

**EPR Spectra of $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]^+$ ($\text{L} = \text{PEt}_3, \text{PPh}_3, \text{P}(\text{OEt})_3, \text{P}(\text{OPh})_3$):
Analysis of Line Widths and Determination of Ground State Configuration from
Interpretation of ^{31}P Couplings**

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Abstract

The preparation and characterization of $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]$ ($\text{L} = \text{PEt}_3, \text{PPh}_3, \text{P}(\text{OEt})_3$ and $\text{P}(\text{OPh})_3$), are reported. One-electron oxidation affords unstable Cr(I) cations, $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]^+$, EPR spectra of which are reported. Detailed analysis of the anisotropic ^{31}P hyperfine interaction indicates that, in frozen $\text{CH}_2\text{Cl}_2/\text{THF}$, the phosphine and phosphite complexes have $^2\text{A}'$ and $^2\text{A}''$ ground states, respectively. The hyperfine anisotropy can be accounted for by dipolar interaction of the ^{31}P nucleus with spin density on Cr and, in the case of the phosphite complexes, with ~ 0.01 P $3p_y$ spin density resulting from π -backbonding. Line width anomalies observed in EPR spectra of these and other Cr(I) and Mn(II) "piano stool" complexes can be understood in terms of molecular distortions resulting from solvation in frozen solutions.