attributed to (η^3-C$_5$Cl$_5$)Mn(CO)$_4$ based on the IR spectra of the allyl species (η^3-C$_3$H$_5$)Mn(CO)$_4$.[14,15] It seemed reasonable that a species which was apparently an intermediate in the η^1 to η^5 rearrangement and had a vibrational spectra similar to that of the three carbon allyl would be the η^3 species.

While the spectra of **D** is similar to that proposed for the (η^3-C$_5$Cl$_5$)Mn(CO)$_4$ species, no feature is observed near 1963 cm^{-1}. To investigate the absence of a peak at 1963 cm^{-1} on the ultrafast timescale, spectra were recorded on the nanosecond to microsecond timescale using a Step-Scan FTIR spectrometer, described elsewhere.[16] On the nanosecond timescale it is possible to detect a peak at 1964 cm^{-1} with a rise time of 136 ± 53 ns. These results suggest the existence of a two-step mechanism for the formation of the ring slipped intermediate.[17] The first step is the formation of **D** on the ultrafast timescale. The second step is

‡ Present Address: Harvard University, Chemical Laboratories, Box 225, 12 Oxford Street, Cambridge, MA 02138.
(1) (a) Basolo, F. *New J. Chem.* **1994**, *18*, 19. (b) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.
(2) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657.
(3) There exists a single crystal structure of a slipped Cp ring. Huttner, G.; Brintzinger, H. H.; Bell, L. G. *J. Organomet. Chem.* **1978**, *145*, 329.
(4) (a) Alt, H. G.; Samuel, E. *Chem. Soc. Rev.* **1998**, *27*, 323. (b) Chowdhury, S. K.; Samanta, U.; Puranik, V. G.; Sarkar, A. *Organometallics* **1997**, *16*, 2618. (c) Heenan, D. P.; Long, C.; Montiel-Palma, V.; Pryce, M. T.; Perutz, R. N. *Organometallics* **2000**, *19*, 3867. (d) Breheny, C. J.; Draper, S. M.; Grevels, F. W.; Klotzbucher, W. E.; Long, C.; Pryce, M. T.; Russell, G. *Organometallics* **1996**, *15*, 3679.
(5) Young, K. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 157.
(6) Lian, T.; Bromberg, S. E.; Asplund, M. C.; Yang, H.; Harris, C. B. *J. Phys. Chem.* **1996**, *100*, 11994.
(7) Reimer, K. J.; Shaver, A. *Inorg. Chem.* **1975**, *14*, 2707.

(8) In general, the excess energy from the pump photon will be lost to the surrounding solvent before a second carbonyl may be dissociated.
(9) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941.
(10) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.
(11) Spectra were measured in pentane, kinetics in undecane. A comparison of spectra taken in both solvents revealed no observable differences.
(12) While **E** may be considered a vibrationally excited state of the parent species, it seems unlikely considering the relatively long timescale for recovery compared to the 150 ps timescale which serves as an approximate upper bound for the vibrational relaxation of similar organometallic compounds. See ref 13.
(13) Dougherty, T. P.; Heilweil, E. *J. Chem. Phys. Lett.* **1994**, *227*, 19.
(14) The spectra of Young and Wrighton showed a peak at 2004 cm^{-1} which was also attributed to (η^3-C$_5$Cl$_5$)Mn(CO)$_4$. It is most likely obscured by the parent bleach at 2010 cm^{-1} in our spectra.
(15) Hitam, R. B.; Mahmoud, K. A.; Rest, A. J. *J. Organomet. Chem.* **1985**, *291*, 321 and references therein.
(16) Sun, H.; Frei, H. *J. Phys. Chem. B* **1997**, *101*, 205.

Scheme 1. Overall Mechanism of Ring Slip Following Photodissociation. Structures Obtained Using DFT
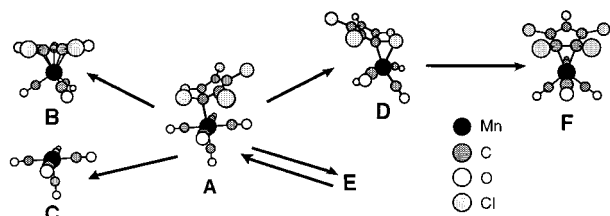
observed on the nanosecond timescale with the rise of **F**, a species with peaks overlapping those of **D** in addition to the 1964 cm^{-1} peak.[18] Young and Wrighton's previous experiments combined with the ultrafast and nanosecond data suggest **F** is the ring slipped intermediate which forms via the intramolecular rearrangement of **D**.

Density functional theory (DFT) was used to determine structures of the intermediate species. All DFT calculations were accomplished with the use of the commercial package JAGUAR[19] with the B3LYP[20] exchange-correlation functional and the LACVP**[21] basis set. Solvation calculations were performed using the cyclohexane model solvent provided with JAGUAR. Optimized geometries were calculated using the two methods described below. The first method for the formation of an intermediate structure began with the optimized parent species, $(\eta^1\text{-}C_5Cl_5)Mn(CO)_5$. It was found that the lowest energy structure resulted from optimization following the removal of a single equatorial carbonyl, in agreement with the studies of Young and Wrighton.[5] The resulting structure, best described as chlorine-coordinated, is shown in Scheme 1 as **D**. Removal of an axial carbonyl produces an η^3 structure with a relative gas-phase energy +19.1 kcal/mol greater than that of the chlorine-coordinated species.

The second method takes the opposite approach, starting with an optimized η^5 structure, $(\eta^5\text{-}Cp)Mn(CO)_3$. A -2 charge is then added and the structure is optimized again. Veiros had used this method to obtain a structure for $[(\eta^3\text{-}Cp)Mn(CO)_3]^{2-}$.[22] Following the same procedure, but with a chlorinated Cp ring, results in an η^2 structure, $[(\eta^2\text{-}C_5Cl_5)Mn(CO)_3]^{2-}$. We replaced the -2 charge with an additional carbonyl on the Mn center of the optimized η^2 structure. This results in an η^2 structure, $(\eta^2\text{-}C_5Cl_5)Mn(CO)_4$, with a planar ring slipped to an η^2 position shown in Scheme 1 as **F**. Despite numerous attempts, we have been unable to converge an η^3 structure for a chlorinated Cp ring using this method.

The use of theoretical data for the determination of **D** is difficult as no real physical picture exists for its description. On the basis of the methods for generating DFT geometries it is possible to consider the chlorine-coordinated species to be the structure of **D**. The DFT frequency calculations suggest that, of possible structures, it is only the chlorine-coordinated species that has the same number of peaks as are experimentally observed. While this does not confirm that the chlorine-coordinated species is the initial photoproduct, it does provide a possible description of **D**.

The assignment of **F** as $(\eta^3\text{-}C_5Cl_5)Mn(CO)_4$ had been based on comparisons to the IR spectra of $(\eta^3\text{-}C_3H_5)Mn(CO)_4$. However, DFT calculations show that the 17-electron species, $(\eta^2\text{-}C_5Cl_5)\text{-}Mn(CO)_4$, is lower in energy that the 18-electron species, $(\eta^3\text{-}C_5Cl_5)Mn(CO)_4$. This is true for both gas-phase and solution-phase calculations. In addition, calculations performed for tetracarbonyl species in which the chlorinated Cp ring was replaced with either Cp or Cp* [Cp* = (CpMe$_5$)] indicate that in both cases a lower energy structure is obtained for the η^2, rather than the η^3 species.[23] These calculations show that the formation of the 17-electron species may be quite general and cannot be attributed to steric or electronic arguments.[24]

Based on experimental observations and DFT calculations the mechanism of the reverse ring slip of $(\eta^1\text{-}C_5Cl_5)Mn(CO)_5$, shown in Scheme 1, can be described as follows: the UV excitation of $(\eta^1\text{-}C_5Cl_5)Mn(CO)_5$, **A**, results in the fast formation (<50 ps) of four species. These four species include the following: **B**, the two-carbonyl loss $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ product; **E**, an electronic excited state of the parent species; **C**, the radical Mn(CO)$_5$; and **D**, a short-lived intermediate that may be described as chlorine-coordinated. On a timescale of 136 ns, **D** rearranges to form **F**, the long-lived $(\eta^2\text{-}C_5Cl_5)Mn(CO)_4$.

One interesting aspect of this mechanism is the consideration of the ring slipped intermediate as a 17-electron species for Group VII transition metals. Although ring slip has previously been proposed to maintain an 18-electron count on a metal center, it appears that the 17-electron η^2 species is the thermodynamically favorable structure for Group VII metals. It is possible that previous studies which have inferred η^3 species by examining peak shifts in infrared data could be reformulated in terms of a 17-electron η^2 species. Also important is the experimental observation of **B**, $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$, on the ultrafast timescale. This is a rare example of a two-carbonyl-loss process in solution and as such conflicts with the widely held convention that excess energy is lost to the solvent before a second carbonyl can be lost. Clearly additional experiments will be necessary to elucidate this process.

Note Added after ASAP. In the last paragraph of the first column on the second page, two chemical formulas were incorrect in the version posted July 10, 2001; the corrected version was posted July 25, 2001.

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(17) Young and Wrighton suggested a "two-step" mechanism in the sense that the unobserved $(\eta^1\text{-}C_5Cl_5)Mn(CO)_4$ was the first step in the formation of the long-lived intermediate. It seems unlikely that the rearrangement would occur on a timescale as long as 136 ns considering that the formation of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ occurs in less than 1 ps.

(18) Kinetic analysis shows that the rise at 1964 cm^{-1} is equal to a rise at 2020 cm^{-1}. No decay of **D** is observed, most likely due to a greater absorption coefficient for **F** than for **D**.

(19) *Jaguar*, 3.5 ed.; Schrodinger, Inc.: Portland, OR, 1998.

(20) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(21) (a) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(22) Veiros, L. F. *J. Organomet. Chem.* **1999**, *587*, 221.

(23) As a check of the methods, $(\eta^2\text{-}Cp)CpW(CO)_2$ has been optimized in the gas-phase. It was found that the ring will rearrange to form the η^3 species, in agreement with the crystal structure.

(24) Calculations comparing the gas-phase energies of the η^2 and η^3 species of the Group VII metals show that the difference in energy ($\eta^3 - \eta^2$) increases as Tc < Mn < Re, with Re least likely to be η^3. It is interesting to note that this ordering is the same as the ionization energy of the metal, i.e. M(I)$-$M(0).