Application of mass spectrometry to study electronic ligand effects on gold organometallic complexes

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Ligand dissociation is a key process in homogenous catalysis and gives access to a wide range of products and reactions. Through their steric and electronic effects, ligands are able to orientate the reactivity of the complexes and can thus influence the selectivity in the chemical transformations. Usually, the metal-ligand bond is depicted by the Dewar-Chatt-Duncanson model [1,2] involving two opposite interactions, a σ-donor and a π-acceptor effect. Over the years, many experimental methods have been developed to measure these electronic effects, the most common being that of Tolman by Tolman electronic parameter (TEP), which is limited to organometallic complexes possessing probe ligands such as CO and based on the A_1-symmetrical CO-stretching frequency shift [3]. We have recently developed the use of new experimental gas-phase approaches to measure these effects, one based on mass spectrometry using activation by higher energy collision dissociation (HCD). Under this method, the satisfying results obtained on model systems [4] have encouraged us to apply this later on gold (III) complexes of the type $[(C^\wedge C)Au(NHC/PPh_3)L]^+$ and $[(C^\wedge N^\wedge C)AuL]^+$ with L a differently substituted pyridine ligand and where a direct measurement of the ligand effect is possible. The effect of pyridine substitution on the enrichment of the metal center was evaluated by determining the dissociation energy (BDE), $M-L^+ \rightarrow M^+ + L$. Rationalization of the experimental results is made using kinetic modelling, density functional theory and bond description methods to get information on the electronic structure of the complexes and thus on the metal-ligand interaction.

References

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