Electronic effects of substituent in *syn* and *anti* isomers of [(1-R-η^3-C$_3$H$_4$)PdCl$_2$]$^-$ anions: comparative DFT study

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Abstract

In the frame of DFT method, the comparative study of two series of anionic allylic complexes of palladium of general formula [(1-R-η^3-C$_3$H$_4$)PdCl$_2$]$^-$ (**1**) with different *syn* or *anti* orientation of substituent have been made. Equilibrium geometries of both *syn* and *anti* isomers of anions **1** in vacuum and in polarizable dielectric continuum (PCM, ε = 78.39) have been calculated with B3LYP functional. Bond length, Milliken charges on atoms, energy and composition of molecular orbitals (MO) in *syn*-**1** and *anti*-**1** have been compared. Correlating equations of general type $E_{MO} = Const + \rho_{R^-} R^- + \rho_F F + \rho_\alpha \sigma_\alpha$, where F and R$^-$ − are Swain-Lupton field and resonance parameters, σ$_\alpha$ − is a polarization constant, have been obtained. The dependence of ρ on the type of MO, *syn* or *anti* substituent orientation, on environment, and destabilizing influence of polarizing continuum as well have been discussed. For complexes **1** (R = Ph, C$_2$H) HOMO and HOMO-3 energies are 0.2 and 0.1 eV consequently above the values obtained from correlating equations. Theoretical NMR ^{13}C chemical shifts values (δ) for *syn*-**1** are in a good accordance with experimental data, for unsubstituted terminal carbon of allyl ligand C^3 they linearly correlate with σ$^+$ and with Swain-Lupton parameters R$^+$ и F as well. These δ values depend on both C^3 atom charge and Pd-C^3 bond length.