Acknowledgment. The author is grateful to the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for support of this work. I also thank Professor M. Cowie of this department for the use of his diffractometer and for helpful discussions on the X-ray crystallographic analysis.

Supplementary Material Available: Analytical and spectroscopic data for **1b**, **1c**, **2b**, **2c**, **3b**, and **3c** and tables of crystal data and details of intensity collection, positional parameters, anisotropic thermal parameters, least-squares planes, and bond lengths and angles (17 pages); a listing of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Flash Photolysis Studies of Lewis Base Addition to $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$

Richard S. Herrick,* Aaron B. Frederick, and Ronald R. Duff, Jr.

Department of Chemistry, College of the Holy Cross
Worcester, Massachusetts 01610

Received September 9, 1988

Summary: Flash photolysis studies on $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in hexane confirm formation of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ following flash photolysis. Decay proceeds with a rate of 151 (10) $M^{-1}\ s^{-1}$ for added CO and of 1.34 (5) $\times\ 10^3\ M^{-1}\ s^{-1}$ for added PPh_3.

The $CpM(CO)_x(\eta^1\text{-}CH_2C_6H_5)$ (M = Fe, x = 2; M = Mo or W, x = 3) system has provoked interest because loss of carbon monoxide leads to the corresponding η^3-benzyl complex[1] in analogy to the $CpM(CO)_x(\eta^1\text{-}C_3H_5)$ allyl system.[2] Recent work has concentrated on the iron derivative which, unlike the corresponding molybdenum and tungsten derivatives,[1] does not have a stable η^3-benzyl intermediate. Wrighton and co-workers[3] have examined the low-temperature infrared spectroscopy of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ which was prepared photochemically from $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$. Brookhart and co-workers[4] have reported some preliminary measurements on the nano- and microsecond flash photolysis of $CpFe(CO)(\eta^1\text{-}CH_2C_6H_5)$ and examined the kinetics of trapping of the η^3-benzyl intermediate by phosphines at low temperature. We wish to report a kinetic study of the room-temperature reaction of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ with carbon monoxide or PPh_3 which clarifies the role of the η^3-intermediate.

Flash photolysis[5] of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in hexane at 22 °C under 1 atm of carbon monoxide produces a transient which decays exponentially back to the original base line in approximately 3 s (Figure 1). The transient is completely formed by the end of the lamp pulse. The transient absorption spectrum, obtained by measuring absorbance changes as a function of wavelength, shows the previously recorded value of 460 nm ± 5 nm as λ_{max}.[3] Solutions under CO are nearly photochromic, but continued flashing produces a new transient which decays much more rapidly. This is attributed to formation of the exo form of $(\eta^4\text{-}C_5H_5CH_2C_6H_5)Fe(CO)_3$ which was observed as a minor product following low-temperature continuous photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ under a CO atmosphere.[3] Similar experiments with excess PPh_3 under a nitrogen atmosphere produce an exponential decay to a new base line of increased absorbance. Solutions containing PPh_3 change from yellow to orange following a single flash. An intense band appearing at 1917 cm^{-1} (hexane) indicates formation of $CpFe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$.[4,6]

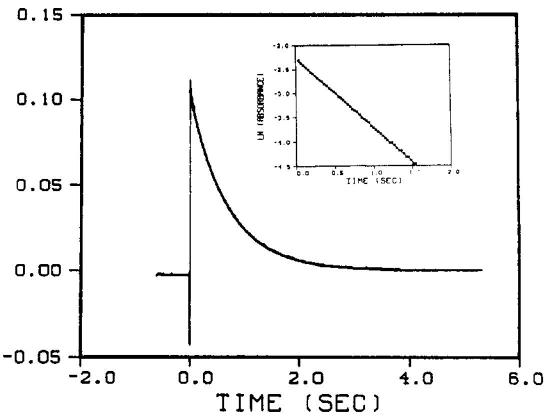


Figure 1. Change in absorbance vs time at 460 nm on flash photolysis of a CO saturated hexane solution of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$. The line through the decay curve represents the nonlinear first-order least-squares fit of the data for the disappearance of the transient. Insert: linear least-squares first-order fit of the data to 3.1 half-lives; $R = -0.9998$.

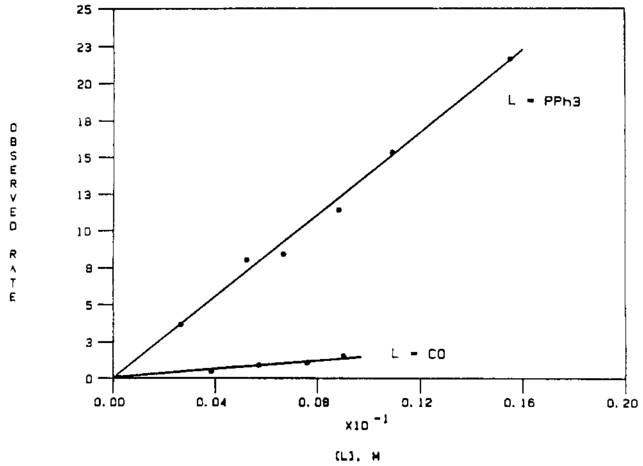
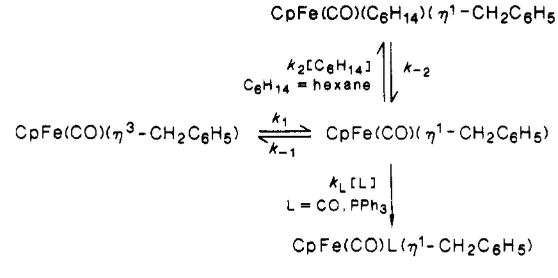


Figure 2. Plot showing the linear dependence of the observed rate constant against PPh_3 concentration (top line) and CO concentration (bottom line) for disappearance of the transient following flash photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$.

Scheme I



---

[1] Selected examples include: (a) King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966**, *88*, 709. (b) Cotton, F. A.; La Prade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418. (c) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339.

[2] (a) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, *189*. (b) Dub, M. *Organometallic Compounds*, 2nd ed.; Springer-Verlag: Berlin, 1966; Vol. 1. (c) Gibson, D. H.; Hsu, W. L.; Lin, D. S. *J. Organomet. Chem.* **1979**, *172*, C7.

[3] Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

[4] (a) Brookhart, M.; Buck, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 559. (b) Brookhart, M.; Buck, R. C.; Danielson, E. *J. Am. Chem. Soc.* **1989**, *111*, 567.

[5] See: Herrick, R. S.; Peters, C. H.; Duff, R. R. *Inorg. Chem.* **1988**, *27*, 2214 for a description of the flash photolysis setup.

0276-7333/89/2308-1120$01.50/0

A linear relationship was observed between k_{obsd} and [L] where L is either CO or PPh_3 (Figure 2),[7] showing the observed rate law is first order in both transient and added ligand. The bimolecular rate constant for recombination with CO is 151 (10) $M^{-1}\ s^{-1}$ and with PPh_3 is 1.34 (5) × 10^3 $M^{-1}\ s^{-1}$. These rate constants are small compared to other processes involving Lewis base addition to a CO-deficient transient. For instance, addition of CO to $Cr(CO)_5(C_6H_{12})$ (C_6H_{12} = cyclohexane) has a rate constant of 3 × 10^6 $M^{-1}\ s^{-1}$.[8] Furthermore, flash photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in perfluorohexane under CO gives an observed rate constant only 5 times faster than that observed in hexane[9] showing that desolvation is not contributing to the activation barrier for CO addition. Thus the η^3-benzyl configuration is implicated as the observed transient.

A mechanism that satisfactorily accounts for this data is shown in Scheme I.[10] While there is no direct evidence in this study for either intermediate ($CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ is not an intermediate in this mechanism), NMR investigations demonstrate that the η^3-benzyl ligand rearranges via an η^1-intermediate.[1b,4,11] Furthermore, others have shown that 16-electron systems, such as $Cr(CO)_5$ and $W(CO)_5$, will be solvated in less than 100 ps[12] with a solvent molecule acting as a "token ligand".[13]

Assuming that the equilibria are rapid relative to the product forming step for the two intermediates in Scheme I, the derived rate law is $R = k_1k_L[CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)][L]/(k_{-1} + k_L[L])$. With $k_{-1} > k_L[L]$, the rate law, $R = k_{app}[CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)][L]$ is obtained with $k_{app} = k_1k_L/k_{-1}$. This is identical with the experimentally observed rate law. The ratio of the two rate constants, $k_{app(PPh_3)}/k_{app(CO)} = 8.9$.[14] Typically, competition ratios of 6 or less have been observed for various ligands competing with CO at organometallic metal centers following ligand loss.[15] A competition ratio of this magnitude is usually interpreted as indicating a high reactivity and low selectivity of a desolvated 16-electron species. It should be noted, however, that while this proposed mechanism is consistent with mechanisms proposed for comparable systems,[13,15e,16] no direct kinetic evidence is available demonstrating that ligand attack occurs on the desolvated 16-electron intermediate rather than on the solvated species or on the η^3-system.

Further studies on this system are currently in progress.

Acknowledgment. We thank Professor M. S. Brookhart for supplying preprints of his work. We acknowledge a William and Flora Hewlet Foundation Grant from the Research Corp. and thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation through Grant No. CHE87-12543 for support of this research.

---

(6) Determined by one flash of a Sunpak 321 S camera flash on a solution of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and PPh_3 in hexane in an IR cell. $CpFe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$, produced by the literature method,[3] exhibits an identical IR spectrum.

(7) (a) The concentration of CO in hexane is obtained from P_{CO}, Henry's Law, and the solubility of CO in hexane. (b) Atwood, J. D. Ph.D. Dissertation, University of Illinois, Urbana, IL, 1976.

(8) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259.

(9) (a) The solubility of CO in perfluorohexane under 1 atm of CO has not been reported. In perfluoroheptane it is 0.017 M which, for the observed rate constant of 14 (1) s^{-1}, corresponds to a bimolecular rate of 820 (60) $M^{-1}\ s^{-1}$. This is about 5 times larger than the rate in hexane but still 6 orders of magnitude smaller than the diffusion-controlled rate constant expected if solvation effects pertain. (b) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220. (c) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344. (d) Herrick, R. S.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 4550.

(10) NMR and other data[1b,4,11] show that the η^3-benzyl ligand exists as the endo form (benzo group trans to cyclopentadienyl) and rapidly fluctuates between enantiomers, and imply that α-H elimination from an η^1-intermediate forms a carbene hydride transient.[4a] This information does not need to be invoked to interpret the data presented here.

(11) Mann, B. E.; Shaw, J. P. *J. Organomet. Chem.* **1987**, *326*, C13.

(12) (a) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751. (b) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1987**, *91*, 5538. (c) Langford, C. H.; Moreljo, C.; Sharma, D. K. *Inorg. Chem. Acta* **1987**, *126*, L11.

(13) The term "token ligand" refers to a weakly interacting ligand, usually a solvent molecule, which occupies a specific coordination site of an organometallic intermediate following ligand loss. See: Dobson, G. R.; Hodges, P. M.; Healy, M. A.; Poliakoff, M.; Turner, J. J.; Firth, S.; Asali, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 4218.

(14) Since k_1/k_{-1} is independent of the ligand, the ratio of the two observed rate constants is equal to the ratio of k_{PPh_3} to k_{CO}.

(15) (a) Day, J. P.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 6927. (b) Cardaci, G.; Narciso, V. *J. Chem. Soc. Chem. Commun.* **1972**, 2289. (c) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820. (d) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286. (e) Asali, K. J.; Basson, S. S.; Tucker, J. S.; Hester, B. C.; Cortes, J. E.; Awad, H. H.; Dobson, G. R. *J. Am. Chem. Soc.* **1987**, *109*, 5386 and references therein.

(16) Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakoff, M. *Organometallics* **1987**, *6*, 2600.

Nucleophilic Catalysis of Organosilicon Substitution Reactions

Patrick J. Lennon,*,[†] David P. Mack, and Quentin E. Thompson

Monsanto Chemical Company
800 N. Lindbergh Blvd.
St. Louis, Missouri 63167

Received February 8, 1989

Summary: Catalytic quantities of cyanide or thiocyanate ions are shown to facilitate the substitution of silyl chlorides by Grignard reagents and dialkylmagnesium reagents, to afford high yields of tetraalkyl- and tetraarylsilanes under extremely mild conditions.

Organolithium reagents are usually preferred to Grignard reagents for the synthesis of tetraorganosilanes. While Grignard reagents might otherwise be the reagents of choice because of greater availability, ease of formation, and cost, their reactions with triorganosilyl chlorides are so sluggish that only the simplest tetraorganosilanes can be obtained in satisfactory yields and purity.[1] We here report that cyanide and thiocyanate ions catalyze the reaction between organomagnesium reagents and chlorosilanes under extremely mild conditions affording tetraorganosilanes in high yield (eq 1).

$$RMgX + R'_nSiCl_{4-n} \xrightarrow[\le 15\ °C]{5\%\ CN^-} R'_nSiR_{4-n} + ClMgX \qquad (1)$$

For example, aryl Grignard reagents have been reported to yield tetraarylsilanes after reaction with $SiCl_4$ above 160 °C.[2] In contrast to these conditions, 5 mol % CuCN promotes the reaction of *p*-tolyltrichlorosilane with phenylmagnesium chloride at 10 °C to afford an 81% yield of *p*-tolyltriphenylsilane[3] after 1 h. This catalyst promotes reaction of both alkyl Grignards and dialkylmagnesium reagents. In the case of R_2Mg reagents, prepared by the excellent method of Bogdanovic,[4] this catalysis is partic-

---

[†] Present address: Central Research Laboratories, Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO 63167.

(1) (a) Eaborn, C. *Organosilicon Compounds*; Butterworths Scientific Publications: London, 1960; pp 22–25. (b) Eaborn, C.; Bott, R. W. In *Organometallic Compounds of the Group IV Elements*; Mac Diarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, Part 1, pp 111–113.

(2) Cusa, N. W.; Kipping, F. *J. Chem. Soc.* **1933**, 1040–1043.

(3) Gilman, H.; Clark, R. N. *J. Am. Chem. Soc.* **1946**, *68*, 1675–1676.