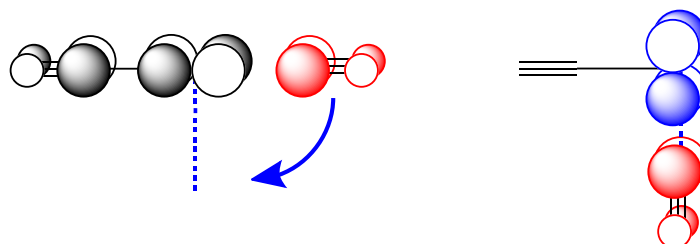


Bite Angles in Catalytic Bond Activation: Steric and Electronic Tuning

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The reaction barrier for oxidative addition of an R–X bond is well-known to depend on the bite angle, that is, the ligand-metal-ligand angle in the catalytic complex ML_2 . Using relativistic density functional theory and quantitative Kohn-Sham MO theory, I will explain why isolated dicoordinated d^{10} transition metal complexes ML_2 are in general linear and, more importantly, why this does not have to be so! The L–M–L angle can be tuned through the electronic and steric properties of the metal center and ligands. And this can be done so without using chelating ligands in which one has to vary the length of the bridge between the coordinating center.



To this end, I present a detailed bonding mechanism in $d^{10} ML_2$ complexes in terms of molecular orbital theory, for different combinations of metal center and ligands. I show that, and explain why, some dicoordinated $d^{10} ML_2$ complexes adopt bent geometries (the illustration is a hint). Secondly, I briefly discuss the effect of tuning the bite angle of the catalytic complex on the energy profile of the oxidative addition of methane to a variety of catalytic complexes.

Literature

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