

Fluxional Behavior in Transition Metal Half-Sandwich Complexes of the Phenalenyl Radical

Robert Sjovold, Noah Walker and Kelling J. Donald

Department of Chemistry, Gottwald Center for the Sciences, University of Richmond,
Richmond, Virginia 23173, United States

Abstract: The phenalenyl radical ($\mathbf{P} = \text{C}_{13}\text{H}_9$) is a relatively stable organic radical. It consists of three fused six membered rings sharing a central carbon. We analyze the thermodynamic and kinetic stability of transition metal complexes with \mathbf{P} bonded to a range of early transition metals known to form stable half sandwich complexes with radicals. \mathbf{PMX}_n ($M = \text{V}, \text{Cr}$; $X = \text{F}, \text{Cl}, \text{CO}$). The MX_n fragments that we employed were chosen because they are similar to known fragments involved in cyclopentadienyl (Cp) or benzene half sandwich complexes - some of which are of continuing interest for catalytic and other potential applications. We report in this poster the outcomes of a series of investigations in the stability of these phenalenyl complexes and the influence of the radical character of the six-membered rings in \mathbf{P} on the bonding in those complexes. The systems are especially interesting for us because they combine the properties of six-membered benzene ring and the radical character of Cp - in relatively simple organometallic species, none of which have been prepared to date. We report computed energy barriers and evidence for a mechanism for hopping of the metal fragment from one ring to the next across the surface of the radical. In general, the hapticity of the metal-phenalenyl coordination is very sensitive to the identity of the metal and the barriers to translation are of the order of $6.0 \text{ kcal.mol}^{-1}$.

