EPR Studies of Catalytically Relevant Four-Coordinate Cobalt(I) Complexes

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Introduction
Cobalt(I) (3d^8) complexes have been far less investigated than those of Co(II) and Co(III), and almost all Co(I) complexes have either trigonal bipyramidal or square pyramidal geometry and are thus diamagnetic, “low-spin”. There is, however, a series of Co(I) complexes of pseudo-tetrahedral geometry, which are thus paramagnetic, $S = 1$, “high-spin”. The general formula of this series is $\text{CoX(PR}_3)_3$, where $R$ = alkyl or aryl groups and $X$ = Cl, Br, I. In addition to being of fundamental interest as a source of information on a relatively unstudied paramagnetic transition metal ion, these complexes are of practical interest. Specifically, $\text{CoCl(PPh}_3)_3$ has been shown to be an effective catalyst for alkene dimerization and hydrogenation [1].

We began the study of these complexes a number of years ago [2]; however, we were hampered by two factors. At Roosevelt U., there was both a lack of equipment for preparation of air-sensitive complexes, and of instrumentation for their parallel characterization by electronic absorption spectroscopy. We now have both an inert atmosphere glove box (pO$_2$ ~ 1 ppm) and a UV-Vis-NIR diffuse reflectance accessory. The former allows handling of these air-sensitive materials and the latter allows recording solid-state absorption spectra. We have thus revisited this project to bring it to completion. Analysis of optical spectra can then be combined with High-Frequency and -Field Electron Paramagnetic Resonance (HFEPR) analysis to provide a complete picture of the electronic structure of Co(I) in these complexes.

Experimental
HFEPR experiments on polycrystalline samples of $\text{CoX(PPh}_3)_3$ (X = Cl, Br) were performed at the EMR Facility using its 15/17 T superconducting magnet. The complexes are very air sensitive, even in the solid state, and care was taken to prevent oxidation during this process. Success at maintaining Co(I) was evidenced by the absence of characteristic Co(II) (3d^7, $S = 3/2$) EPR signals, which had not been the case in our earlier studies.

Results and Discussion
Very strong and well-defined responses were obtained from both samples under study. The spectra are characteristic for a triplet ($S = 1$) spin state; however, they also indicate a presence of multiple sites differing by their spin Hamiltonian parameters. Figure 1 presents an experimental EPR spectrum of $\text{CoCl(PPh}_3)_3$ accompanied by powder-pattern simulations using parameters for each of three identified sites, and the sum of those. The parameters are listed in the caption. The agreement between the summary simulation and experiment can be considered as very good.

Conclusions
The ability to extract spin Hamiltonian parameters from three separate sites is a testament to the quality of the HFEPR spectrometer. Multiple sites with slightly different electronic structure is expected based on the crystal structure of $\text{CoCl(PPh}_3)_3$, which has three distinct molecules per unit cell [3].

Acknowledgements
The NHMFL UGCP grant #5062 is kindly acknowledged.

References