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Synthesis of gold(III) organometallics complexes and determination of their dissociation energy by mass spectrometry

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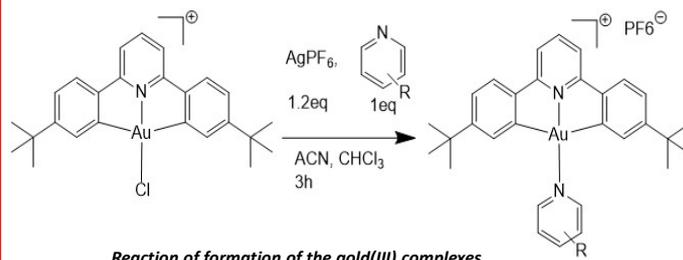
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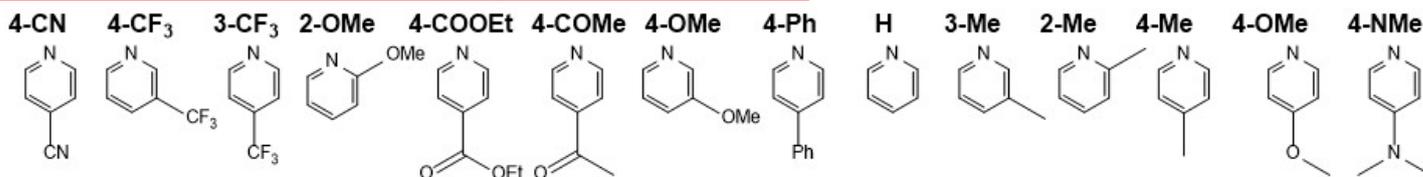


Introduction

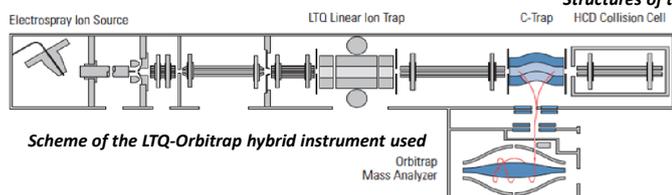
- Organometallics complexes are widely used in homogenous catalysis [1].
- By their steric and electronic effects, ligands have the ability to impact the reactivity of the metal center they are bound with.
- It is important to know these effects to choose the most adapted ligand for the design of a reaction.
- Only indirect experimental methods are available (IR, NMR) [2-3] using probe ligands. In our group, a method was developed using mass spectrometry to evaluate the Bond Dissociation Energy (BDE) of the Au-CO bond of $[(PR_3)Au-CO]^+$ complexes and classify the donor ability of the Phosphine ligands [4].
- But what about direct M-L BDE measurement?



Reaction of formation of the gold(III) complexes



Structures of the various substituents studied



Scheme of the LTQ-Orbitrap hybrid instrument used

Experimental setup

- Ions are formed by an electrospray source and analyzed in a LTQ-Orbitrap hybrid instrument ThermoFisher Corporation, San Jose, USA).
- Precursor ions are isolated in the Linear Ion Trap and accelerated into a collision cell containing N_2 leading to the formation of fragments.

Kinetic modelling and theoretical calculations

Determination of the Survival Yield (SY) of the precursor ion: $SY = \frac{I_{(P^+)}}{I_{(P^+)} + \sum I_{(F^+)}}$, $I_{(P^+)}$ the abundance of the precursor ion, $\sum I_{(F^+)}$ the sum of abundances of fragment ions.

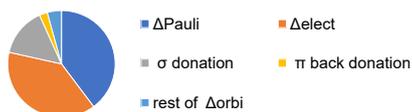
Kinetic treatment based on the RRKM theory [5] with the MassKinetics software [6] to obtain the difference between the dissociation barrier and that of the precursor ion (E_0).

Theoretical values of BDEs obtained using the Density Functional Theory (B3PW91/ SDD (+f) (Au), 6-31G** (other atoms) with the GAUSSIAN 16 software) [7].

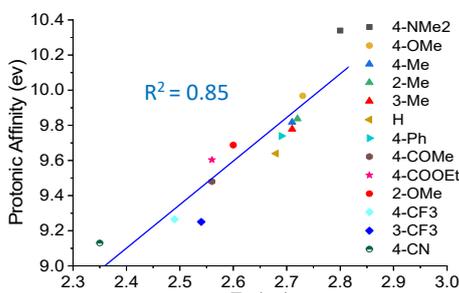
The Au-L bond was analyzed using the Energy Decomposition Analysis (EDA) [8] to compute the interaction energy ΔE_{int} :

$$\Delta E_{int} = \Delta E_{elect} + \Delta E_{Pauli} + \Delta E_{orb}$$

ΔE_{elect} is the electrostatic interaction, ΔE_{Pauli} , the Pauli repulsion and ΔE_{orb} , the orbital interaction. This term can be further decomposed into the different contributions as σ donation, π back donation, ...

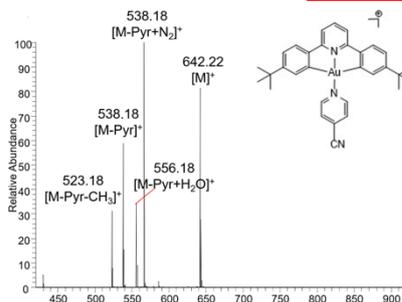


EDA results for the $[(C^*N^C)Au-(PyrH)]^+$ bond

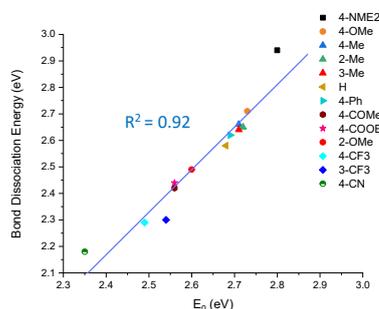


Correlation of the protonic affinity (eV) of the substituted pyridines versus E_0 (eV)

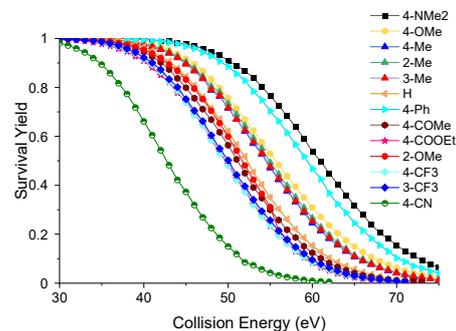
Results



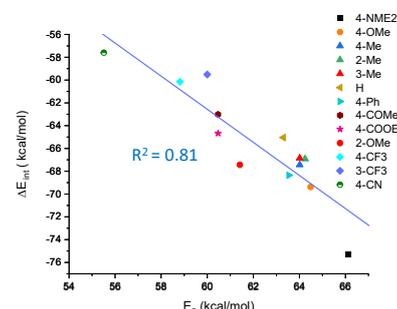
HCD fragmentation spectrum of: $[(C^*N^C)Au(Pyr-CN)]^+$ at 46 eV



Experimental measurements E_0 (eV) versus calculated BDEs in eV



Survival yield of the complexes as a function of the collision energy



E_0 (kcal/mol) versus ΔE_{int} (kcal/mol)

Conclusion and Perspectives

- A series of 14 $[(C^*N^C)Au(Pyr-R)]^+$ complexes were synthesised, isolated and characterized.
- Experimental and theoretical values of bond dissociation energies of the M-L bond were obtained and correlated well. They confirm the expected trends of the ligand donating effects: the richest pyridines are able to donate more to the metal and thus renders the Au-L bond stronger.
- EDA-NOCV analysis of the Au-L bond indicates that the σ -donor component of the bond dominates the bonding and that the π -acceptor backbonding is negligible.
- This finding is confirmed by the good correlation observed between the proton affinity of the ligands and E_0 .
- Catalytic tests are in progress to determine the relation between the electronic donor capability of the ligand and the yield of the reaction.