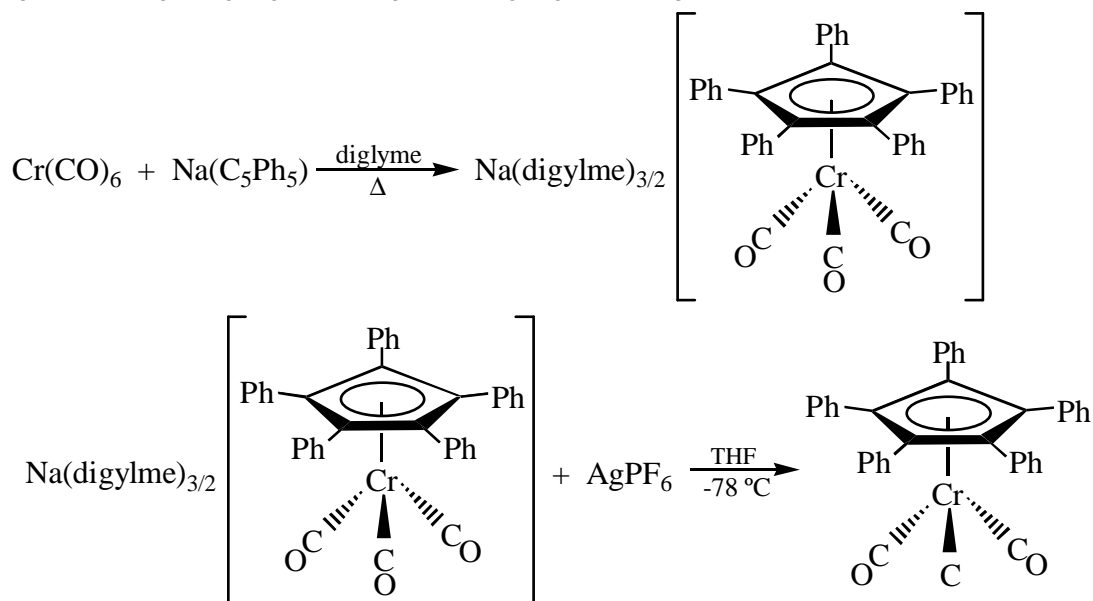


# Synthesis, Characterization, and Crystal Structure of the ( $\eta^5$ -C<sub>5</sub>Ph<sub>5</sub>)Cr(CO)<sub>3</sub> Radical

R.J. Hoobler,\* M.A. Hutton,\* M.M. Dillard,\* M.P. Castellani, A.L. Rheingold,  
A.L. Rieger, P.H. Rieger, T.C. Richards, and William E. Geiger

## Abstract

The reaction between Cr(CO)<sub>6</sub> and Na(C<sub>5</sub>Ph<sub>5</sub>) in refluxing diglyme yields [Na(diglyme)<sub>3/2</sub>][(C<sub>5</sub>Ph<sub>5</sub>)Cr(CO)<sub>3</sub>], **1**. Metathesis of **1** with [Ph<sub>3</sub>P=N=PPh<sub>3</sub>]Cl in CH<sub>2</sub>Cl<sub>2</sub> yields [Ph<sub>3</sub>P=N=PPh<sub>3</sub>][(C<sub>5</sub>Ph<sub>5</sub>)Cr(CO)<sub>3</sub>], **2**. Oxidation of **1** by AgBF<sub>4</sub> in cold THF under an argon atmosphere produces (C<sub>5</sub>Ph<sub>5</sub>)Cr(CO)<sub>3</sub>, **3**. Complexes **2** and **3** form a redox pair connected by a quasireversible one-electron process, E<sub>0</sub> = -0.69 V vs ferrocene in CH<sub>2</sub>Cl<sub>2</sub>, E<sub>0</sub> = -0.50 V in CH<sub>3</sub>CN, k<sub>r</sub> = 0.12 cm/s. ESR spectra of (C<sub>5</sub>Ph<sub>5</sub>)Cr(CO)<sub>3</sub> in toluene at 90 K gave a rhombic g-tensor with components 2.1366, 2.0224, and 1.9953, consistent with the expected low-spin d<sup>5</sup> electronic configuration. The largest g-tensor component was significantly temperature dependent, suggesting an equilibrium between conformations with <sup>2</sup>A' and <sup>2</sup>A'' ground states. Crystal structures of [Ph<sub>3</sub>P=N=PPh<sub>3</sub>][(C<sub>5</sub>Ph<sub>5</sub>)Cr(CO)<sub>3</sub>] and (C<sub>5</sub>Ph<sub>5</sub>)Cr(CO)<sub>3</sub> were obtained.



\*Marshall University undergraduate student.