

Competing Reaction Pathways in the Photochemical
Reactions of Manganese Carbonyl Compounds

Richard Sullivan

Final Seminar

April 20, 1990

Reactive metal carbonyl intermediates exist as coordinatively unsaturated 16-species [1] or as 17-e and 19-e radicals [2]. These intermediates are capable of reacting with main group metal hydrides by any of several pathways. Coordinatively unsaturated 16-e intermediates react via an oxidative addition pathway [3]. 17-e radicals undergo either H-atom transfer [4] or oxidative addition [5], whereas, 19-e radicals react via direct H-atom transfer [6].

It has been shown in several studies that irradiation of $Mn_2(CO)_{10}$ leads to two primary photoproducts, $Mn_2(CO)_9$ and $Mn(CO)_5\cdot$ [7-13]. The photochemical reaction of $Mn_2(CO)_{10}$ and its bis(phosphine) substituted analogs with a main group metal hydride such as $HSnBu_3$ represent a case of competing reaction pathways since both intermediates can potentially exhibit reactivity. To date, the mechanistic details of such reactions remain unclear. In this seminar, results from a continuous photolysis study and a flash photolysis study of the photochemical reaction of $Mn_2(CO)_{10}$ and its bis(phosphine) substituted analogs with $HSnBu_3$ will be presented.

Sunlamp irradiation of a CO-saturated hexane solution of $Mn_2(CO)_{10}$ and $HSnBu_3$ results in formation of $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$ in equimolar quantities. The rate of disappearance of $Mn_2(CO)_{10}$ and formation of products exhibit an inverse $[CO]$ dependence. These results are inconsistent with a direct H-atom transfer to $Mn(CO)_5\cdot$ as well as oxidative addition of $HSnBu_3$ to $Mn(CO)_5\cdot$ via the Brown-Wegman mechanism [5].

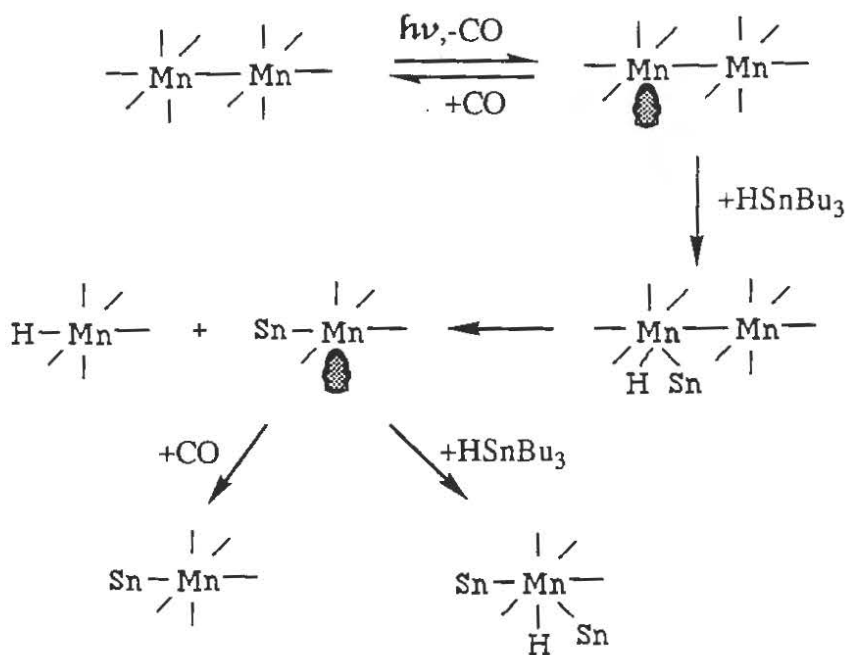
When the reaction of $Mn_2(CO)_{10}$ with $HSnBu_3$ is performed under 1 atm Ar, the rate of disappearance of $Mn_2(CO)_{10}$ is much faster than when CO is present, $HMn(CO)_5$ forms in much greater quantities than $Bu_3SnMn(CO)_5$, and a third product, identified as $HMn(CO)_4(SnBu_3)_2$, forms as the other major product. The above observations are consistent with a mechanism involving oxidative addition of $HSnBu_3$ to $Mn_2(CO)_9$ as shown in Scheme I.

The wavelength dependence of the quantum yield for product formation is also in accord with a mechanism involving oxidative addition of $HSnBu_3$ to $Mn_2(CO)_9$; the quantum yields for product formation and CO loss both increase with decreasing wavelength of radiation, which is opposite to the trend followed for Mn-Mn bond homolysis.

The reactions of $HSnBu_3$ with $Mn(CO)_4L\cdot$ ($L = CO$ or PR_3) and $Mn_2(CO)_7L_2$ were studied by flash photolysis. In every case examined, $HSnBu_3$ undergoes oxidative addition with $Mn_2(CO)_7L_2$. However, H-atom transfer to $Mn(CO)_4L\cdot$ does not occur. For $L = CO$, PMe_3 , $P(i-Bu)_3$, and $P(O-i-Pr)_3$, the initial product of oxidative addition, $Mn_2(CO)_7L_2(H)(SnBu_3)$, is observed. At longer time intervals, this intermediate disappears by reductive elimination of $HMn(CO)_4L$. $Mn_2(CO)_7L_2(H)(SnBu_3)$ is not observed when the metal center is crowded as in the cases of $L = P(i-Pr)_3$ and $P(C_6H_{11})_3$ because oxidative addition is slow relative to reductive elimination.

The transient absorbance decay of $\text{Mn}_2(\text{CO})_7\text{L}_2$ in the presence of HSnBu_3 obeys pseudo-first-order kinetics. Plots of k_{obs} vs. $[\text{HSnBu}_3]$ are linear for $\text{L} = \text{P}(\text{i-Bu})_3$, $\text{P}(\text{i-Pr})_3$, and $\text{P}(\text{C}_6\text{H}_{11})_3$. However, for $\text{L} = \text{PMe}_3$ and $\text{P}(\text{n-Bu})_3$, the k_{obs} vs. $[\text{HSnBu}_3]$ plot is non-linear throughout the entire $[\text{HSnBu}_3]$ range. A mechanism involving a rate determining equilibrium between unbridged $\text{Mn}_2(\text{CO})_7\text{L}_2$ and semi-bridged $\text{Mn}_2(\text{CO})_7\text{L}_2$ prior to oxidative addition of HSnBu_3 accounts for the experimental observations.

Scheme I



References

1. Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure App. Chem.*, Vol. 49, Pergamon Press: Great Britain, 1977; p. 271.
2. (a) Brown, T. L. *Ann. N. Y. Acad. Sci.* **1980**, 333, 80.
 (b) Stiegman, A. E.; Tyler, D. R. *Acc. Chem. Res.* **1986**, 5, 215.
 (c) Trogler, W. C. *Int. J. Chem. Kin.* **1987**, 19, 1025.
3. (a) Dong, D. F.; Hoyano, J. K.; Graham, W. A. G. *Can. J. Chem.* **1981**, 59, 1455.
 (b) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, 10, 4.
 (c) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, 10, 1.
 (d) Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, 91, 3375.
4. McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, 104, 7476.
5. Wegman, R. W.; Brown, T. L. *Organometallics* **1982**, 1, 47.

6. (a) Kuchynka, D. J.; Armatore, C.; Kochi, J. K. *Inorg. Chem.* 1986, 25, 4087.
(b) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* 1987, 6, 129.
(c) Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Organometallics* 1987, 6, 1886.
7. Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. J. *Am. Chem. Soc.* 1982, 104, 3536.
8. Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* 1983, 105, 6249.
9. Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* 1983, 105, 5934.
10. Fox, A.; Poë, A. J. *Am. Chem. Soc.* 1980, 102, 2497.
11. Dunkin, I. A.; Härter, P.; Shields, C. J. *J. Am. Chem. Soc.* 1984, 106, 7248.
12. Seder, T. A.; Church, S. P.; Weitz, E. J. *Am. Chem. Soc.* 1986, 108, 7518.
13. Kobayashi, T.; Ohtani, H.; Noda, H.; Teretani, S.; Yamazaki, H.; Yasufuku, K. *Organometallics* 1986, 5, 110.