

**Journal of Structural Chemistry & Crystallography Communication****Michael B. Hall**

**N**on-innocent ligands play important roles in a variety of catalytic reactions. However, the ambiguous nature of their electronic structure causes a problem for the assignment of the metal's oxidation state and for a clear-cut role of the metal in their reaction mechanisms. Nickel bis(dithiolene) complexes, which exist in three oxidation states  $[\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2]_n$  ( $n = 2-, 1-, 0$ ), are all square-planar Ni(II) with redox active ligands. The neutral complex reacts with an alkene to produce the cis-interligand adduct, which upon reduction releases the alkene. Among the related ruthenium tris(thiolate) complexes,  $[\text{Ru}(\text{dppbt})_3]_n$  ( $n = 1-, 0, 1+$ ) (dppbt = diphenylphosphinobenzenethiolate), the most oxidized form also reacts with alkenes, a reaction attributed to thiyl-diradical character involving two S atoms. Although it seems clear that  $[\text{Ru}(\text{dppbt})_3]1-$  is Ru(II) with three thiolate ligands, the nature of the most oxidized form,  $[\text{Ru}(\text{dppbt})_3]1+$  appears elusive. High-level ab initio methods (CASSCF and CASPT2) predict its ground state electronic structure to be an open shell diradical singlet state with a Ru(III) ( $d^5$ ,  $S = 1/2$ ) antiferromagnetically (AF) coupled to a thiyl radical ( $S = 1/2$ ), rather than the previous description based on a dithiyl state involving two S 3p orbitals. These new results

provide an improved understanding of this system's experimental behavior. Furthermore, the related Re complexes  $[\text{Re}(\text{dppbt})_3]_n$  ( $n = 0, 1+, 2+$ ) span two additional higher oxidation states. High-level ab initio methods confirm a CS singlet with a Re(III) ( $d^4$ ,  $S = 0$ ) center as the ground state of  $[\text{Re}(\text{dppbt})_3]0$ . Thus, this neutral Re species has considerably less thiyl radical character than the valence isoelectronic  $[\text{Ru}(\text{dppbt})_3]1+$ . On the other hand, the more oxidized derivatives  $[\text{Re}(\text{dppbt})_3]1+$  and  $[\text{Re}(\text{dppbt})_3]2+$  show significant metal-stabilized thiyl radical character; both have major contributions from Re(III) ( $d^4$ ,  $S = 1$ ) centers AF coupled to thiyl- and dithiyl-dppbt ligands. These findings are consistent with the experimental chemistry as  $[\text{Ru}(\text{dppbt})_3]1+$ ,  $[\text{Re}(\text{dppbt})_3]1+$ , and  $[\text{Re}(\text{dppbt})_3]2+$  can add ethylene to form the new C-S bonds, but  $[\text{Re}(\text{dppbt})_3]0$  cannot. These complexes have been extensively studied as electrochemical catalysts for both proton reduction and H<sub>2</sub> oxidation. The interesting protonated intermediate,  $[\text{HRe}(\text{dppbt})_3]1+$ , has been studied by x-ray crystallography that shows a protonated S. However, DFT calculations and the experimental structure appear to disagree on which S is actually protonated.