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Oxidation Studies of Cu(II) Phenolate Compounds

Transition metals and phenoxide groups play crucial roles in many biological systems such as the copper-containing enzyme tyrosinase. High oxidation state transition metal centers are often required for reactivity; therefore, model studies of the oxidation of copper(II) phenolate compounds to proposed copper(III) phenolate products are of interest. Two ligands, pentafluorophenoxide ($\text{OAr}^{\text{F}} = \text{OC}_6\text{F}_5$) and 3,5-bis(trifluoromethyl)phenoxide ($\text{OAr}' = 3,5\text{-OC}_6\text{H}_3(\text{CF}_3)_2$), have been used to synthesize various metal phenolate compounds in the Doerrer group. Salts containing the anions $[\text{Cu}^{\text{II}}(\text{OAr}')_4]^{2-}$ and $[\text{Cu}^{\text{II}}(\text{OAr}^{\text{F}})_4]^{2-}$ were reacted with strong two-electron oxidants pyridine-*N* oxide, Me_3NO , and PhIO or one-electron oxidants NO^+ , $\text{Ce}(\text{OTf})_4$, and PhICl_2 . Initial ^1H and ^{19}F nuclear magnetic resonance data have shown that the yellow product from the reaction of $[\text{Cu}^{\text{II}}(\text{OAr}^{\text{F}})_4]^{2-}$ with PhIO is diamagnetic. Because copper(II) has a paramagnetic d^9 electron configuration and copper(III) has diamagnetic d^8 electron configuration, we propose that this yellow compound is a copper(III) complex. Further isolation schemes are being carried out to increase the yield of this putative Cu(III) product for additional spectroscopic and reactivity characterization.