Mono- and Di-nuclear Rhenium(I) Complexes and their Application as a Photocatalyst for Reduction of CO2 to CO

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**Abstract**

 In this thesis, two mononuclear complexes of Re(I), [ReCl(CO)3(py)2] and [ReCl(CO)3(phen-dione)] and one dinuclear complex, [ReCl(CO)3(*μ*-tptzH)Re(CO)3], (where tptz-H is 2,4,6-tri(pyridine-2-yl)-2H-1,3,5 triazine-1-ide)have been prepared and characterized by elemental analysis, FT-IR, UV-vis and NMR spectroscopies. Solid state structure of [ReCl(CO)3(*μ*-tptzH)Re(CO)3] complex was determined by single crystal X-ray crystallography. Red crystals of [ReCl(CO)3(*μ*-tptzH)Re(CO)3] were grown by slow evaporation in chloroform and toluene. This complex crystallized in monoclinic crystal system with space group of *P 21/c,* with the following unit-cell parameters: *a* (Å) = 10.445(11), *b* (Å) = 18.133(19), *c* (Å) = 16.803(17), *α* (˚) = 90, *β* (˚) = 90.125, *γ* (˚) = 90, *Z* = 4 and *V*(Å3) = 3182(6). In the dinuclear complex, coordination geometry around each of Re(I) is distorted octahedral, with bite angles of N(4)–Re(2)–N(5) (75˚), N(2)–Re(1)–N(3) (74.04˚) and N(2)–Re(1)–N(1) (71.70˚) for the tptz-H ligand. Due to the configuration, the pyridyl group on the *sp3*-hybridized C(1) is tilted to such an extent that it is almost perpendicular to both the central triazine ring (76.18˚) and the other pyridyl group (74.69˚).

 The partially saturated triazine ligand, tptz-H, is coordinated as tridentate and bidentate chelate to each Re(I). Saturation of C(1) in tptz disturbs the aromaticity of triazine ring followed by two consecutive redox reactions.

 Due to the activation of the dinuclear complexes in the presence of alumina, an anation reaction occurs and one chloro ligand substiutes to one of Re(I) center.

 The thermodynamic parameters, 1H-NMR, 15N-NMR, 13C-NMR, IR and Raman spectra, frontier orbitals (FOs) energy and modified structure of the unsaturated and partially saturated dinuclear complex were calculated by DFT method.

 Photocatalytic activity of mono- and dinuclear complexes for reduction of CO2 to CO in the presence of TEA, TEOA and NHEt3Cl was also studied. The results indicate a significant photocatalytic activity for each of complexes. Two catalytic cycles were proposed for reduction of CO2 to CO by these complexes. In these catalytic cycles, Under photochemical conditions, the catalyst is initially excited with incident light, which allows for a metal-to-ligand charge transfer. Back-electron transfer is prevented by excited state quenching with triethylamine (TEA). This results in the radical ion pair [ReCl(CO)3(*μ*-tptzH)Re(CO)3]•– and Et3N•+, which is the beginning of our catalytic cycle. Both radical ions must undergo immediate reaction to continue the process. Radical anion rhenium dissociates to a rhenium radical plus chloride, while Et3N•+ transfers a proton to a second molecule of TEA, generating a neutral radical CH3C•HNEt2 and the triethylammonium ion. The two radicals then undergo a disproportionation reaction through TS1 to generate rhenium hydride and diethylvinylamine. At this point, insertion of CO2 into the Re–H bond via TS2 yields rhenium complex with Re–O bond. This step forms the critical C–H bond. Dissociation of Re–O bond yields formate and rhenium cation. The final step regenerates catalyst through reassociation of rhenium cation with chloride.

 ***Keyword***

Rhenium(I) complexes, polypyridyl ligand, redox reaction, computational chemistry, photocatalytic reaction, reduction of CO2