Synthesis, Characterization, and Molecular Structure of Bis(tetraphenylcyclopentdienyl)rhodium(II)

J.E. Collins,[†] M.P. Castellani, A.L. Rheingold, E.J. Miller, W.E. Geiger, A.L. Rieger, and P.H. Rieger

Abstract

A 5 day diglyme reflux of Rh(acac)₃ and K(C₅HPh₄), followed by treatment with aqueous HPF₆, produces orange-yellow [(C₅HPh₄)₂Rh]PF₆ in 40 - 50% yield. Reduction of [(C₅HPh₄)₂Rh]PF₆ with sodium amalgam in THF yields olive green (C₅HPh₄)₂Rh in 70% yield. An X-ray crystal structure of (C₅HPh₄)₂Rh was obtained. The metal-centroid distance is 1.904 Å and all other bond lengths and angles are similar to known octaphenylmetallocenes. ESR spectra of (C₅HPh₄)₂Rh in low-temperature glasses display a rhombic *g*-tensor with resolution of Rh hyperfine splitting on one-*g*-component. Analysis of the spectral parameters is consistent with a d⁷ configuration derived from a nearly degenerate d_{xz} , d_{yz} ground state. Voltammetry and coulometry establish the electron-transfer series (C₅HPh₄)₂Rh^{1+/0/1-} with E° values of -1.44 V and -2.13 V vs ferrocene. The heterogeneous charge transfer rate of the second reduction is about three orders of magnitude lower than that of the first.



[†]Marshall University Masters student