

Bo Research Group



Group Leader: Carles Bo
Postdoctoral Researchers: Nuno A. G. Bandeira
PhD Students: Fernando S. Castro / M^a Dolores Melgar / Xavier Sanz
System Administrator: Martín Gumbau
Programmer: Moisés Álvarez
Administrative Support: Núria Vendrell

Abstract

Our research deals with the application of computational chemistry methods to a variety of subjects. In most cases, we work in close collaboration with experimental groups both at ICIQ and at other institutions. Research topics fall into three main categories:

-Structure and reactivity of organometallic compounds and homogeneous catalysis-related issues, such as characterisation in-silico of

reactive intermediates, elucidation of reaction mechanisms, origin of the chemo-, regio- and enantioselectivity, ligand effects, ligand design and structure-selectivity relationships.

-Supramolecular Chemistry: structure of host-guest systems, assessment of non-bonding interactions and supramolecular catalysis.

-Polyoxometalates (POMs): electronic structure, mechanisms of catalytic oxidation reactions, dynamic structure of cations and solvent water molecules around and inside POMs.

Homogeneous Catalysis

In 2013 we continued exploring the reactivity of borane reagents both computationally and experimentally in collaboration with Dr. Elena Fernandez (URV). Two main topics were studied: the catalytic activity of transition metal complexes and the metal-free version of this chemistry. Our goals are to open the application of these new reactions to a wider scope of substrates by understanding the reaction mechanisms in detail.

In rhodium catalysed borylation of cyclic alkenes,[1] the synergy between bidentate N-heterocyclic carbene (NHC) ligands, that modify cationic Rh(I) species, and the use of non-polar solvents, such as cyclohexane, is the key factor to favour a less energetically demanding route towards the formation of diborated products versus allyl boronate esters. Differences between the two computed reaction pathways were found to be not very large (Fig. 1), thus subtle changes in the solvent and in the ligands can switch reactivity. Indeed, polarity and coordination ability of the solvent are key factors to explain the differences observed in selectivity.

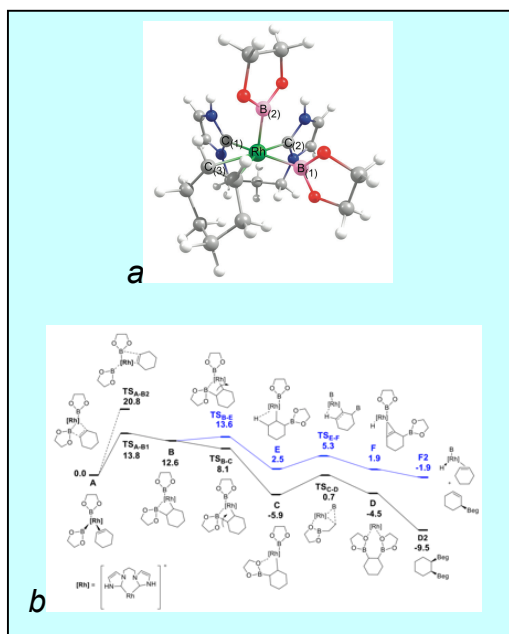


Fig. 1 – Top: Model structure for the cationic bisboryl Rh(III)-NHC species cyclohexene complex. Bottom: *Gibbs Free Energy profiles for the formation of the diborated and allyl boronate ester compounds (values in kcal.mol⁻¹)*

In last years, we unravelled the mechanism of activation of diborons in the absence of

transition metal complexes, with the sole use of a base. The basic principles of these new chemical reactions are now fully understood and our theoretical studies demonstrated common features in the diboration reactions of unactivated alkenes and the β -boration of activates olefins. We expanded the application of these principles to other substrates such are vinyl epoxides and aziridines. [2] Consequently, the nucleophilic boryl moiety generated by activating the diborane reagent with the base attacked at the alkene carbon-carbon thus opening the three member heterocyclic ring. The molecular orbitals of the transition state structures enabled visualizing such interactions, as shown in Fig.2 for 3,4-epoxy-1-cyclohexene.

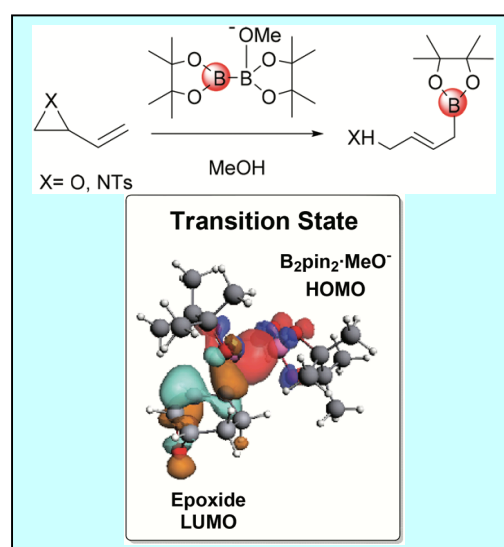


Fig. 2 - *Metal-free approach towards borylative ring-opening of vinyl epoxides and aziridines.*

Much more complexity is found in the reaction mechanisms of some organo-catalytic reactions. There was a lack of basic understanding of the mechanisms of cinchona-based primary amino-catalysts, which enable stereo-selective functionalization of a variety of sterically hindered carbonyl compounds. In collaboration with Prof. Melchiorre's group (ICIQ), we succeeded in explaining the origin of the stereo-selectivity of the Friedel-Crafts alkylation of indoles with α,β -unsaturated ketones catalyzed by 9-amino(9-deoxy)epi quinine. An essential role for the achiral acid cocatalyst was uncovered: upon condensation of the cinchona catalyst with the enone, the resulting covalent imine intermediate and the acid interact to build-up a well-structured ion-pair supramolecular catalytic assembly, which is

stabilized by multiple attractive noncovalent interactions. All the components of the assembly cooperatively participate in the stereocontrolling event, with the anion of the achiral acid being the structural element responsible for the π -facial discrimination of the iminium ion intermediate.[3]

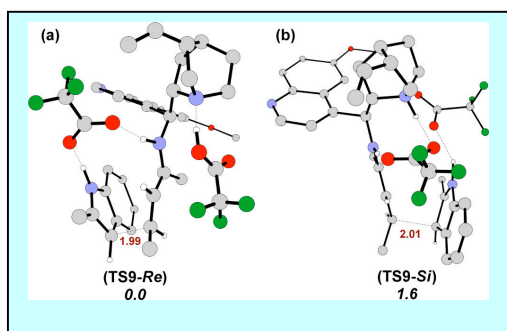


Fig. 3 - Transition-state structures for the (a) Re and (b) Si face addition of indole to the iminium ion assembly. Selected bond distances are in Å. Relative free energies ($\Delta\Delta G^{318}$) given in $\text{kcal}\cdot\text{mol}^{-1}$.

Fig. 3 shows the two transition state structures for the addition of indole to the β -carbon of the ketone, when it is in its iminium ion form with the cinchona catalyst. Two molecules of TFA protonate the supramolecular assembly and effectively block one face of the alkene. It is worth mentioning that the multi-step mechanism for iminium formation also required the active presence of the two TFA molecules. Our studies established a decisive role for the acid cocatalyst, which induces the building up of a well-structured supramolecular catalytic assembly by means of electrostatic interactions. The resulting hydrogen-bonding network rigidifies the covalently bound catalyst-imine intermediate, providing the conformational constraints of the transition-state assembly required for high stereoselection.

Bradshaw and Bonjoch (UB) applied organocatalytic methodologies for the design of the diastereoselective synthesis of cis-5-oxodecahydroquinolines, in which three stereocenters were generated in a one-pot reaction. We helped in solving issues related to the mechanism of some reaction steps and the relative stability of several reaction intermediates by performing computational studies. [4]

Ruthenium complexes played until recently a crucial role as catalysts for water oxidation. Prof. Lobet (ICIQ) synthesized a new family of Ru

complexes with varying number of NHC carbene ligands, and measured their redox properties. We found that our computed $\Delta E_{1/2}$ values followed the same linear trend as found experimentally, and that the trend presented in Fig. 4 is a combination of the two linear crossing trends of the mono-electronic half-oxidation potentials E°_1 and E°_2 . Thus, when these two redox potentials cross, the complex becomes unstable with regard to disproportionation of the oxidation state III.[5]

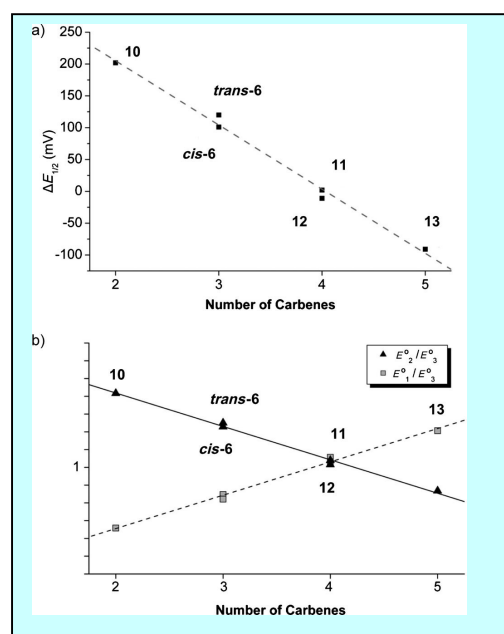


Fig. 4 (a) Plot of calculated $\Delta E_{1/2}$ versus the number of carbenes for several Ru. (b) Plot of the ratios between oxidation potentials versus the number of carbenes.

In the framework of a long-term collaborative project with Prof. Kleij's group at ICIQ, we studied the mechanism of the Zn(Salphen) catalysed reaction for the chemical fixation of CO_2 with epoxides to produce cyclic carbonates. Fig 5 shows the transition state for the last reaction step, i.e., the formation of the last C-O bond that closes the ring. This step is a $\text{S}_{\text{N}}2$ nucleophilic substitution reaction that releases the iodine co-catalyst. [6] On the other hand, this sort of Zn-salphen complexes have been studied too by means of IM-MS spectrometry in collaboration with Prof. Creaser (Loughborough University, UK). We computed the collision cross-sections from our structural parameters and atomic charges and found excellent agreement with experimental values. [7]

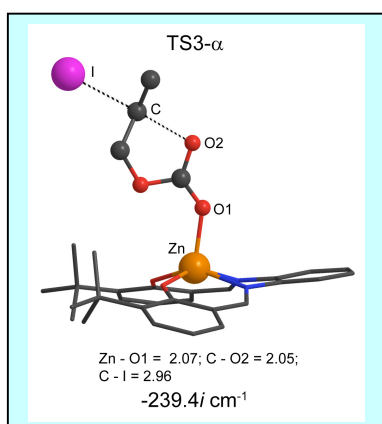


Fig. 5 – Transition state structure for the ring closing step in the Zn-salen catalyzed reaction of CO₂ and epoxides for forming cyclic carbonates.

Supramolecular Chemistry

In collaboration with Prof. Ballester (ICIQ), we had predicted that a native resorcin[4]arene-based host could bind [Rh(nbd)₂]⁺ complexes, and demonstrated that, for hydrogenation reactions, the encapsulated complex reacts

differently than when the metal complex is in free form, being norbornene the major reaction product. This last year we could complete a theoretical study about the hydrogenation of norbornadiene (nbd), outside and inside the capsule, that enabled understanding the effect of the confinement on the reactivity. [8]

Polyoxometalates

During this year, the group has continued studying several aspects of polyoxometalates nanocapsules, and actively participated in the launching of the PoCheMoN COST Action, which gathers around 20 European research groups. Our group is in charge of the design and maintenance of the project web site.

On the other hand, we have reviewed the latest theoretical and computational studies on structural aspects and reactivity of these metal-oxide anionic clusters, putting special emphasis to oxidation reactions and to water splitting.[9]

Articles

1-“Rhodium–NHC complexes mediate diboration versus dehydrogenative borylation of cyclic olefins: a theoretical explanation”

Dalton Trans. (2013) 42, 746

C. Pubill-Ulldemolins, M. Poyatos, C. Bo, E. Fernández

2-“Metal-free borylative ring-opening of vinyl epoxides and aziridines”

Org. Biomol. Chem. (2013) 11, 7004 – 7010

X. Sanz, G.M. Lee, C. Pubill-Ulldemolins, A. Bonet, H. Gulyás, S. A. Westcott, C. Bo, E. Fernández

3-“A Mechanistic Rationale for the 9-Amino(9-deoxy)epi Cinchona Alkaloids Catalyzed Asymmetric Reactions via Iminium Ion Activation of Enones”

J. Am. Chem. Soc., (2013) 135, 9091 – 9098

A. Moran, A. Hamilton, C. Bo, P. Melchiorre

4-“Synthetic and DFT Studies Towards a Unified Approach to Phlegmarine Alkaloids: Aza-Michael Intramolecular Processes Leading to 5-Oxodecahydroquinolines”

Chem. Eur. J. (2013) 19, 13881–13892

B. Bradshaw, C. Luque-Corredera, G. Saborit, C. Catiuela, R. Dorel, C. Bo, J. Bonjoch

5-“Understanding electronic ligand perturbation over successive metal-based redox potentials in mononuclear ruthenium-aqua complexes”

ChemPlusChem (2013) 78, 235 – 243

L. Vaquer, P. Miró, X. Sala, F. Bozoglian, E. Masllorens, J. Benet-Buchholz, X. Fontrodona, T. Parella, I. Romero, A. Roglans, M. Rodríguez, C. Bo, A. Llobet

6-“A DFT Study on the Mechanism of the Cycloaddition Reaction of CO₂ to Epoxides Catalyzed by Zn(Salphen) Complexes”

Chem. Eur. J. (2013) 19, 6289 – 6298

F. Castro-Gómez, G. Salassa, A. W. Kleij, C. Bo

7-“Structural studies of metal ligand complexes by ion mobility-mass spectrometry”

Int. J. Ion. Mobil. Spec. (2013) 16, 61 – 67

V. E. Wright, F. Castro-Gómez, E. Jurneczko, J. C. Reynolds, A. Poulton, S. D. R. Christie, P. Barran, C. Bo, C. S. Creaser

2013 Annual Scientific Report

8-“Mechanisms of Catalysis in Confined Spaces: Hydrogenation of Norbornadiene with a Rhodium Complex included in a Self-Folding Cavitand”

Curr. Org. Chem., **(2013)** 7, 1499 –1506

A. Hamilton, M. Gicquel, P. Ballester, C. Bo