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Rearrangement of η^5-CpMn(CO)$_2$(HSiEt$_3$): A Missing Step in the Energy Surface for the Oxidative Addition of Silane to CpMn(CO)$_2$(heptane)

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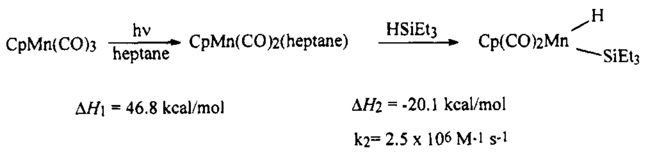
Summary: The rearrangement of a triethylsilane adduct with η^5-CpMn(CO)$_2$ has been detected by photoacoustic calorimetry. The energetics and kinetics of this process in neat triethylsilane, heptane, and perfluorodecalin are reported.

The oxidative addition of a silane to a metal center is a key step in hydrosilation of olefins and is analogous to the oxidation addition of alkanes to metal centers. The results of a recent study on the energetics of triethylsilane addition to η^5-CpMn(CO)$_2$ were found to disagree with those previously published in our laboratory.[1,2] In the most recent study using photoacoustic calorimetry (PAC), the enthalpies of CO displacement by heptane (ΔH_1) and heptane displacement by silane (ΔH_2, Scheme 1) were reported to be 46.8 ± 2.1 and −20.1 ± 2.1 kcal/mol, respectively, giving an overall enthalpy of 26.7 ± 3.0 kcal/mol.[1] This was in contrast to the more endothermic result (also using PAC) we obtained in neat triethylsilane (30.9 ± 1.0 kcal/mol),[2] where only a reaction with silane is possible. Thermochemically the results in heptane and neat silane should be identical since the overall reaction is the same,[3] but it was argued that the oxidative addition was too slow ($<10^7$ s) to be detected entirely by our experiment.[1] By analogy to Cr(CO)$_5$(EtX),[4] we reasoned that η^5-Cp(CO)$_2$-Mn(Et$_3$SiH) rearranges to η^5-Cp(CO)$_2$Mn(HSiEt$_3$) in less than 1 ns; therefore the total heat of CO displacement by the SiH group would be observed in our neat silane PAC experiment. If this were true, then it was not clear why the results were different for the two PAC studies, so we have reinvestigated the reaction under a variety of conditions. With further investigation, we have discovered that the adduct undergoes a rearrangement that was not reported by either of the previous studies. The rate of the rearrangement occurs on a time scale between that of the two studies and accounts for the reported discrepancies.

Scheme 1



We have confirmed the results of Yang *et al.* by repeating their experiments in heptane using deconvolution of the PAC signals (0.1 Mhz transducer):[5] ϕ_1 = 0.650 ± 0.005, ϕ_2 = 0.142 ± 0.010, k_2 = (1.4 ± 0.3) × 10^6 M^{-1} s^{-1}, ΔH_1 = 45.7 ± 0.7 kcal/mol, ΔH_2 = −18.5 ± 1.3 kcal/mol. The amplitudes of two consecutive decays

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[®] Abstract published in *Advance ACS Abstracts,* September 15, 1994.

[1] Hester, D.; Sun, J.; Harper, A. W.; Yang, G. K. *J. Am. Chem. Soc.* **1992**, *114*, 5234.

[2] Burkey, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8239.

[3] We found the quantum yield for substitution of η^5-CpMn(CO)$_3$ in silane (0.66 ± 0.09) to be the same as in alkane solvent (0.65). See: Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160.

[4] (a) Xie, X.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 1130. (b) O'Driscoll, E.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 6580.

[5] The apparatus and methods have been recently described: Nayak, S. K.; Burkey, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 6391.

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(ϕ_1 and ϕ_2) are expressed as a fraction of the light energy absorbed, and the second-order rate constant (k_2) and lifetimes (τ_2) correspond to ϕ_2. Processes that are much faster than the transducer response ($\tau_1 < 10^{-7}$ s) contribute to ϕ_1, and those whose rates are similar to the transducer response (10^{-7} s $< \tau_2 < 10^{-5}$ s) contribute to ϕ_2. The enthalpies of reaction (ΔH_1 and ΔH_2) are calculated from eqs 1 and 2, where $E_{h\nu}$ is the photon energy (84.8 kcal/mol) and Φ is the quantum yield (0.65).[3]

$$\Delta H_1 = E_{h\nu}(1 - \phi_1)/\Phi \tag{1}$$

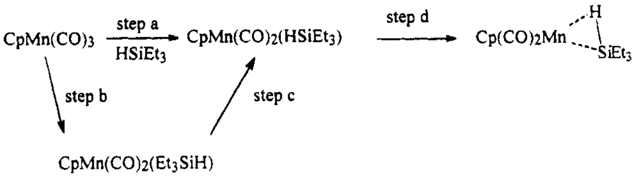
$$\Delta H_2 = -E_{h\nu}\phi_2/\Phi \tag{2}$$

$$1/\tau_2 = k_0 + k_2[\mathrm{L}] \tag{3}$$

We also repeated our experiments in neat triethylsilane, but in this case we analyzed the signals for the presence of more than one heat decay.[2] Two heat decays were detected, but the magnitudes are different than in heptane (1 Mhz transducer, $\phi_1 = 0.734 \pm 0.010$ and $\phi_2 = 0.071 \pm 0.006$, $\tau_2 = (1.3 \pm 0.3) \times 10^{-7}$ s). This yields $\Delta H_1 = 34.7 \pm 1.3$, $\Delta H_2 = -9.1 \pm 0.8$, and $k_{\mathrm{obs}} = (8 \pm 2) \times 10^6$ s^{-1}. Since silane is the solvent the reaction with it must contribute to the first heat decay; thus the detection of a second heat decay indicates a rearrangement on the time scale of the transducer. Furthermore the overall enthalpy is the same as that observed in heptane indicating that the same overall reaction is being observed.

It may be concluded that the rearrangement was not resolved in heptane because the rearrangement was faster than the displacement of heptane (compare k_2 and k_{obs}); that is, the heats of displacement and rearrangement are observed as a single heat decay (ϕ_2). If this were the case, carrying out the reaction in a solvent that is more readily displaced[6] would accelerate the initial adduct formation allowing the resolution of a rearrangement as a slower process. Photolysis of η^5-CpMn(CO)$_3$ with 5 or 15 mM triethylsilane in perfluorodecalin yielded two heat decays essentially identical to that observed in neat silane and independent of silane concentration (1 Mhz transducer, $\phi_1 = 0.733 \pm 0.030$, $\phi_2 = 0.08 \pm 0.03$), $\tau_2 = (2.1 \pm 0.2) \times 10^{-7}$ s, $k_{\mathrm{obs}} = (4.7 \pm 0.5) \times 10^6$ s^{-1}). Again, the detection of a second heat decay is consistent with a rearrangement since displacement of PFD is near the diffusion-controlled limit.[7] Note that an associative process, where Cp(CO)$_2$Mn(Et$_3$SiH) reacts with Et$_3$SiH, is not consistent with τ_2 being independent of silane concentration.

Scheme 2



The nature of the rearrangement is not clear, but at least two mechanisms fit the available results. On the basis of studies of Cr(CO)$_5$ species, it is clear that both η^5-Cp(CO)$_2$Mn(Et$_3$SiH) and η^5-Cp(CO)$_2$Mn(HSiEt$_3$) will be formed upon initial encounter (Scheme 2, steps a and b). In the first mechanism, step c is assigned to the second heat decay. This would mean that η^5-CpMn(CO)$_2$ walks along an alkyl chain (or alternatively dissociates from an alkyl and reassociates) much slower than Cr(CO)$_5$. For this mechanism, ΔH_1 is more exothermic in silane than in heptane because some SiH adduct is formed in addition to alkyl adduct during the first heat decay, and ΔH_2 is less exothermic because less SiH adduct is formed during the second heat decay than in heptane. In the second mechanism, step c is fast ($>10^7$ s^{-1} as it is for Cr(CO)$_5$(EtX) and contributes to the first heat decay) requiring an additional step to account for the second heat decay. Step d is proposed to involve an elongation of the SiH bond and/or rearrangement of ancillary ligands[8] and is analogous to rearrangements recently reported for dihydrogen complexes (L$_n$M(H$_2$) → L$_n$M(H)$_2$).[9] We are currently investigating other metal complexes and silicon compounds to determine the generality and details of this rearrangement.

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Supplementary Material Available: Text giving detailed experimental procedures and a table giving ϕ_1, ϕ_2, and τ_2 for each experiment (4 pages). Ordering information is given on any current masthead page.

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(6) Nayak, S. K.; Burkey, T. J. *Organometallics* **1991**, *10*, 3745.

(7) A bimolecular reaction faster than the transducer response is indicated by the observation of only one decay; for example, only a single heat decay was observed for 16 and 42 mM tetraethylsilane.

(8) The structures of related silane adducts indicate that complete scission of the SiH bond does not occur. See: (a) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4. (b) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1989**, *111*, 3583. (c) Lichtenberger, D. L.; Rai-Chaudhuri, A. *Inorg. Chem.* **1990**, *29*, 975. (d) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1990**, *112*, 2492. (e) Carre, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics* **1984**, *3*, 1272. (f) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81.

(9) (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.