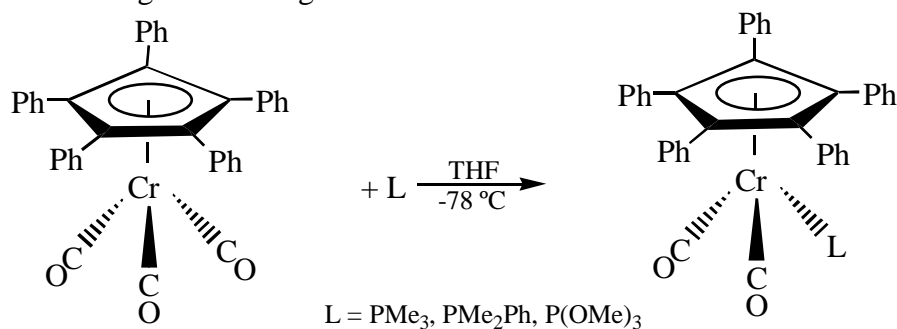


Substitution Reactions of $(C_5Ph_5)Cr(CO)_3$: Structural, Electrochemical, and Spectroscopic Characterization of $(C_5Ph_5)Cr(CO)_2L$, $L = PMe_3, PMe_2Ph, P(OMe)_3$

D.J. Hammack,* M.M. Dillard,* M.P. Castellani, A.L. Rheingold, A.L. Rieger and P.H. Rieger

Abstract

The radical complex, $(C_5Ph_5)Cr(CO)_3$, reacts with small, neutral, monodentate Lewis bases (PMe_3 , PMe_2Ph , and $P(OMe)_3$) in THF at $-78\text{ }^\circ\text{C}$ (PMe_2Ph reacts at ambient temperature) to yield the monomeric substitution products, $(C_5Ph_5)Cr(CO)_2L \cdot THF$ as thermally stable solids. Electrochemical and spectroscopic data are provided. An X-ray crystal structure of the hemisolvate $(C_5Ph_5)Cr(CO)_2PMe_3 \cdot 0.5THF$ was obtained. Frozen solution ESR spectra of $(C_5Ph_5)Cr(CO)_2L$ in toluene are comparable to those of other low-spin d^5 "piano-stool" complexes. Rotation of the $Cr(CO)_2L$ moiety relative to the C_5Ph_5 ring is rapid on the ESR time scale in low-temperature liquid solutions and leads to axial powder-like spectra. Analysis of this effect leads to significant insights into the electronic structure.



*Marshall University undergraduate student