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Alkyne hydroarylation catalyzed by (P,C)-cyclometalated Au(III) complexes : energetic aspects

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Over the last decade, gold(III) catalysis has grown intensively. It offers now many innovative synthetic routes. For most of them, mechanistic insights are yet to be investigated. We particularly focused on the intermolecular hydroarylation of alkynes catalyzed by (P,C)-cyclometalated Au(III) complexes. Experimental studies, supported by DFT, showed that a Wheland intermediate can be easily obtained (resting state). In solution, different aryle/alkyne combinations have been tested, and their relative anti-addition product have been obtained, indicating an outer-sphere mechanism[1]. So, the endothermic exchange between the electron-rich aryle and the incoming alkyne takes place, before the outer-sphere attack of the aryle. This study therefore concerns both the determination of dissociation energies between the Au(III) complexes and the different substrates, and the comparison of electronic properties of the ligand/substrate.

Complexes have been generated in the gas phase in a triple quadrupole (Quattro II, Waters) by ion-molecule reaction, and then fragmented by CID. We have chosen to work under high-pressure conditions with argon as collision gas, since the formed complexes are very fragile and T-CID conditions have not been met. Kinetic modeling of the survival yield curves using MassKinetics software has been applied to collect critical energies of dissociation[2,3]. A good agreement was found between these experimental critical energies and bond dissociation energies obtained by molecular modeling. That consolidates both the models used and the mechanistic insights.

References

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