

# Reactivity Studies of a Proposed Metal-Coordinated Thiyl Radical: C-S Bond Formation

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Transition-metal thiolate complexes represent are instrumental in numerous biological systems. Understanding the reactivity and function of these compounds is important in modeling biologically relevant activity and in the development of catalytic systems. A significant challenge in the study and synthesis of metal thiolate complexes arises from complicated oxidation chemistry attributed to the electron rich character of the metal as well as the thiolate. Oxidation can be metal- or ligand-centered, with the latter resulting in ametal coordinated thiyl radical. Metal coordinated thiyl radicals tend to be reactive and difficult to observe.<sup>3</sup> This reactivity reportedly results from the sulfur character of the SOMO. This S-centered localization of electron density is utilized in the current study for bond formation. Herein we report oxidation of  $[\text{Ru}^{\text{III}}(\text{DPPBT})_3]$  (**1**), (DPPBT= 2-diphenylphosphinobenzenethiolate), to yield a spectroscopically observable thiyl radical  $[\text{Ru}(\text{SR}\cdot)]$ . DFT calculations indicate the HOMO of the precursor complex contains significant sulfur p-character. The radical, in the absence of a reactive substrate, decays to a disulfide with observed rate of  $10^{-3} \text{ s}^{-1}$  as determined by chronoamperometry. However, in the presence of ketones such as acetone, acetophenone and 2-butanone, at applied potential of +620mV a novel C-S bond formation at single sulfur is observed, equation 1. A reaction pathway is proposed that yields complex **2**. An insight into potential utility of this radical is offered.

