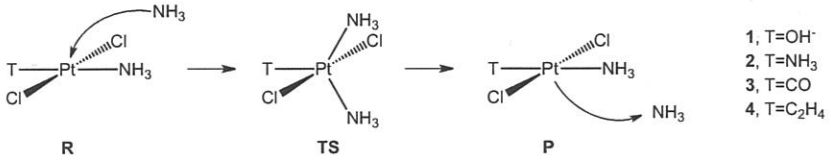
Trans effect: withdrawing electrons from the reactive region

Balazs Pinter[‡], Veronique Van Speybroeck[#], Michel Waroquier[#], Paul Geerlings[‡], Frank De Proft[‡]

[‡]*Algemene Chemie, Vrije Universiteit Brussel,* [#]*Center for Molecular Modeling, Ghent University, pbalazs@vub.ac.be*

The aminolysis of four square planar platinum complexes (**1-4**) differing only in the properties of the trans ligand (T), depicted in scheme 1, were investigated. Analyzed trans ligands include pure σ-donors of various strength (NH_3 and OH^-) as well as π-accepting ligands, *i.e.* π-acids (CO and C_2H_4). In good accordance with the experimentally determined trans directing strength (OH^-<NH_3<<CO<C_2H_4) the activation energies of the corresponding aminolysis reactions decrease along the **1**, **2**, **3** and **4** series. Moreover, for T=C_2H_4 the π-back donation stabilizes the trigonal bipyramid structure (denoted as **TS** in scheme 1) to such extent that it appears to be a minimum (intermediate) on the potential energy surface. The fortunate separation of the systems into [NH_3...NH_3] and [$TPtCl_2$] fragments that results in almost identical activation strain for the four systems allows the unambiguous determination of the origin of the trans effect in terms of electrostatic, orbital and steric interactions. Utilizing the Ziegler-Rauk decomposition scheme we found that interaction energy differences in systems **1-4** are clearly reflected in the orbital interaction contribution, *i.e.* the trans effect can be interpreted in the MO framework. Using the natural orbital for chemical valence technique we separated the contributions of the π and σ-subspaces to the difference in the orbital energy interaction. The significant increase in the trans effecting strength when going from OH^- and NH_3 to CO and C_2H_4 can be attributed to the π-backdonation in the latter systems.



Scheme1. Investigated substrates **1-4** for the aminolysis.