

REACTIONS OF MANGANESE CARBONYL RADICALS:
HYDROGEN ATOM TRANSFER AND SUBSTITUTION.

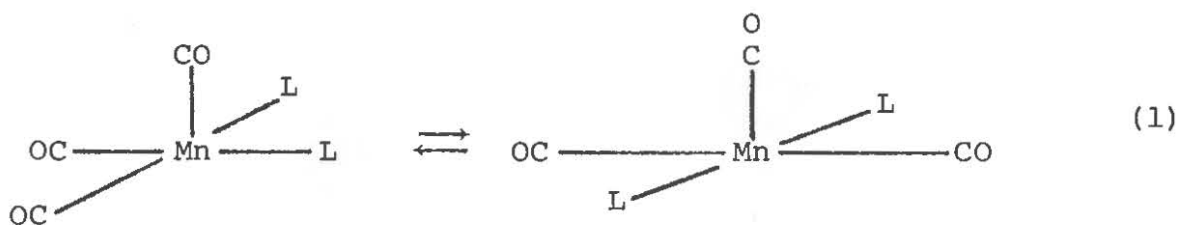
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The UV-visible spectra of dinuclear metal carbonyl compounds exhibit an intense absorption ($\epsilon \sim 10^4 \text{M}^{-1} \text{cm}^{-1}$) in the range of 300 to 500 nm. Gray has assigned this absorption to a $\sigma \rightarrow \sigma^*$ electron transition of the metal-metal bond. (1) Irradiation at wavelengths near the $\sigma \rightarrow \sigma^*$ transition leads to a lowering of the bond order from one to zero, resulting in homolysis of the metal-metal bond. The metal carbonyl radicals formed in this photochemical process have very short half lives, recombining at diffusion controlled rates. (2) In several cases, such as $[\eta^3\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3]_2$, weakening of the metal-metal bond interaction as a result of steric crowding leads to the existence of an equilibrium between the dinuclear compound and its paramagnetic monomers. (3) Dimerization does not occur for $\eta^3\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2\text{PPh}_3$ because the bulky PPh₃ ligand prevents recombination of the monomers. (4)

The extended photolysis of $\text{Mn}_2(\text{CO})_8\text{L}_2$ with L (L=phosphorus donor ligand) in hexane, with periodic removal of CO results in formation of $\text{Mn}(\text{CO})_3\text{L}_2$. The room temperature EPR spectrum of the irradiated solution is an overlapping sextet of triplets, consistent with the assignment $\text{Mn}(\text{CO})_3\text{L}_2$. This $17e^-$ species exhibits broad absorptions in its electronic spectrum ($\lambda_{\text{max}} = 750$ and 1120 nm) similar to that reported for $\text{Mn}(\text{CO})_5$ ($\lambda_{\text{max}} = 830$ nm). (5) Molecular orbital considerations predict a square pyramidal geometry for $\text{Mn}(\text{CO})_5$, (6) therefore it is likely that $\text{Mn}(\text{CO})_3\text{L}_2$ also has square pyramidal geometry. $\text{Mn}(\text{CO})_3\text{L}_2$ probably undergoes rapid isomerization as shown in Eqn (1)



The reaction of $\text{Mn}(\text{CO})_3\text{L}_2$ with CCl_4 leads to $2,4\text{-L}_2\text{-1-ClMn}(\text{CO})_3$ as the major reaction product along with small amounts of $2,3\text{-L}_2\text{-1-ClMn}(\text{CO})_3$ (7) suggesting that the equilibrium shown in Eqn. 1 favors trans basal positions for L in the radical. In the absence of trace amounts of oxygen the $\text{Mn}(\text{CO})_3\text{L}_2$ radicals are stable for several weeks making it possible to study the reactions of $\text{Mn}(\text{CO})_3\text{L}_2$ with HSnBu_3 and CO.

The reaction of $\text{Mn}(\text{CO})_3\text{L}_2$ with HSnBu_3 results in $\text{HMn}(\text{CO})_3\text{L}_2$ as the major reaction product based on IR and NMR data. The rate of reaction exhibits first order dependence upon the concentrations of $\text{Mn}(\text{CO})_3\text{L}_2$ and HSnBu_3 and decreases with the increasing cone angle of L for a series of phosphorus donor ligands with similar electronic properties. (8) For ligands with similar steric requirements, increasing the π -acceptor ability of L results in a slower rate of reaction. These observations

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support hydrogen atom transfer from HSnBu_3 to $\text{Mn}(\text{CO})_3\text{L}_2$ as the rate determining step in the reaction pathway.

The reaction of $\text{Mn}(\text{CO})_3\text{L}_2$ ($\text{L} = \text{P}(\text{n-Bu})_3, \text{P}(\text{i-Bu})_3$) with CO results in formation of $\text{Mn}_2(\text{CO})_8\text{L}_2$. The reaction of $\text{Mn}(\text{CO})_3[\text{P}(\text{i-Bu})_3]_2$ with CO exhibits first order dependence upon the concentrations of CO and $\text{Mn}(\text{CO})_3\text{L}_2$ and inverse dependence upon the concentration of free ligand. For a smaller ligand such as $\text{P}(\text{n-Bu})_3$ on $\text{Mn}(\text{CO})_3\text{L}_2$ reaction with CO is much faster. These observations support an associative reaction pathway for the substitution of L by CO on $\text{Mn}(\text{CO})_3\text{L}_2$.

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