Synthesis, Characterization, and Crystal Structure of the \((\eta^5-C_5Ph_5)Cr(CO)_3\) Radical


Abstract

The reaction between Cr(CO)\(_6\) and Na(C\(_5\)Ph\(_5\)) in refluxing diglyme yields [Na(diglyme)\(_{3/2}\)][(C\(_5\)Ph\(_5\))Cr(CO)\(_3\)], 1. Metathesis of 1 with [Ph\(_3\)P=N=PPh\(_3\)]Cl in CH\(_2\)Cl\(_2\) yields [Ph\(_3\)P=N=PPh\(_3\)][(C\(_5\)Ph\(_5\))Cr(CO)\(_3\)], 2. Oxidation of 1 by AgBF\(_4\) in cold THF under an argon atmosphere produces (C\(_5\)Ph\(_5\))Cr(CO)\(_3\), 3. Complexes 2 and 3 form a redox pair connected by a quasireversible one-electron process, \(E_0 = -0.69\) V vs ferrocene in CH\(_2\)Cl\(_2\), \(E_0 = -0.50\) V in CH\(_3\)CN, \(k_\tau = 0.12\) cm/s. ESR spectra of (C\(_5\)Ph\(_5\))Cr(CO)\(_3\) 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 \(d^5\) electronic configuration. The largest g-tensor component was significantly temperature dependent, suggesting an equilibrium between conformations with \(^2\)A' and \(^2\)A" ground states. Crystal structures of [Ph\(_3\)P=N=PPh\(_3\)][(C\(_5\)Ph\(_5\))Cr(CO)\(_3\)] and (C\(_5\)Ph\(_5\))Cr(CO)\(_3\) were obtained.

\[
\text{Cr(CO)}_6 + \text{Na(C}_5\text{Ph}_5) \xrightarrow{\Delta \text{diglyme}} \text{Na(diglyme)}_{3/2}
\]

\[
\text{Na(diglyme)}_{3/2} + \text{AgPF}_6 \xrightarrow{\text{THF, -78 } ^\circ\text{C}} \text{(C}_5\text{Ph}_5)\text{Cr(CO)}_3
\]

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