

Photodissociation Dynamics of Gaseous $\text{CpCo}(\text{CO})_2$ and Ligand Exchange Reactions of CpCoH_2 with C_3H_6 , C_3H_4 and NH_3

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Abstract

The photodissociation dynamics of $\text{CpCo}(\text{CO})_2$ in a molecular beam was studied using photofragment translational energy spectroscopy with 157nm photoionization detection of the metallic products. At all wavelengths studied, including 532 nm, 355 nm, and 290 nm, the dominant one-photon channel involved loss of a single CO ligand producing CpCoCO . The product angular distributions were isotropic and a large fraction of excess energy appeared as product vibrational excitation. Production of $\text{CpCO} + 2\text{CO}$ resulted from two-photon absorption processes.

Photolysis of $\text{CpCo}(\text{CO})_2$ seeded in H_2 carrier gas at the orifice of a supersonic expansion at 355nm led to efficient production of the novel 16-electron unsaturated species CpCoH_2 . By crossing the CpCoH_2 beam with a molecular beam containing reactant molecules (M) such as propene (C_3H_6), propyne (C_3H_4), or ammonia (NH_3), transition metal ligand exchange reactions $\text{CpCoH}_2 + \text{M} \rightarrow \text{CpCoM} + \text{H}_2$ were studied under single-collision conditions for the first time. In all cases, ligand exchange was found to proceed via short-lived 18-electron association complexes. Although no ligand exchange reactions were detected from CpCoH_2 collisions with methane (M = CH_4), by photolyzing $\text{CpCo}(\text{CO})_2$ mixtures with CH_4 , the methane complex CpCoCH_4 was produced.