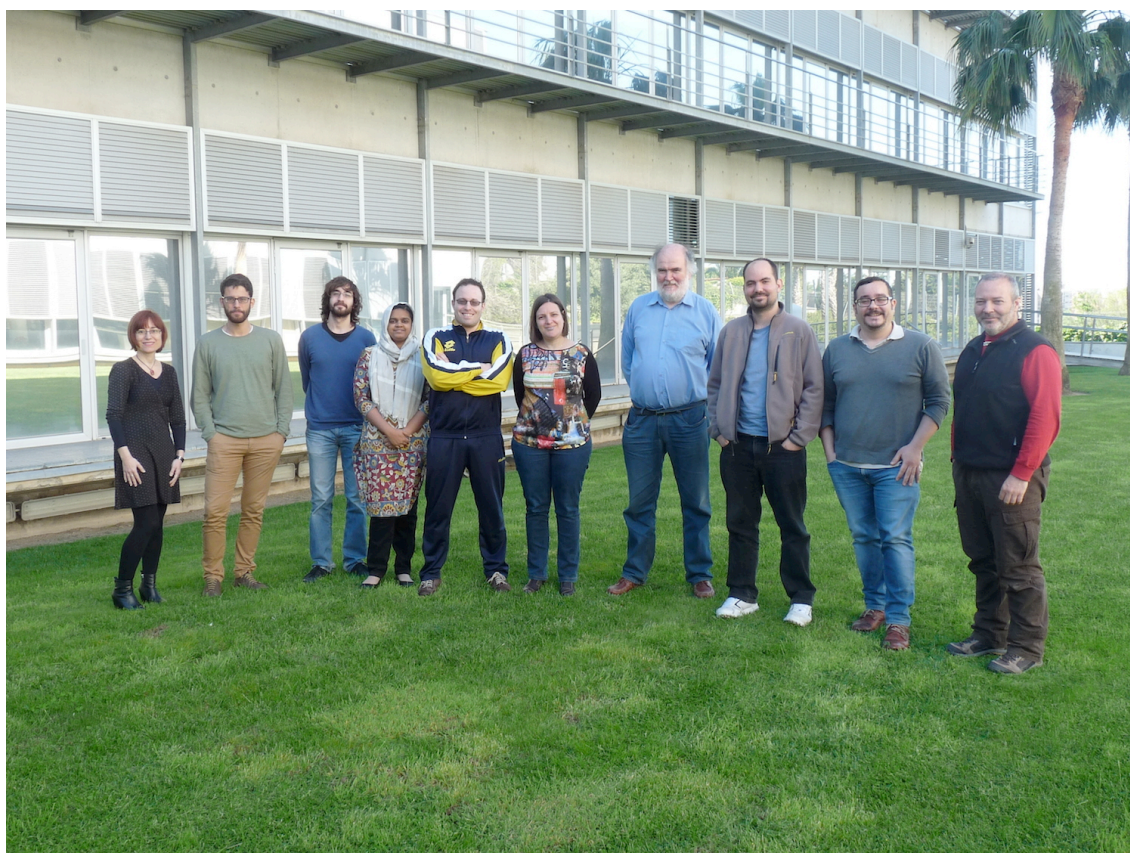# Maseras Research Group

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Abstract

Computational chemistry is applied to the study of different chemical processes of practical interest. DFT and DFT/MM methods are used on different processes in homogeneous catalysis, in most cases in collaboration with experimental groups. Studies in 2015 focused on homogeneous catalytic processes with involvement of photons, dioxygen and carbon dioxide. Previous reserarch lines, such as host-guest catalysis and C-H activation, were also continued.

Photocatalysis

The last few years have witnessed a resurgence of interest in visible light-driven photoreactions. Synthetic chemists recognize that light excitation can open new dimensions to chemistry, since molecular excited states can react in completely different ways compared with the ground state. In addition, visible light photochemistry holds great potential for the design of more sustainable and environmentally responsible chemical processes. This has resulted in the recent development a variety of synthetically valuable photochemical reactions, mainly exploiting the ability of photoredox-active transition metal complexes to excite organic molecules toward the generation of radical intermediates.

In a collaboration with the group of Melchiorre (ICIQ), we were able to successfully apply DFT methods to elucidate the mechanism and understand the origin of the regio-selectivity of the photochemical aromatic perfluoroalkylation of ethyl α-cyano phenylacetate **1** (Fig. 1). This metal-free, light-driven process, recently reported by Melchiorre's group, had two appealing features that made it suitable as test system for the efficiency of DFT modeling: i) the availability of a variety of experimental mechanistic data, and ii) the existence of some experimental observations that remained unexplained. A combination of DFT calculations and kinetic models was shown to be necessary to fully elucidate the seemingly complex reactivity of the system. The resulting mechanistic framework rationalized the observed quantum yield, as well as the differences in reactivity and/or selectivity of seemingly similar substrates. The use of a kinetic model for the chemical interpretation of the DFT-computed reaction constants was shown to be critical.
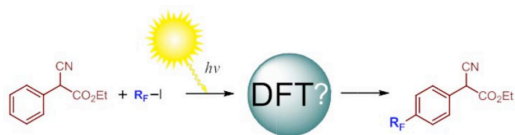

Fig. 1 - The photochemical process computed with DFT and microkinetic models.

Dioxygen chemistry

Molecular water oxidation catalysis by transition metal complexes is a highly active field of research at present due to its implications in new energy conversion schemes based on water splitting with sunlight. In addition water oxidation is also of interest in biology because it is the reaction that takes place at the oxygen evolving complex of photosystem II in green plants and algae. The very high thermodynamic potential needed for water oxidation (1.23 V vs NHE at pH = 0.0) implies necessarily the use transition metal complexes containing oxidatively rugged ligands, in order to come up with long lasting systems that can have potential commercial applications In addition these complexes need to be working in water as a solvent imposing and additional requirement for the auxiliary ligands that have to be substitutionally inert at the pH of action since otherwise they end up generating the corresponding aqua/hydroxo complexes and the free ligand. This is especially critical for first row transition metal complexes as has been previously shown in the literature because there will only be a limited pH range were the integrity of the complex is maintained. In addition ligand liberation from the metal complex is an additional driving force towards the formation of metal oxides and/or mixed oxo-hydroxides that will be highly dependent on working pH. On the other hand, an interesting feature of a water oxidation catalyst design is the use of redox non-innocent ligands that can help on the difficult task of managing the multiproton-multielectron needed to carry out the water oxidation reaction. This feature would be particularly useful if the ligand based redox process are tied to the rate determining step of the catalytic process and is not linked to unwanted radical based reactions leading to fast decomposition.
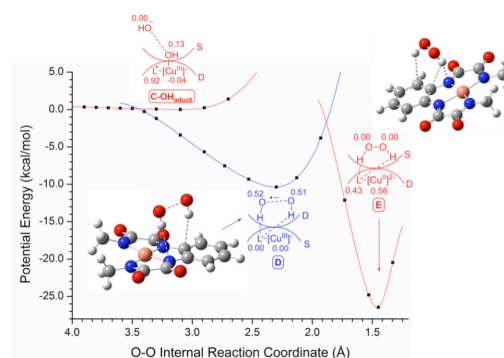

Fig. 2 - Computed potential energy relaxed scan for the O-O bond formation step in the reaction between the species resulting from [(opban)Cu^{II}]$^{2-}$ oxidation and two hydroxyl groups.

In order to explore the options of water oxidation catalysis based on oxidatively rugged but redox

active ligands, the group of Llobet (ICIQ) was able to prepare a family of four Cu(II) complexes containing tetraanionic tetradentate amidate acyclic ligands. We carried out a computational study on the reaction mechanism corresponding to one of these complexes, $[(opban)Cu^{II}]^{2-}$ (opban= o-phenylenebis(oxamidate)). Our DFT calculations allowed us to propose a complete catalytic cycle uncovering an unprecedented pathway in which crucial O−O bond formation occurs in a two-step, one-electron process where the peroxo intermediate generated has no formal M−O bond but is strongly hydrogen bonded to the auxiliary ligand (see Fig. 2). We have labeled such mechanism as Single Electron Transfer - Water Nucleophilic Attack (SET-WNA), and we intend to explore its eventual generality in the near future.

Carbon dioxide chemistry

The functionalization of primary sites of alkanes is yet one of the more challenging areas in catalysis. In this context, a novel effect has been discovered, being responsible of the enhancement of the reactivity of the primary C-H bonds of alkanes in a catalytic system. Experimental work by the group of Pérez (Huelva) showed that the copper complex $Tp^{(CF3)2,Br}Cu(NCMe)$ catalyses the functionalization of C_nH_{2n+2} with ethyl diazoacetate upon inserting the $CHCO_2Et$ unit into their C-H bonds. In addition, the selectivity of the reaction toward the primary sites significantly increased when using supercritical carbon dioxide as the reaction medium when compared to that in neat alkane. Our DFT calculations showed that this be is attributed to the effect of carbon dioxide molecules that retire electron density from the ligand fluorine atoms, enhancing the electrophilic nature of the metal centre (Fig. 3).
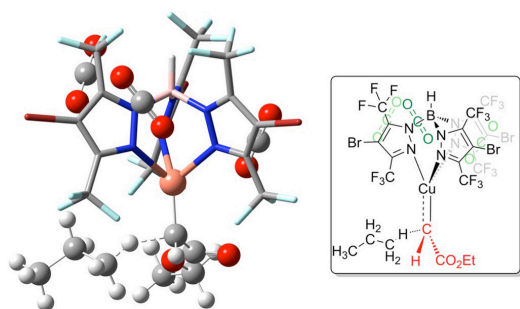

Fig. 3 - Optimized structure of the transition state of the primary C-H activation of propane by $Tp^{(CF3)2,Br}Cu(CHCO_2Et)(CO_2)_3$.

Host-guest catalysis

Supramolecular catalysis is a well established research field that encompasses a variety of catalytic processes where non-covalent binding interactions play an important role. A particularly interesting area of supramolecular catalysis is that of host-guest catalysis, where the reactants are introduced in a supramolecular nanovessel, or molecular container, where the reaction takes place with a rate higher than that outside the supramolecule. Host-guest catalysis has an appealing intuitive connection to enzymatic catalysis, which is well-known for its high efficiency, and has been applied successfully in a variety of systems. A further expansion of host-guest catalysis would in any case be largely helped by a better mechanistic understanding of the processes.
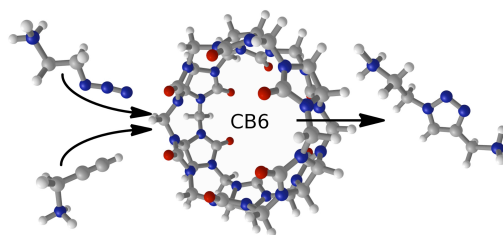

Fig. 4 - The cycloaddition reaction inside a cucurbit[6]uril which was studied.

The enhanced reactivity of the Huisgen 1,3-dipolar cycloaddition between the protonated forms of azidoethylamine and propargylamine inside the cucurbit[6]uril host was computationally studied in our group (see Fig. 4). A DFT approach was applied to explore the relative stabilities and connections of a large variety of possible host-guest aggregates that may be formed in solution, as well as their reactivity. The free energies resulting from the DFT calculations were converted to rate and dissociation constants, and introduced, together with the experimentally reported initial concentrations, in a kinetic simulation. The results reproduce the experimental observations, and provide a detailed description of the behavior of a large host-guest system over time. The major cause of the rate acceleration inside the nanovessel is the reduction of the entropic component of the free energy barrier, and the existence of stable non-productive host-guest adducts was identified as a major obstacle to improved catalysis.

C-H activation

Hydrocarbons are cheap and abundant materials. They are not only used as energy sources (mostly as fossil fuels), but also play a substantial role as feedstock in chemical industry. The latter application is however hindered by the stability itself of the compounds, which make them difficult to functionalize. This functionalization is vital, because it enables the conversion of cheap and abundant substrates into valuable functionalized organic compounds.
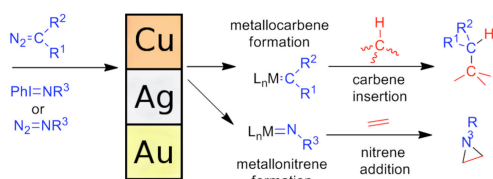
Computational chemistry plays a key role in the construction of the current understanding of the reaction mechanisms for the reaction of coinage metal complexes with hydrocarbons. Carbene precursors (diazo compounds) or nitrene precursors (hypervalent iodine compounds or azides) react with the catalyst complexes giving rise to highly reactive metallocarbene or metallonitrene intermediates, which are difficult to observe experimentally. DFT calculations allow the characterization of these intermediates and of their reactivity with hydrocarbons, leading to C-H insertion, aziridination or oxazole synthesis. We published in 2015 a review in collaboration with the group of Pérez (Huelva) summarizing computational work in the last decade in this research field, which has progressed in collaboration with experimental knowledge on these systems.

Fig. 5 - Coinage metal complexes are among the most successful catalysts for C-H activation.

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