Substitution Reactions of (C₅Ph₅)Cr(CO)₃: Structural, Electrochemical, and Spectroscopic Characterization of (C₅Ph₅)Cr(CO)₂L, L = PMe₃, PMe₂Ph, P(OMe)₃

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Abstract

The radical complex, (C₅Ph₅)Cr(CO)₃, reacts with small, neutral, monodentate Lewis bases (PMe₃, PMe₂Ph, and P(OMe)₃) in THF at -78 ºC (PMe₂Ph reacts at ambient temperature) to yield the monomeric substitution products, (C₅Ph₅)Cr(CO)₂L•THF as thermally stable solids. Electrochemical and spectroscopic data are provided. An X-ray crystal structure of the hemisolvate (C₅Ph₅)Cr(CO)₂PMe₃•0.5THF was obtained. Frozen solution ESR spectra of (C₅Ph₅)Cr(CO)₂L in toluene are comparable to those of other low-spin d⁵ “piano-stool” complexes. Rotation of the Cr(CO)₂L moiety relative to the C₅Ph₅ 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.

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