

Syntheses, Ground-State and Excited-State Properties of Monomeric and Bridged Re (I) Tricarbonyl Complexes

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Several monomeric and bridged rhenium (I) tricarbonyl complexes containing 2,2'-bipyridine (bpy), 2,2'-bipyrazine (bpz) and 1,10-phenanthroline (phen), monodentate ligands pyridine (py) and [OCH₂CH₃]⁻ (OAc) and bridging ligands isonicotinate (isonic) and diphenylphosphinoethane (dppe) are shown in Figure 1. The compounds were synthesized from Re(CO)₅Cl by first replacing two carbonyl groups with one of the bidentate heterocyclic ligands, then removal of the coordinated chloride ligand and replacing it with a monodentate or bridging ligand. The cationic complexes were isolated as [CF₃SO₃]⁻ salts.

All compounds were characterized by ¹H NMR, IR and elemental analysis. The complexes underwent reversible electrochemical reduction associated with the heterocyclic ligand. The Re (I) complexes absorb in the near UV region of the spectrum and emit near 600 nm when excited into the lowest energy absorption band. Emission lifetimes determined in a glassy matrix or in solution varied from 100 to 400 ns. An X-ray structure reveals coordination of the nitrogen atom of pyridine to one rhenium center and coordination of one of the oxygen atoms of the carboxyl group to the other rhenium center resulting in two nonequivalent centers in the dimer. To understand the consequence of this, the properties of the two monomer pairs, [Re(bpy)(py)(CO)₃]⁺ / [Re(bpy)(OAc)], [Re(bpz)(py)(CO)₃]⁺ / [Re(bpz)(OAc)] and [Re(phen)(py)(CO)₃]⁺ / [Re(phen)(OAc)] are compared.

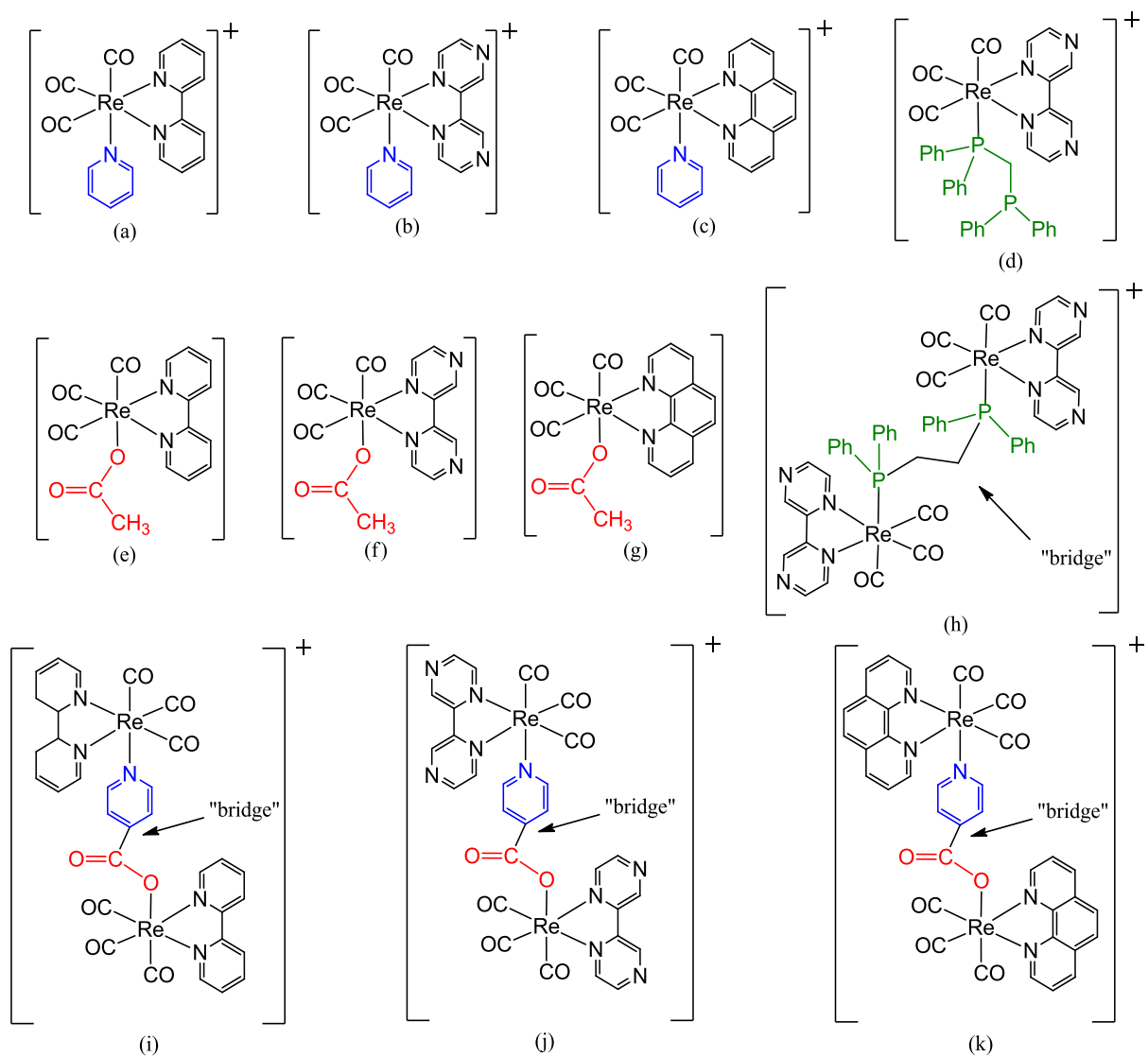


Figure 1 Structure of complexes: a) $[\text{Re}(\text{bpy})(\text{py})(\text{CO})_3]^+$, b) $[\text{Re}(\text{bpz})(\text{py})(\text{CO})_3]^+$, c) $[\text{Re}(\text{phen})(\text{py})(\text{CO})_3]^+$, d) $[\text{Re}(\text{bpz})(\text{dppm})(\text{CO})_3]^+$, e) $[\text{Re}(\text{bpy})(\text{OAc})(\text{CO})_3]$, f) $[\text{Re}(\text{bpz})(\text{OAc})(\text{CO})_3]$, g) $[\text{Re}(\text{phen})(\text{OAc})(\text{CO})_3]$, h) $[\{\text{Re}(\text{bpz})(\text{CO})_3\}_2(\text{dppe})]^{2+}$, i) $[\{\text{Re}(\text{bpy})(\text{CO})_3\}_2(\text{isonic})]^+$, j) $[\{\text{Re}(\text{bpz})(\text{CO})_3\}_2(\text{isonic})]^+$, k) $[\{\text{Re}(\text{phen})(\text{CO})_3\}_2(\text{isonic})]^+$

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