

## Femtosecond Infrared Studies of Silane Silicon–Hydrogen Bond Activation

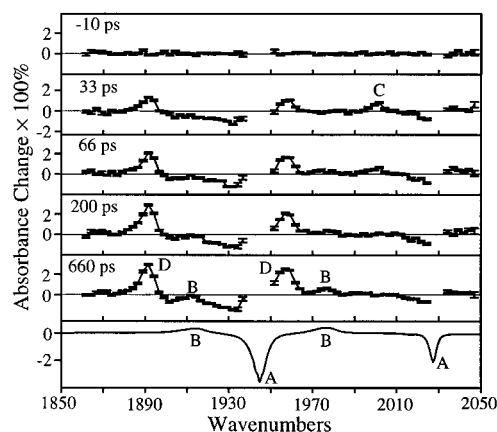
H. Yang, K. T. Kotz, M. C. Asplund, and C. B. Harris\*

Department of Chemistry, University of California  
Berkeley, California 94720

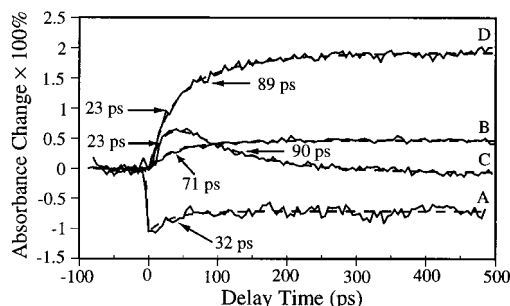
Received May 20, 1997

Cleavage, or activation, of the silicon–hydrogen bond of a silane by a metal center has been the focus of many recent studies.<sup>1–6</sup> Knowledge of this type of reaction is relevant to the central ideas of chemical bonding in general and is essential to the development of catalytic reactions such as hydrosilylation. It is commonly accepted that the photochemical reaction for the oxidative addition of  $\text{Et}_3\text{SiH}$  ( $\text{Et} = \text{C}_2\text{H}_5$ ) to  $\text{CpMn}(\text{CO})_3$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ) begins with the loss of a CO ligand as the result of UV irradiation, producing a coordinatively unsaturated dicarbonyl species<sup>7,8</sup> which further reacts to activate the Si–H bond to form  $\text{CpMn}(\text{CO})_2(\text{H})(\text{SiEt}_3)$ . Due to the fast reaction rates, however, the detailed reaction mechanism including the initial solvation of the nascent photogenerated chemical species has remained unclear. With the advent of ultrafast spectroscopy, especially in the infrared, it is now possible to identify such events which occur on a time scale shorter than diffusion to reveal the underlying elementary reaction steps.<sup>9</sup> In this communication, we report the first ultrafast infrared study on silicon–hydrogen bond cleavage by  $\text{CpMn}(\text{CO})_3$ .

As a result of photodissociating one CO ligand,<sup>10</sup> the kinetics of the parent molecule recorded at  $2028\text{ cm}^{-1}$  (A, Figure 1) shows an instrument limited bleach, 31% of which recovers in  $32 \pm 7.4\text{ ps}$  (Figure 2A).<sup>12</sup> This rapid recovery of the parent bleach is due to vibrational relaxation in the ground electronic manifold of the parent molecule.<sup>9,13,14</sup> The 31% recovery is in good agreement with reported CO loss quantum yields of 0.65 measured at 313-nm excitation.<sup>15</sup> Subsequent spectral evolution suggests that photolysis of the parent molecules leads to two transient species including  $\eta^5\text{-CpMn}(\text{CO})_2$  and a previously unreported intermediate. These reactive intermediates are solvated within a few picoseconds.<sup>16</sup> The initial solvation of the nascent species through either the ethyl moiety or the Si–H bond of the solvent partitions the reaction into two channels of



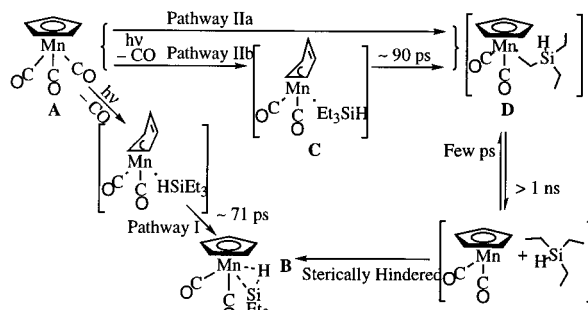
**Figure 1.** Transient difference spectra in the CO stretching region for  $\text{CpMn}(\text{CO})_3$  in neat triethylsilane at  $-10$ ,  $33$ ,  $66$ ,  $200$ , and  $660\text{ ps}$  following  $295\text{-nm}$  UV photolysis. The weak, broad bleaches in the regions  $1900\text{--}1937$  and  $2010\text{--}2015\text{ cm}^{-1}$  can be attributed to the dissociation of naturally abundant  $^{13}\text{CO}$  ligands from  $\text{CpMn}(\text{CO})_3$  (ref 33). The last panel is an FTIR difference spectrum before and after UV photolysis at  $308\text{ nm}$ . Notice that the absorption cross-section of the product (B) is much smaller than that of the parent molecule (A). The large absorption cross-section of the parent CO bands and the solvent Si–H band ( $\sim 2100\text{ cm}^{-1}$ ) made it very difficult to access some regions of the spectrum under the experimental conditions. A broad, wavelength independent background signal from  $\text{CaF}_2$  windows has been subtracted from the transient spectra and kinetics.



**Figure 2.** Kinetics (solid lines) of  $\text{CpMn}(\text{CO})_3$  in neat triethylsilane after  $295\text{-nm}$  UV photolysis at (A)  $2028\text{ cm}^{-1}$ , the parent molecule CO stretch, (B)  $1977\text{ cm}^{-1}$ , the CO stretch of the silyl adduct  $\text{CpMn}(\text{CO})_2(\text{H})(\text{SiEt}_3)$ , (C)  $2002\text{ cm}^{-1}$ , and (D)  $1892\text{ cm}^{-1}$ . The wavelengths were chosen to minimize overlap with adjacent peaks. The time constants for the exponential fits (dashed lines) are shown in the graph.

\* Author to whom correspondence should be addressed.

- (1) Palmer, B. J.; Hill, R. S. *Can. J. Chem.* **1996**, *74*, 1959.
- (2) Breckenridge, W. H. *J. Phys. Chem.* **1996**, *100*, 14840.
- (3) Hu, S.; Farrell, G. J.; Cook, C.; Johnston, R.; Burkey, T. J. *Organometallics* **1994**, *13*, 4127.
- (4) Hester, D.; Sun, J.; Harper, A. W.; Yang, G. K. *J. Am. Chem. Soc.* **1992**, *114*, 5234.
- (5) Burkey, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8329.
- (6) Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 799.
- (7) Young, K. M.; Wrighton, M. S. *Organometallics* **1989**, *8*, 1063.
- (8) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.
- (9) Lian, T.; Bromberg, S. E.; Yang, H.; Proulx, G.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **1996**, *118*, 3769.
- (10) The sample  $\eta^5\text{-CpMn}(\text{CO})_3$  (99%) was purchased from Strem, Inc. and dissolved in dried, oxygen-free triethylsilane acquired from Gelest, Inc. Unless otherwise specified, the sample was prepared under nitrogen atmosphere in a  $500\text{ }\mu\text{m}$  thick, air-tight flow cell. Its concentration,  $\sim 18\text{ mM}$ , was adjusted such that the absorbance was approximately 0.6 OD at  $295\text{ nm}$ . The femtosecond IR spectrometer setup with  $\sim 300\text{ fs}$  temporal resolution and  $\sim 4\text{ cm}^{-1}$  spectral resolution has been described in ref 11. In brief, the sample was photoexcited by  $30\text{ Hz}$ ,  $\sim 6\text{ }\mu\text{J}$  pulses at  $295\text{ nm}$ , and the subsequent spectral changes in the CO stretching region were monitored by a broad band IR probe. The polarizations of the pump and the probe pulse were set at the magic angle ( $54.7^\circ$ ) to make sure that all transient signals were due to population dynamics.
- (11) Lian, T.; Bromberg, S. E.; Asplund, M. C.; Yang, H.; Harris, C. B. *J. Phys. Chem.* **1996**, *100*, 11994.
- (12) Uncertainties represent one standard deviation.
- (13) Dougherty, T. P.; Grubbs, W. T.; Heilweil, E. J. *J. Phys. Chem.* **1994**, *98*, 9396.
- (14) Arrivo, S. M.; Dougherty, T. P.; Grubbs, W. Y.; Heilweil, E. J. *Chem. Phys. Lett.* **1995**, *235*, 247.
- (15) Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160.
- (16) King, J. C.; Zhang, J. Z.; Schwartz, B. J.; Harris, C. B. *J. Chem. Phys.* **1993**, *99*, 7595 and references therein.



**Figure 3.** A proposed reaction mechanism for the photochemical Si–H bond activation of  $\text{Et}_3\text{SiH}$  by  $\text{CpMn}(\text{CO})_3$ . Suggestive chemical structures are in brackets.

*disparate time scales.* One channel involves a dissociative rearrangement to form the final adduct (pathway II, Figure 3), while the other channel includes a direct addition of the Si–H bond to the new intermediate, possibly a ring-slipped  $\eta^3$  dicarbonyl (pathway I, Figure 3). Solvation of  $\eta^5\text{-CpMn}(\text{CO})_2$  and the new intermediate through the ethyl group of  $\text{Et}_3\text{SiH}$  gives rise to a pair of bands at  $1892$  and  $1957\text{ cm}^{-1}$  (D, Figure

1) and a peak at 2002  $\text{cm}^{-1}$  (**C**, Figure 1), respectively. Assigned to  $\eta^5\text{-CpMn}(\text{CO})_2(\text{Et}_3\text{SiH})$ , **D** has also been observed in the low-temperature-glass studies.<sup>17</sup> Its kinetics displays a biexponential rise of time constants  $23 \pm 6.4$  and  $89 \pm 20$  ps (Figure 2D), and maintains the intensity up to  $\sim 1$  ns. On the other hand, the new transient species **C** shows a rise time of  $23 \pm 2.3$  ps and a decay time of  $90 \pm 6.7$  ps (Figure 2C). While the 23-ps component of both **C** and **D** is consistent with vibrational relaxation, the similarity between the decay of **C** (90 ps) and the rise time of **D** (89 ps) indicates that **C** and **D** are kinetically coupled (pathway IIb, Figure 3). The identity of **C** cannot be a vibrationally excited **A** since the latter time constant is greater than the bleach recovery time of **A**. However, it is very likely that the **C** band is due to a dicarbonyl species with the second CO stretching band buried in the weak, broad bleach ( $1900\text{--}1937\text{ cm}^{-1}$ ).<sup>18</sup> Considering its  $\sim 45\text{ cm}^{-1}$  blue-shift from the higher energy band of **D** and the chemical reactivity of the electron donating Cp ligand, we tentatively assign **C** as an ethyl-solvated  $\eta^3$  dicarbonyl.<sup>19,20</sup> This assignment is consistent with the observed  $30\text{ cm}^{-1}$  blue-shifting of the CO stretching frequency resulting from lowering of the hapticity of  $\eta^3\text{-Tp}^*\text{Rh}(\text{CO})_2$  ( $\text{Tp}^* = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borato}$ ) to form  $\eta^2\text{-Tp}^*\text{Rh}(\text{CO})_2$ .<sup>24,25</sup> With this assignment, the  $\sim 90$ -ps component can be related to re-chelation from an  $\eta^3$  to an  $\eta^5$  species (pathway IIb, Figure 3).

Eventually, on a time scale  $> 1$  ns as indicated by the absence of **D** in the static difference FTIR spectrum (bottom panel, Figure 1), **D** must further rearrange to form the product. For this rearrangement, two mechanisms have been proposed which are the "chain-walk" mechanism<sup>26</sup> and the "dissociative" mechanism.<sup>27</sup> The chain-walk mechanism was first proposed to account for the observed  $\sim 100$ -ps rearrangement from an alkyl-solvated  $\text{Cr}(\text{CO})_5(\text{ROH})$  to the more stable hydroxyl-solvated  $\text{Cr}(\text{CO})_5(\text{HOR})$ , where ROH is 1-propanol. If this is the case in our study, assuming that complexed  $\text{Et}_3\text{SiH}$  migrates from the terminal carbon of one ethyl group to the silicon atom, one would expect the rearrangement to be complete within 100 ps. However, the observed decay time of **D** is longer than 100 ps, suggesting that a "dissociative" mechanism is dominant. In such a pathway,  $\text{CpMn}(\text{CO})_2(\text{Et}_3\text{SiH})$  thermally dissociates slowly into a loosely bound  $\text{CpMn}(\text{CO})_2 \cdots (\text{Et}_3\text{SiH})$  complex, allowing the metal center to interact with the Si-H bond of possibly another solvent molecule. The minimum activation energy for such a dissociative process is then expected to be

(17) Hill, R. H.; Wrighton, M. S. *Organometallics* **1987**, *6*, 632.

(18) The gas-phase CO stretch frequency of the monocarbonyl  $\text{CpMn}(\text{CO})$  has been reported to be  $1948\text{ cm}^{-1}$ . Zheng, Y.; Wang, W.; Lin, J.; She, Y.; Fu, K.-J. *J. Phys. Chem.* **1992**, *96*, 7650.

(19) Lees, A. J.; Purwoko, A. A. *Coord. Chem. Rev.* **1994**, *132*, 155.

(20) Presently, we do not know the detailed structure of this intermediate **C**. Nevertheless, in a separate experiment on  $\text{CpMn}(\text{CO})_3$  in neat *n*-pentane, a transient absorption at  $2000\text{ cm}^{-1}$  with similar kinetic behavior was observed, which supports our assigning **C** as an ethyl solvate. With these data, however, we cannot exclude possible involvement of other electronic states in explaining the intermediate **C**. Metastable triplet states have been observed for Fe and Co complexes (refs 21 and 22), and experimental evidence as well as theoretical modeling (ref 23) suggests that transition metal complexes in electronic states of different multiplicity may assume different geometry, which in turn may affect the vibrational frequencies.

(21) (a) Ryther, R. J.; Weitz, E. J. *J. Phys. Chem.* **1991**, *95*, 9842. (b) Maciejewski, A.; Jawoska-Augustyniak, A.; Szeluga, Z.; Karolczak, J. *J. Chem. Phys. Lett.* **1988**, *153*, 227.

(22) (a) Bengali, A. A.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 3879. (b) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1996**, *118*, 1487.

(23) Rawlins, K. A.; Lees, A. J. *Inorg. Chem.* **1989**, *28*, 2154 and references therein.

(24) Generally, the CO stretching frequency of a metal carbonyl complex reflects the charge density on the metal center: the less charge the metal center has to back donate to CO  $\pi^*$  orbitals, the higher the CO stretching frequency will be. Therefore, the  $45\text{ cm}^{-1}$  blue-shift implies an electron deficient metal center for **C**.

(25) Bloyce, P. E.; Mascetti, J.; Rest, A. J. *J. Organomet. Chem.* **1993**, *444*, 223.

(26) Xie, X.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 1130.

(27) Ladogana, S.; Nayak, S. K.; Smit, J. P.; Dobson, G. R. *Inorg. Chem.* **1997**, *36*, 650.

dictated by the complexation enthalpy of a  $\text{CpMn}(\text{CO})_2$  and an alkyl group, which is estimated to be  $\sim 8\text{ kcal/mol}$ .<sup>28</sup> At room temperature, this barrier height corresponds to a reaction time scale of  $\sim 120\text{ ns}$ .<sup>29</sup> The observed rearrangement time ( $> 1\text{ ns}$ ) in this study therefore supports the "dissociative" mechanism (pathway II, Figure 3).

Potentially, the bare  $\eta^3$  species may also be solvated through the Si-H bond of the solvent and lead to the product  $\eta^5\text{-CpMn}(\text{CO})_2(\text{H})(\text{SiEt}_3)$  on a time scale similar to the decay of **C**, when the complex changes its hapticity from  $\eta^3$  to  $\eta^5$  thus providing sufficient electron density for the activation process. Indeed, the product band (**B**, Figure 1) exhibits a rise time of  $71 \pm 5.4$  ps (Figure 2B),<sup>30</sup> indicating that the Si-H bond may be activated by direct solvation through the Si-H bond of the solvent (pathway I, Figure 3). Furthermore, if the activation barrier of a Si-H bond is comparably small,<sup>6</sup> the apparent rate determining step would be the dissociative rearrangement from **D** to **B**. Our measured rates for the formation of **B** are also consistent with the observation that the overall enthalpy of activation is dominated by the enthalpy of dissociating the solvent from the reaction site, and that the transition state consists of a very loosely bound  $\text{R}_3\text{SiH}$ .<sup>17,31</sup>

In the light of the above discussion, the overall reaction mechanism is summarized in Figure 3. Upon UV excitation, **A** may lose one CO ligand to form  $\eta^5\text{-CpMn}(\text{CO})_2$ , or lose one CO ligand and at the same time undergo a change in its hapticity to an  $\eta^3$  species; both dicarbonyls are solvated within a few picoseconds. Solvation of the nascent  $\eta^3$  species via the Si-H bond of the solvent leads to the activated product on a time scale of 71 ps (pathway I). Solvation of the  $\eta^3$  and  $\eta^5$  dicarbonyls through the ethyl groups of the solvent results in **C** and **D**, respectively, where **C** evolves to form **D** on a time scale of 90 ps (pathway II). Finally, **D** rearranges dissociatively to form the product on a time scale greater than 1 ns.

This work represents the first study of Si-H bond activation at room temperature with ultrafast infrared spectroscopic methods, which are proving to be general and powerful means for studying complex chemical reaction dynamics in condensed phases. Our results suggest that the formation of  $\eta^5\text{-CpMn}(\text{CO})_2(\text{H})(\text{SiEt}_3)$  is partitioned by the initial solvation into two possible pathways: (1) formation through a new intermediate, possibly a photogenerated ring-slipped species, which decays to form the product on a time scale of about 71 ps; and (2) formation through an ethyl-solvated dicarbonyl species  $\text{CpMn}(\text{CO})_2(\text{Et}_3\text{SiH})$ , which eventually dissociatively rearranges to form the product on a time scale greater than 1 ns. This observation is consistent with the low reaction barrier for Si-H bond activation, in sharp contrast to the  $\sim 10\text{ kcal/mol}$  barrier in activating an isoelectronic C-H bond.<sup>32</sup>

**Acknowledgment.** This work was supported by a grant from the National Science Foundation. We are grateful to P. J. Alaimo for much assistance with the sample. We also thank C. B. Moore for use of the FTIR spectrometer and R. G. Bergman for fruitful discussions.

JA9716362

(28) Klassen, J. K.; Selke, M.; Sorensen, A. A.; Yang, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 1267.

(29) This time scale was estimated from simple transition state theory:  $1/\tau \cong k_{\text{TST}} = (k_{\text{B}}T/h)e^{-\Delta G^\ddagger/RT}$ , using the activation parameters from ref 28.

(30) For the product band, one may expect a biexponential rise similar to **D** if the  $\eta^5$  dicarbonyl is also solvated through the Si-H bond of the solvent. However, we did not observe such behavior. The reason is perhaps due to the statistical favor for the ethyl groups over the Si-H  $\sigma$ -bond in a triethylsilane. Furthermore, one would expect more steric hindrance for the  $\eta^5$  dicarbonyl to be solvated via the solvent's Si-H bond.

(31) Hart-Davis, A. J.; Graham, W. A. G. *J. Am. Chem. Soc.* **1971**, *93*, 4388.

(32) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science*. Accepted for publication.

(33) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1973**, *51*, 307.