Fluxional Behavior in Transition Metal Half-Sandwich Complexes with the Phenalenyl Radical: A case study with MX_n.

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Abstract: The Phenalenyl ligand ($C_{13}H_9$) is an unusually stable radical. It is made up of three benzene rings in a plane which share a central carbon. Following up on previous work in our group on sandwich complexes of this polycyclic ring system, we investigate in this phase of our work the structure, bonding, and fluxional behavior of a set of half-sandwich complexes. For these investigations, including a detailed analysis of a slice of the potential energy surface using the 'linear transit' option in the Amsterdam Density Functional (ADF) suite of programs, we used the scandium halides as our systems of choice for our initial cases studies. An analysis of the organometallic complexes has allowed us to assess the thermodynamic stability of the complexes, and to identify an optimized path for the hopping from one ring to the next with barriers of the order of -4.405 kcal·mol^{-1}. This work provides a way in for us to study and understand better the catalytic properties of these transition metal half-sandwich complexes, the nature of the fluxional behavior of metals on polycyclic ring surfaces, and the dependence of the hapticity in stable transition metal complexes on the identity of the metal.