

Electronic and Photophysical Properties of Re I (CO)₃Br Complexes Modulated by Pyrazolyl-Pyridazine Ligands

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The direct reaction of a series of substituted (1H-pyrazol-1-yl)pyridazine (L I : 6-(1H-pyrazolyl)pyridazine; L II : 3-chloro-6-(1H-pyrazole-1-yl)-pyridazine; L III : 6-(1H-3,5-dimethylpyrazolyl)pyridazine-3-carboxylic acid; L IV : 3,6-bis-N-pyrazolyl-pyridazine; and L V : 3,6-bis-N-3-methylpyrazolyl-pyridazine) with the bromotricarbonyl(tetrahydrofuran)-rhenium(I) dimer leads to the monometallic complexes [(L X)Re(CO)₃Br] (I-V), which displays a nonregular octahedral geometry around the Re I center and a fac-isomerism for the carbonyl groups, whereas pyridazine and pyrazolyl rings remain highly coplanar after coordination to rhenium. Cyclic voltammetry shows one irreversible oxidation and one irreversible reduction for each compound as measured in N,N-dimethylformamide. Oxidation ranges from 0.94 V for III to 1.04 V for I and have been attributed to the Re I /Re II couple. In contrast, the reductions are ligand centered, ranging from -1.64 V for II to -1.90 V for III and V. Density functional theory calculations on the vertical one electron oxidized and one electron reduced species, using the gas-phase optimized geometry for the neutral complex confirm this assignment. Compounds I-V show two absorption bands, one around 410 nm (metal-to-ligand charge transfer (MLCT), Re d⁵ → π*) and the other at ~300 nm (intraligand, π → π*). Excitation at 400 nm at 77 K leads to unstructured and monoexponential emission with large Stokes shift, whose maxima vary between 570 (III) and 636 (II) nm. The quantum yields for these emissions in solution are intensified strongly going from air to argon

equilibrated solution. Singlet oxygen quantum yields change from 0.03 (III) to 0.21 (IV). These data are consistent with emission from 3MLCT . The emission undergoes a bathochromic shift when R 1 is a π -donating group (Cl or N-pyrazolyl) and a hypsochromic shift for a π -acceptor (COOH). The bimolecular emission quenching rate constant by triethylamine (TEA) for II, IV, and V is 1.09, 0.745, and $0.583 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Photolysis in dichloromethane- CO_2 saturated solution with TEA as a sacrificial electron donor leads in all cases to formic acid generation.