## ABSTRACT

Synthesis and Electrochemical reactions of Rhenium(I) di- and tri-carbonyl compounds containing polypyridyl like ligands.

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The tricarbonyl compound, *fac*-$Re(CO)_3(dpk)Cl$ (dpk = $[(C_5H_4N)_2C(O)]$ was obtained in a good yield from the reaction $Re(CO)_5Cl$ and dpk, in refluxing toluene. When 2,2'-dipyridyl amine, dpa, $[(C_5H_4N)_2NH]$ was used in place of dpk, $Re(CO)_5Cl$ was recovered unreacted. Various methods were tried in order to prepare *fac*-$Re(CO)_3(dpa)Cl$, reactions in higher boiling solvents as well as melt reactions. This resulted in the isolation of the starting material at the end of the reaction. However when a mixture of $Re(CO)_5Cl$ and triphenylphosphine, $PPh_3$ was refluxed in toluene for an extended period of time, an intermediate was formed which reacted with a $CH_2Cl_2$ solution of dpa to give *cis*-$Re(CO)_2(PPh_3)[(C_5H_4N)_2NH)]$. This method was then used as a general procedure for the incorporation of the chromophore *cis*-$Re^I(CO)_2(PPh_3)Cl$ into other bidentate donor ligands such as dpk and bipy resulting in the isolation of *cis*-$Re(CO)_2(PPh_3)(dpk)Cl$ and *cis*-$Re(CO)_2(PPh_3)(bipy)Cl$.

Nucleophilic addition of water at the carbonylic carbon atom of coordinated dpk resulted in the hydration of the keto group to form *fac*-$Re(CO)_3[(C_5H_4N)_2C(O)(OH)]$. Coordinated dpk also reacted with absolute ethanol to give *cis*-$Re(CO)_2[(C_5H_4N)_2C(O)(OC_2H_5)](PPh_3)$. Nucleophilic

addition resulted in a change of coordination mode in dpk from a bidentate to a terdentate ligand.

The lowest absorption band in these compounds exhibits a marked solvatochromic behavior due to metal ligand charge transfer (MLCT) transitions. The solvent dependence of the MLCT was investigated in three classes of solvents, nonchlorinated aliphatics, chlorinated and aromatics. The solvent dependence was studied using Tafts solvent polarity scale $\pi^*$, and $E_T$, the molar transitional energy. The compounds *fac*-$Re(CO)_3(dpk)Cl$ and *cis*-$Re(CO)_2(dpk)(PPh_3)Cl$ when studied, gave good linear free energy relationships with slopes of 24.30 and 12.70 respectively in nonchlorinated aliphatic solvents when $E_{MLCT}$ was plotted against $\pi^*$.

The electrochemical reactions of *fac*-$Re(CO)_3(dpk)Cl$ and dpk with $CO_2$ and $H_2O$ are reported. The reaction of $CO_2$ with *fac*-$Re(CO)_3(dpk)Cl$ is solvent dependent and is controlled by the rate of diffusion of the electroactive species from the surface of the electrode. When studied by chronoamperommetry (CA), by use of the Cottrell equation, $i(t) = nFAcD^{1/2} / \pi^{1/2}t^{1/2}$, the rate of diffusion of the electrochemically species was estimated to be ~ 2.5 times faster in $CH_3CN$ than in DMF.