

**Electrochemical Oxidation of  $\text{Mo}(\text{CO})_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})$ : Infrared Spectroelectrochemical Studies of the Reactivity of  $[\text{Mo}(\text{CO})_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})]^+$  Complexes**

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A series of  $\text{Mo}(\text{CO})_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})$  compounds ( $\alpha$ -diimine ligands used include 2,2'-bipyridine, 2,2'-biquinoline, 1,10-phenanthroline and substituted derivatives) was prepared from the corresponding  $\text{Mo}(\text{CO})_4(\alpha\text{-diimine})$  complexes via reflux in acetonitrile. These compounds all exhibit quasi-reversible one-electron oxidations in acetonitrile yielding the corresponding  $[\text{Mo}(\text{CO})_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})]^+$  radicals. The electrogenerated seventeen-electron complexes can be oxidized in a second, irreversible, one-electron process which is coupled to coordination by solvent, yielding the seven-coordinate  $\text{Mo}^{2+}$  complex,  $[\text{Mo}(\text{CO})_3(\text{bpy})(\text{CH}_3\text{CN})_2]^{2+}$ . In addition, the  $[\text{Mo}(\text{CO})_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})]^+$  species are susceptible to nucleophilic attack by the solvent, resulting in net disproportionation reactions. These ligand-induced disproportionations follow first order kinetics, the rate constants of which were found to be influenced by steric and electronic factors. In addition to the  $\text{Mo}^0$  starting compound, disproportionation yields the same seven-coordinate  $\text{Mo}^{2+}$  species that is formed by direct oxidation of  $[\text{Mo}(\text{CO})_3(\alpha\text{-diimine})(\text{CH}_3\text{CN})]^+$ . This compound is unstable toward additional acetonitrile substitution and decomposes to  $[\text{Mo}(\text{CO})_2(\alpha\text{-diimine})(\text{CH}_3\text{CN})_3]^{2+}$ . The infrared spectra of the  $\text{Mo}^{2+}$  oxidation products, as well those of the electrogenerated  $\text{Mo}^+$  complexes, were obtained via infrared spectroelectrochemistry and will be discussed.