Catalytic Conversations:

Integrating Theory and Experiment in Homogeneous Catalysis

Dear colleagues and friends,

It is our great pleasure to welcome you to **Catalytic Conversations: Integrating Theory and Experiment in Homogeneous Catalysis**, taking place on **17 and 18 July 2025** at the **Catalan Chemical Society** (Institut d'Estudis Catalans), Barcelona. This symposium has been organized to celebrate our esteemed colleague and mentor **Agustí Lledós**, marking his 70th birthday and acknowledging his leadership and contributions to the field.

Our goal over these two days is to bring together leading theorists, experimentalists, and young scientists—each working at the cutting edge of homogeneous catalysis. The program includes engaging invited lectures and lively poster sessions, covering topics from computational modeling to experimental mechanistic insights and beyond.

We are fortunate to host a lineup of excellent speakers, including Miquel Solà, Esteban Urriolabeitia, Ainara Nova, Pedro J. Pérez, José Luis Mascareñas, Odile Eisenstein, Ana Albéniz, Fahmi Himo, Eduardo Peris, Max García Melchor, Salva Conejero, Maria Besora, and Rinaldo Poli. These presentations, along with time for discussion, will foster productive exchanges and spark collaborative ideas across disciplinary boundaries.

We extend sincere thanks to our sponsors: Societat Catalana de Química, Grupo Especializado de Química Organometálica, Departament de Química de la UAB, Institut Català d'Investigació Química, and Institut d'Estudis Catalans. We also commend everyone involved in preparing the scientific program and logistical arrangements.

Once again, thank you for joining us in celebrating Agustí Lledós and advancing the science of homogeneous catalysis. Let this symposium inspire future collaborations and deepen our shared appreciation for this dynamic field.

Welcome to **Catalytic Conversations**—let the conversations begin!

Warm regards,

Feliu Maseras and Gregori Ujaque

Lectures

Aromaticity of Annulenes, Acenes, Phenacenes, and Hexabenzenoids in their Ground and Lowest-Lying Triplet States

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The first rule of aromaticity to be established was the famous '(4n+2) .-electron' rule, which states that a cyclic and π-conjugated molecule with (4n+2) .-electrons is aromatic. In 1972, Colin Baird showed [1] that cyclic Dnh annulenes with 4n .-electrons in their lowest triplet excited state (T1) have an aromatic character, whereas those with (4n+2) .-electrons possess an antiaromatic character. The Hückel rule holds strictly only for monocyclic π-conjugated systems such as benzene and cyclooctatetraene. It was noticed early on that polycyclic aromatic hydrocarbons (PAHs) do not obey this rule. The .-sextet rule, proposed in 1972 by Clar to describe aromaticity in PAHs [2], proved to be a more versatile model. In this work, we start analyzing the aromaticity of the T1 state in cyclic annulenes to then move to PAHs such as acenes and phenacenes. Using several measures of aromaticity, we show how Baird's and Hückel/Clar's rules can be combined to explain the triplet state energies of PAHs with fused (4n+2).-electron rings [3].

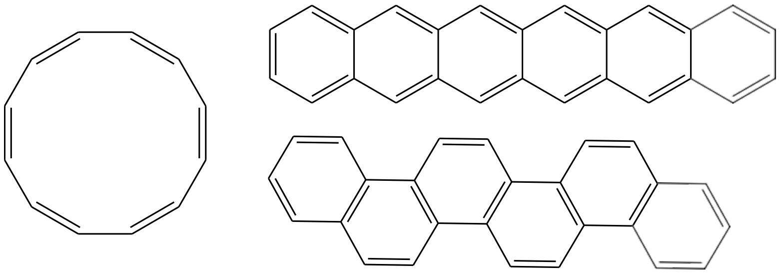

Figure 1: Type of systems studied.

References:
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Exploring the frontier: 25 years of synergy between experiment and theory

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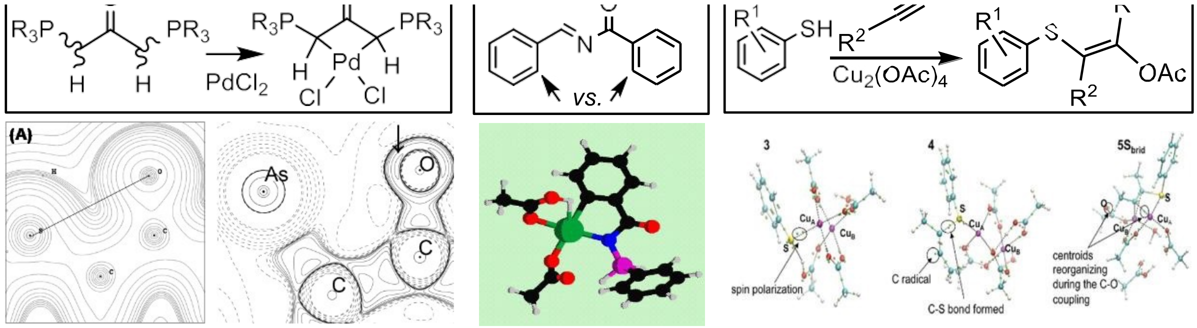
Dialogues between theoretical and experimental chemists have proven to be fundamental when tackling the resolution of problems of diverse nature, ranging from the determination of reaction mechanisms to the explanation of photophysical properties or the evaluation of relative energies of various isomers of a compound. This exchange of information, in addition to helping to understand experimental facts, allows predictions to be made about the behavior of related species at a much lower cost than would be required to do so experimentally in the laboratory.

This talk aims to illustrate, using three very different examples, how the dialogues between Agustí (theory) and myself (experimental) have solved problems of interest in organometallic chemistry. The first was the stereoselectivity observed in the coordination to Pd(II) of bis-ylides of P, N, or S, due to the existence of conformational preferences in the free ligands. Particularly interesting was the characterization of these conformational preferences using Bader's AIM theory, which demonstrated the existence of intramolecular S...O and P...O contacts.[1] A second example analyzes the regioselectivity involved in the C–H activation promoted by Pd in iminophosphoranes.[2] The final case illustrates the stereoselectivity found in the acetoxythiolation of internal alkynes promoted by $Cu_2(OAc)_4$ to give tetrasubstituted olefins. In this case, the key factor was the role played by the cooperation between the two copper centers in the controlled capture of the excess electrons following the incorporation of the acetate and thiolate fragments into the triple bond.[3]



It is obvious that by presenting these works I have strayed from the topic of the conference (catalytic conversations), but I believe they contain enough chemical insight to be of interest to both theoretical and experimental audiences. These studies have been carried out over 25 years of close collaboration, during which I would arrive to Barcelona with an experimental problem that seemed unsolvable, and Agustí would quickly find the solution. For me, it has been a privilege to work under your guidance all these years. Thank you so much!

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Modelling catalysis using computational methods

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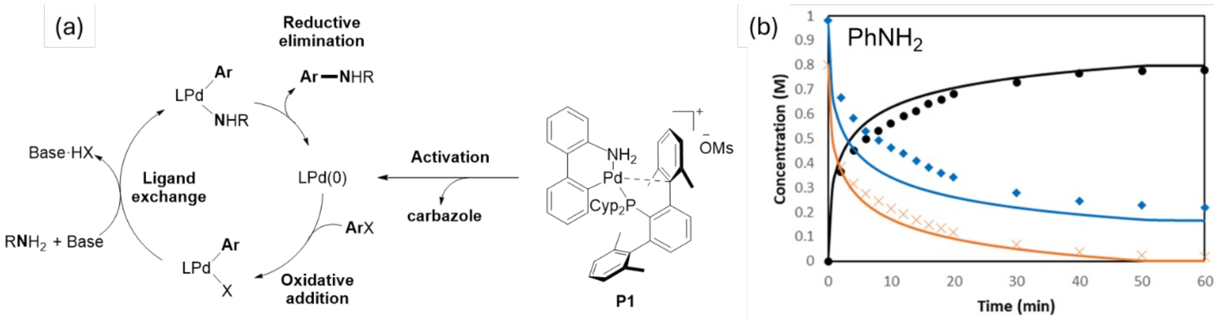
I learnt the art of modelling catalysis using computational methods during my PhD at the Autonomous University of Barcelona with Agustí Lledós and Gregori Ujaque. Since then, the development of computational methods and the increase of computational capabilities have allowed the use of more realistic models to describe chemical systems. The accessibility to accurate energies for medium-sized metal-organic complexes has enabled building microkinetic models that can reproduce the time evolution of reactant, intermediates, and product concentrations over time in highly complex reaction networks.[1] These models provide rich information, such as the catalyst resting state or the kinetically and thermodynamically determining steps, which can be used to design more active, selective, and robust catalysts. While this way of modelling reactions has many advantages, it still has some drawbacks. In this presentation, I will show some examples from our group that utilize this approach and discuss our strategies for overcoming these challenges.[2]



Figures: (a) Key steps for the palladium-catalyzed aryl amination reaction. (b) The concentration of reactants and products over time obtained experimentally and by microkinetic simulations.

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To calculate, or not to calculate, that is the question

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DFT calculations have become a somewhat trivial tool in chemistry from the beginning of this century. In the early days it was frequent to provide calculations with model systems that were actually far from the real thing. Also, in many cases the experimental data collected were sufficient to propose a mechanistic proposal, leaving the DFT calculation as a somewhat decorative part of the article.

Knowing Agustí for many years, I am certain that he does not like trivial calculations but challenging chemical systems. Even more, the perfect work for him would be that in which the calculation predicts experimental work yet to be done or that provide an unexpected explanation for a set of experimental data that cannot be interpreted properly. It is in those cases when to calculate or not to calculate makes the difference.

In this contribution a series of examples related to homogeneous catalytic systems [1-6] developed in our laboratory which either have been predicted by calculations or have been explained via unexpected reaction pathways only reached from calculations will be presented.

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Transition Metal Catalysis: From flasks to living systems

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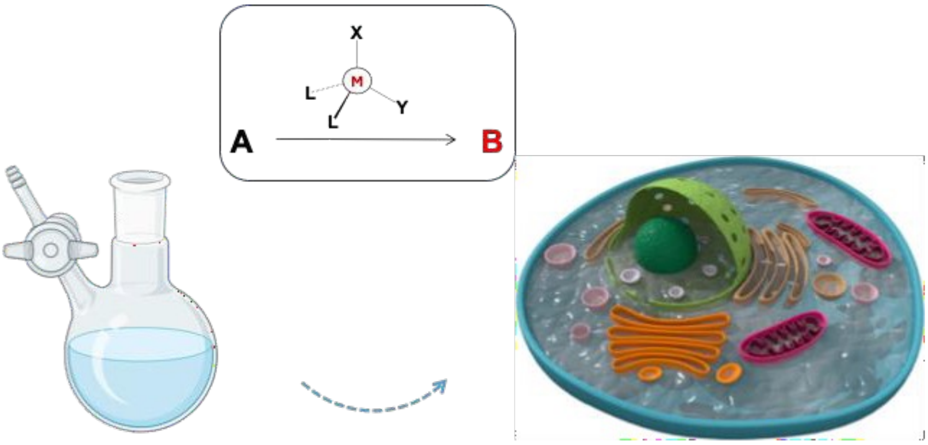
Transition metal complexes have proven invaluable across a broad spectrum of scientific dis- ciplines, including catalysis, synthesis, photophysics, and supramolecular chemistry. Their di- verse coordination geometries and redox properties, combined with the ability to fine-tune these characteristics through ligand modification, offer extensive opportunities for developing novel reactivities and tailored physicochemical responses.

Building on these unique features, our research has focused on leveraging transition metal complexes in catalysis, synthesis, and chemical biology. In recent years, we have explored the feasibility of adapting organometallic catalysis to function in biological environments, including within living mammalian cells. This endeavor poses significant challenges, particularly due to the sensitivity of many metal-catalyzed reactions to air and water, as well as the stringent demands for orthogonality and biocompatibility. Nonetheless, we have successfully developed several intracellular reactions promoted by palladium, ruthenium, and gold complexes. We will summarize our recent advances in these endeavours.



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Searching for the right model: The case of the nucleophilic addition in the past and today

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Many years ago, calculations could be performed using very simplified models of the reagents. [1] These very simplified models of the chemical systems were successful in providing qualitative insights for many reactions. Thus, for instance, it was possible to establish some key aspects of the nucleophilic addition (regio and stereoselectivity) with extremely simple computational models and a molecular orbital analysis. [2,3] This study, while able to interpret experimental data, could be considered as frustrating as the chemical species were very far from what they are in the experimental conditions.

Today, it is possible to model reactions using realistic representations of the chemical species and methods that represent properly the thermodynamics of complex systems. Thus, we have studied the Grignard reaction, a reaction in which a Grignard reagent, RMgX reacts with a carbonyl carbon by making a new C-R bond and form an alcohol after hydrolysis. This reaction, discovered in 1900 by Victor Grignard, Nobel Prize 1912, enables the controlled formation of C-C bond and is thus essential for organic synthesis in the academic and industrial laboratories. Despite extensive studies, this reaction has remained elusive. [4]

In an attempt to provide insights into this reaction, we have used ab initio molecular dynamics to study the species that are present when CH_3MgCl is added to an organic solvent (tetrahydrofuran). We present the arguments that led us to believe that the Grignard reagent is present in a large number of forms in solution [5] and that the Grignard reaction occurs via numerous parallel pathways [6]. We pursue with the presentation of the complex structures of lithium salts (LiX, X = halide) in organic solvent [7] with the goal to understand the role of additives such as LiCl [8] in the reaction (turbo-Grignard).

A perspective on this topic has been published [9].

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Looking deep into palladium chemistry and C–H functionalization catalysis

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The C–H functionalization of arenes catalyzed by palladium complexes is emerging as a new synthetic strategy to complement or substitute the conventional C–C cross coupling processes. The advantages of the direct C–H functionalization stem from the step economy of the method, which does not require the preparation of the reactant partners in common C–C couplings. On the other hand, the still harsh conditions required and the abundance of C–H bonds in a molecule makes attaining selectivity a real challenge. The detailed understanding of the mechanistic pathways of these reactions is crucial to devise systems that overcome their problematic issues and to improve the activity of the catalysts. For this, the tandem experimental-computational effort is necessary and in this talk an example of this type of work will be presented, applied to the chemo- and regioselective direct arylation of unprotected anilines catalyzed by palladium complexes with bipiridone ligands via metal-ligand cooperation (Figure 1).[1]

Besides the study of catalytic processes, the analysis of isolated fundamental organometallic reactions, relevant to catalysis, in a combined experimental- computational approach is extremely useful and examples will be discussed.[2]

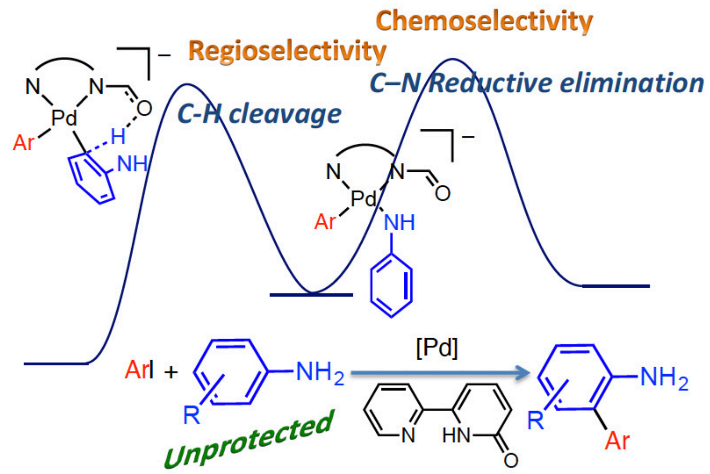

Figure 1. Selective direct arylation of unprotected anilines.

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Modeling Reactions in Capsules and Cavitands

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This talk will present our recent work in the field of modeling reactions inside cavitands and self-assembled capsules.[1-6] Understanding of these host-guest systems requires detailed structural and energetic characterization of the host, accurate calculation of binding free energies of all possible guests, and a detailed investigation of the reaction pathways both inside and outside the host. It is shown that standard density functional theory methodology, in combination with molecular dynamics simulations, offers a reasonable approach for this purpose.

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A short story about carbenes, clippanes and shuttles

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Poly-N-heterocyclic carbene (NHC) ligands have recently emerged as highly versatile compo- nents in the construction of supramolecular organometallic complexes.[1] Particularly, those bridged by polycyclic aromatic hydrocarbons have exhibited intriguing features in terms of their host-guest chemistry properties.[2] Our recent work has focused on expanding the applications of planar, extended π-conjugated NHC ligands in the preparation of organometallic-based su- pramolecular structures.[2] These efforts include utilizing such ligands as hosts for carefully selected organic and inorganic guests. We have also explored a series of di-gold(I)-based metallotweezers,[3] and even developed a new mechanically interlocked molecule (MIM) that we termed clippane.[4] More recently, we introduced a nanosized 'slit-like' metallobox, within which guests such as coronene can shuttle back and forth along the length of the box, effec- tively acting as a molecular shuttle.[5]

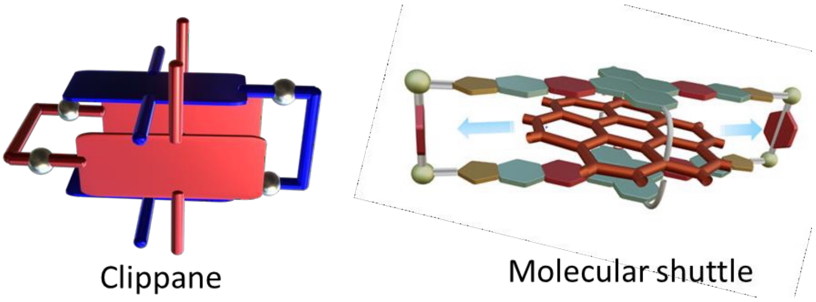

Figure 1. A Clippane and a Molecular Shuttle.

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When the Usual Suspects Talk Back: Uncovering Solution Effects in Wacker Oxidations

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This lecture is both a scientific presentation and a personal tribute to Prof. Agustí Lledós, whose mentorship—alongside that of Prof. Gregori Ujaque—profoundly shaped my early development as a researcher. I will begin with brief reflections on the lessons learned during my PhD, from the value of strong collaborations and a positive research environment to the excitement of scientific discovery, and which continue to influence how I interrogate chemical reactions today.

I will then present recent work from our group on the Wacker oxidation of styrene using hydrogen peroxide (H_2O_2) and tert-butyl hydroperoxide (TBHP) as oxidants.[1] This ostensibly well-understood transformation reveals new mechanistic complexity under computational scrutiny. By combining density functional theory with microkinetic modelling, and interpreting prior D-labeling experiments, we uncover a novel proton shuttle mechanism mediated by triflate counterions that competes with, and ultimately supersedes, the classical 1,2-hydride shift in the H_2O_2-promoted reaction. In contrast, the reaction with TBHP proceeds through an intramolecular protonation pathway, sourced from in situ generated HOtBu. These mechanistic shifts explain the contrasting deuterium incorporation patterns observed experimentally.

Beyond providing insight into the catalytic role of oxidants and the non-innocent behavior of counterions, this work exemplifies a broader message championed by Prof. Lledós: the need to interrogate the "usual suspects" in complex catalytic systems, such as solvent molecules, anions, or minor species. These components are often not merely spectators but may act as mechanistic protagonists.[2],[3] The findings underscore how a well-balanced computational approach, attentive to solution-phase interactions and chemical environment, can bring us closer to understanding the underlying reactivity observed in experiments.

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Low Coordination Number Platinum Complexes: From Structural Analysis to Highly Efficient

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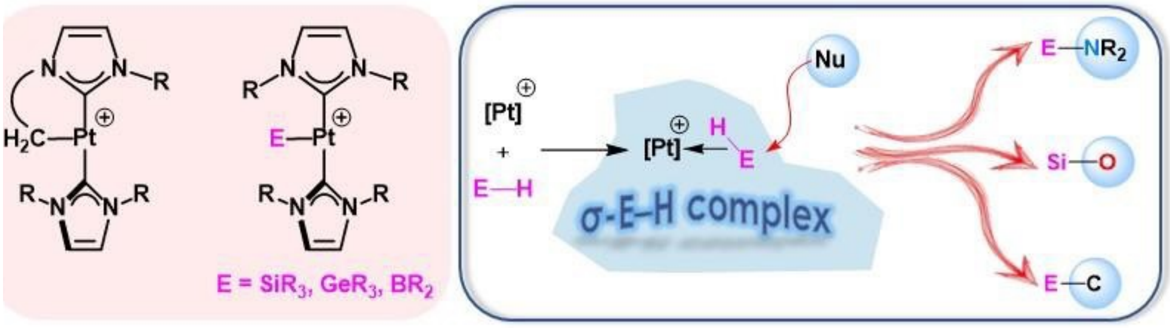
Platinum complexes with low coordination numbers and/or pronounced electrophilic character have been proposed as key intermediates in a wide range of catalytic and stoichiometric transformations.[1] However, their isolation remains a significant challenge. Our research group has been working for several years on the isolation and characterization of these elusive and highly reactive species, using N-heterocyclic carbene (NHC) ligands to form complexes of the general formula $[Pt(X)(NHC)_2][BArF]$.[2] Remarkably, many of these complexes are air- stable, and their steric and electronic properties can be readily fine-tuned. Despite their stability, these highly electrophilic, three-coordinate platinum(II) complexes display enhanced reactivity towards the activation and functionalization of H−E bonds (E = B, Si, Ge). In this presentation,

I will highlight our efforts to understand the reactivity of low-electron-count platinum(II) species through the isolation of key intermediates, mainly σ-EH complexes. These findings, supported by computational studies, have enabled us to elucidate reaction mechanisms and apply this knowledge to catalytic processes that form N−E, O−E, and C−E bonds via electrophilic pathways.



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Learning Chemistry with a Computer

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Dihydrogen (η2-H2) complexes are key in many homogeneous catalytic processes. This species is of fundamental interest in organometallic chemistry, and have numerous practical applications, particularly in catalytic reactions such as hydrogenations. Computational chemistry is essential for studying reaction mechanisms, analyzing molecular structures, and understanding binding modes, making it a crucial tool for investigating these organometallic systems. For some of us, it is impossible to discuss dihydrogen complexes without recalling the influence of Prof. Lledós. In this talk, I will present a brief overview of selected computational studies, both past and recent, that involve dihydrogen (η^2-H_2) complexes.

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Cp*Co^{III}-catalysts further expand the (de) hydrogenation and hydrogen transfer mechanistic landscape

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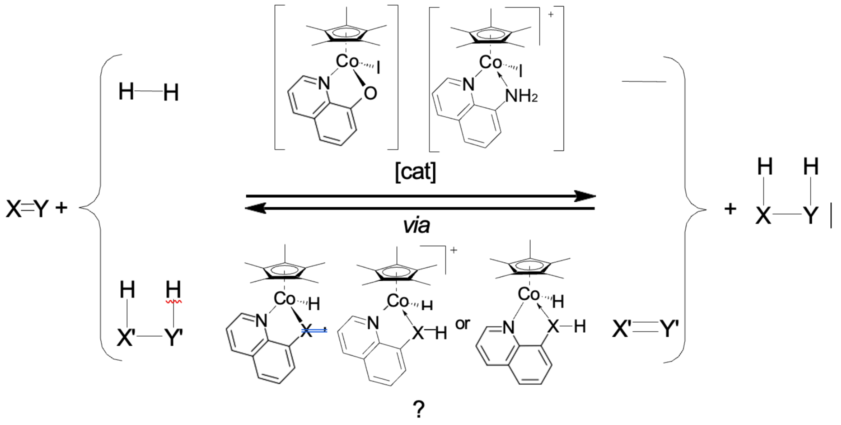
The shuttling of H atoms to and from a substrate in (de)hydrogenations and hydrogen transfer reactions (Scheme) display a very rich mechanistic landscape. These are also key steps in a growing number of transformations that follow the “hydrogen borrowing” principle. The various possible pathways involve either an inner-sphere or an outer-sphere substrate activation, homolytic or ionic dihydrogen activation, the involvement of internal or external protons, etc. The hydrogen donor molecule (H_2 in hydrogenations; an alcohol, formic acid or other donors in hydrogen transfers) transfers the two H atoms to the catalyst system as either two hydride ligands (with the metal being formally oxidized from n to n+2) or as a hydride and a proton (with the metal maintaining the same formal oxidation state). This presentation will highlight a new mode of activation of the hydrogen donor molecule,[1] discovered for transformations catalyzed by Cp*Co systems,[2-4] whereby the two H atoms are transferred to the catalyst system as two protons and the metal is formally reduced by two electrons. The two protons are captured by either internal or external bases. The catalyst resting state, formally Cp*Co^{I}, has an unusual electronic structure.



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Posters

Mechanistic Insights on Metal-Free Light-Mediated Difunctionalization of Unactivated Alkenes

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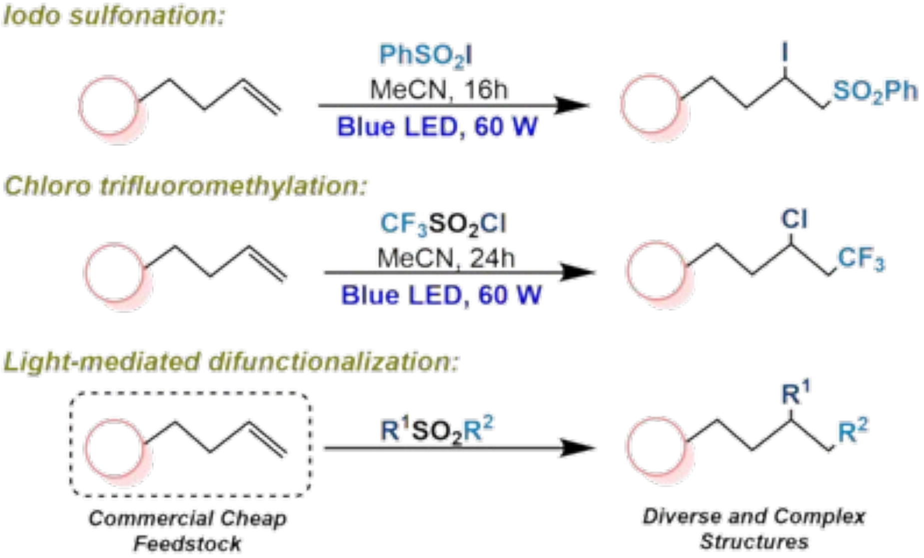
P01

The difunctionalization of alkenes is a straightforward and powerful approach for constructing structurally complex molecules with versatile reactive groups. While numerous difunctionalization strategies have been developed, most rely on transition-metal catalysis, such as Erchinger process [1].
To address these limitations, we propose a metal-free, photocatalyzed approach based on DFT calculations. This method facilitates the generation of two reactive radical intermediates that undergo predictable reactions with unactivated alkenes. The computed mechanisms reveal the formation of transient open-shell species, enabling selective double functionalization.

Our strategy leverages the unique properties of sulfonyl compounds, which can either undergo direct excitation or form an electron donor-acceptor (EDA) complex. The resulting radical intermediates react with unactivated alkenes, enabling polarity-driven selective funcionalization without requiring prior activation steps.



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Computational Insights into the Rh(III)-Catalyzed peri-C−H Alkynylation of Polyaromatic Carbamates

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P02

In recent years, several methods to regioselectively functionalize naphthalene derivatives have been reported.[1] Based on our previous work on the alkynylation of arenes,[2-4] we have developed a Rh(III)-catalyzed carbamate-mediated peri-C−H alkynylation of polyaromatic carbamates. The reaction proceeds regioselectively at the peri position, and it tolerates a broad range of bromoacetylenes. However, with triethylsilyl- and n-hexyl-bromoacetylenes, a cyclization product was obtained as the major product, along with the *peri*-alkyne product.

A computational study to elucidate the origin of this different reactivity has been conducted. Based on the DFT results, two possible pathways emerge depending on the alkyne insertion step, one of which involves the intermediacy of a rhodium vinylidene. To the best of our knowledge, the regioselectivity of the alkyne insertion of bromoacetylenes had previously only been studied computationally in the context of Ir(III)- and Pd(II)-catalyzed reactions.[5-6]

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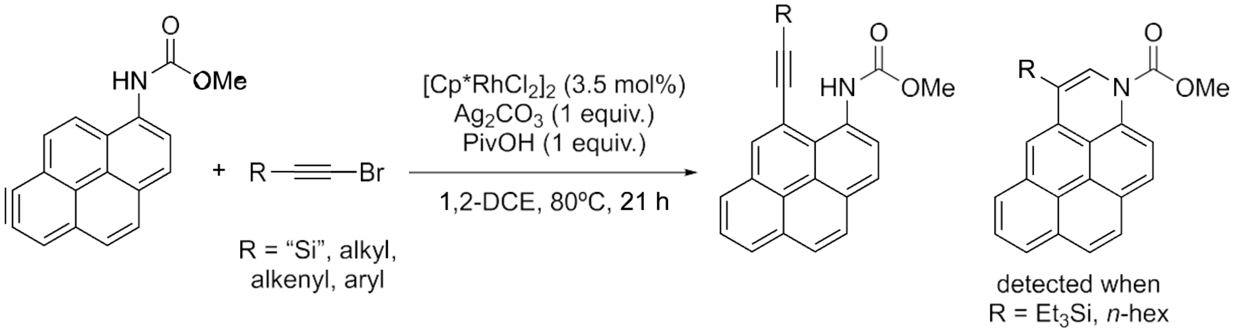

Exploring the Impact of Topological Variations on the Stability of the Ground Singlet and Lowest-Lying Triplet States of Catacondensed Hexabenzenoids

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P03

Polybenzenoid hydrocarbons (PBHs) are very popular in material science[1], organic electronics and spintronics[2] due to aromaticity and unique electronic properties. The impact of topological variations on the relative stability of PAH isomers in different electronic states is poorly understood, with limited insights into how Clar π-sextets[3] and topological features[4] like bay, cove, fjord, and K-regions influence stability in their ground singlet (S_0) and lowest-lying triplet (T_1) states. In this work, we perform density functional theory calculations of the S_0 and T_1 states of the 37 catacondensed hexabenzenoids. We use a multivariate linear regression model with relative energy as the dependent variable and a series of topological parameters as the independent variables to quantify the effect of topology in the relative stability of the catacondensed hexabenzenoids. Our analysis shows that, in S_0, stability is enhanced by an increase in the number of Clar π-sextets and K-regions and decreased by the presence of coves and fjords. In T_1, the main stabilizing factors are the number of Clar π-sextets and the number of rings involved in the antiaromatic region, whereas topological regions like K-edges, bays, coves, or fjords are destabilizing.

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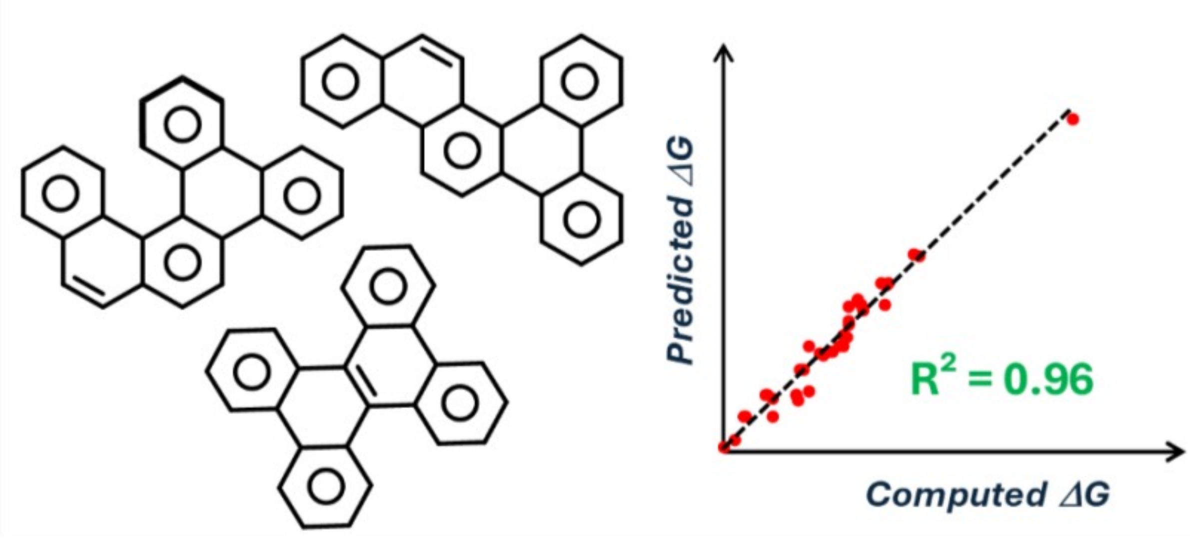

The influence of topological features on the stability of 37 catacondensed hexabenzenoids in their S_0 and T_1 states using a multivariate regression model.

rPAMP: data-driven design of diphosphanes for intermolecular hydroacylation

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P04

Typically, progress in the development of highly efficient ligands for homogeneous catalysis is still based exclusively on chemical intuition, aided by computational tools to study the mechanism and performance. This is especially true for the subset of P-stereogenic phosphanes, with their synthesis being a particularly arduous task, requiring optimization of multistep syntheses, dealing with hazardous reagents and handling several sensitive intermediates.[1]

Fortunately, machine learning techniques have fully made their way into the systematic exploration of the chemical space and have already yielded "machine-proposed" ligands that defy intuition but give very good results.[2],[3]

In this context, we have developed an *in silico* library of reported diphosphanes to map the chemical space around a synthetically accessible set of ligands to determine whether its synthesis is worth exploring. Following this approach, a suitable family of five diphosphanes, named **rPAMP**, has been identified, successfully synthesized, complexed to rhodium, and the complexes tested in the catalytic intermolecular hydroacylation of olefins, with good results.[4]

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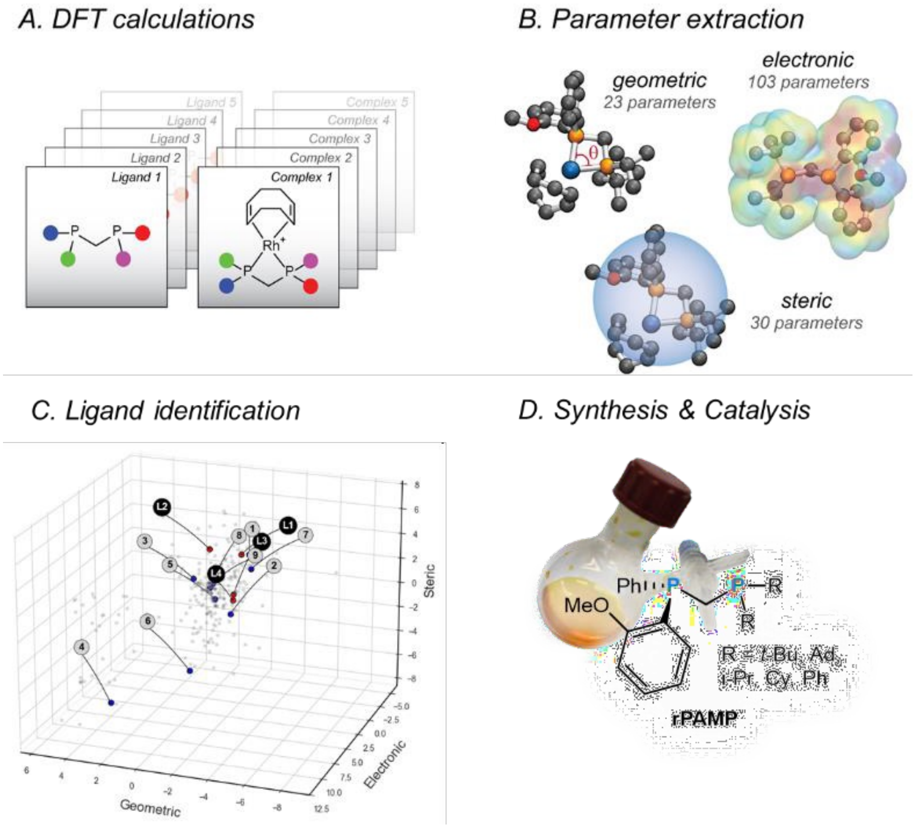

A. DFT calculations

B. Parameter extraction

C. Ligand identification

D. Synthesis & Catalysis

Group 1 Redox Interchange: An Alumanyl Case Study

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P05

Since early 19th Century, group 1 alkali metals have widely served as powerful reducing agents in all fields of chemistry. Notwithstanding Dye and co-workers' startling identification of alkalide (M^-; M = Na, K, Rb, Cs) anions,[1] little consideration is applied to the redox behaviour of these group 1 elements in molecular systems. Their use is often guided more by synthetic expedience than by the origin of reducing electrons, with the resulting M^+ typically regarded as an innocent bystander – either incorporated into the target compound or relegated to a by- product salt.

Across the years, a series of isolable aluminium(I) anions ("alumanyls") have been reported.[2] Very recently, the Hill group have introduced a new series of alumanyls incorporating different alkali metals counterions ($[\{SiN^{Dipp}\}AlM]_2$, 1^M) and demonstrated that the identity of M^+ plays a pivotal role in their stability and reactivity.[3] A combined thermodynamical model is presented that is derived from both theoretical (DFT) and empirical data to accurately evaluate the feasibility of the redox interchange of group 1 elements in alumanyl anions derivatives, through the use of elemental alkali metals (M0) as reducing agents

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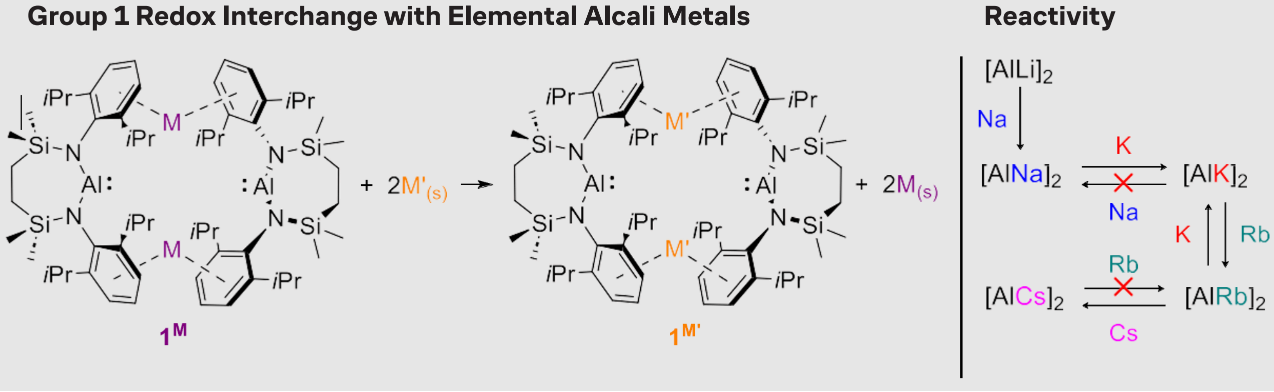

Group 1 Redox Interchange with Elemental Alcali Metals

Reactivity

Enhanced photoreduction of water catalyzed by a cucurbit[8]uril-secured platinum dimer

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P06

The design of artificial photosynthetic systems that split water into molecular hydrogen and oxygen remains a major challenge of our times.[1] The photoreduction of water requires a photosensitizer, an electron relay and a hydrogen-evolving catalyst, either as a three- component system, or with one or two multifunctional components. Platinum(II)terpyridyl (tpy) chlorides can be used both as a photosensitizer and H2-evolving catalyst in the presence of ethylenediaminetetraacetic acid (EDTA) as the sacrificial electron donor. It is known that photosensitization is mostly achieved by the Pt(II)-tpy dimer via a proton-coupled electron transfer (PCET) to the corresponding Pt(II)–Pt(III)–H hydride (Figure 1a).

A cucurbit[8]uril (CB[8])-secured platinum terpyridyl chloride dimer was used in this work as a photosensitizer and hydrogen-evolving catalyst for the photoreduction of water (Figure 1b–d). Volumes of produced hydrogen were up to 25 and 6 times larger than those obtained with the corresponding free and cucurbit[7]uril-bound platinum monomer, respectively. The thermodynamics of the proton-coupled electron transfer from the Pt(II)–Pt(II) dimer to the corresponding Pt(II)–Pt(III)–H hydride key intermediate, as quantified by density functional theory, suggest that CB[8] secures the Pt(II)–Pt(II) dimer in a particularly reactive conformation that promotes hydrogen formation.[2]

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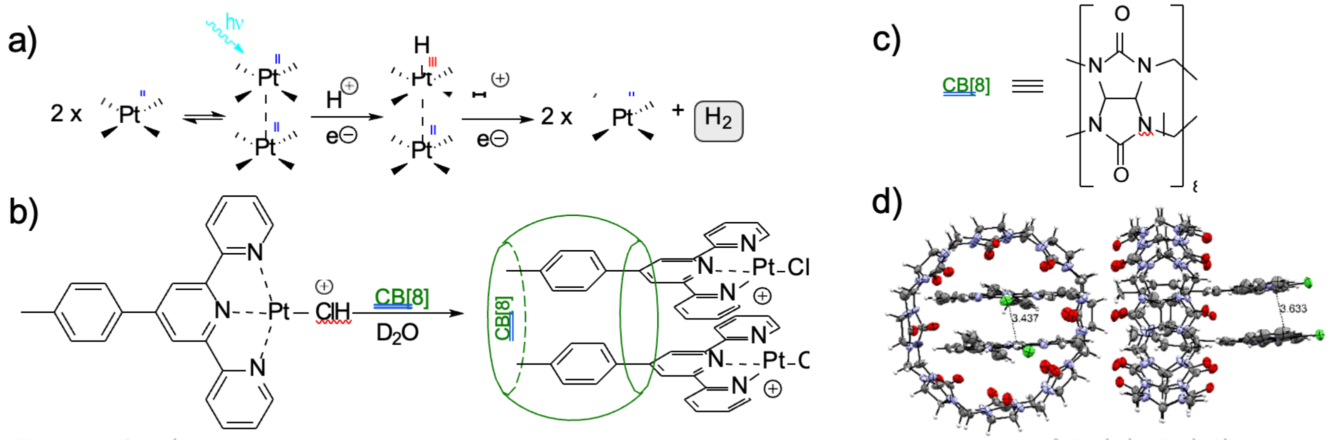

Figure 1. a) Hydrogen-evolving mechanism through photosensitization of Pt(II)–Pt(III)–H hy- dride dimer; b) Formation of a supramolecular homoternary assembly of two Pt(II)-tpy com- plexes by CB[8] in aqueous media; c) structure of CB[8]; (d) single-crystal X-ray diffraction structure of the homoternary assembly showing the two conformations within the unit cell.

Molecular Cucurbit[6] uril-Enhanced Electrochemical Sensor for Sensitive Detection of Hazardous Air Pollutants

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P07

Rapid industrialization has led to a significant increase in air pollutants such as hydrogen cyanide, ammonia, ozone, sulphur dioxide, and sulphur trioxide. This highlights the need for efficient methods to absorb these contaminants. The 3D nanostructure of cucurbit [6] uril (CB [6]) emerges as a promising system due to its potential to interact effectively with various industrial pollutants, as investigated using density functional theory (DFT). Structural and electronic analyses indicate that the analytes exhibit favourable adsorption on the CB [6] framework. Among them, SO_3@CB [6] demonstrates the highest interaction energy (-18.66 kcal/mol). Furthermore, electronic property assessments—including frontier molecular orbital (FMO) analysis, natural bond orbital (NBO) analysis, non-covalent interaction (NCI) plots, electron density difference (EDD) maps, and quantum theory of atoms in molecules (QTAIM)— support the role of CB [6] as an effective electrochemical sensor for diverse pollutants. Overall, the study reveals that ozone (O_3) shows the highest selectivity toward CB [6], as evidenced by its significant bandgap reduction, suggesting that CB [6] is particularly sensitive to O_3 among all the examined species.

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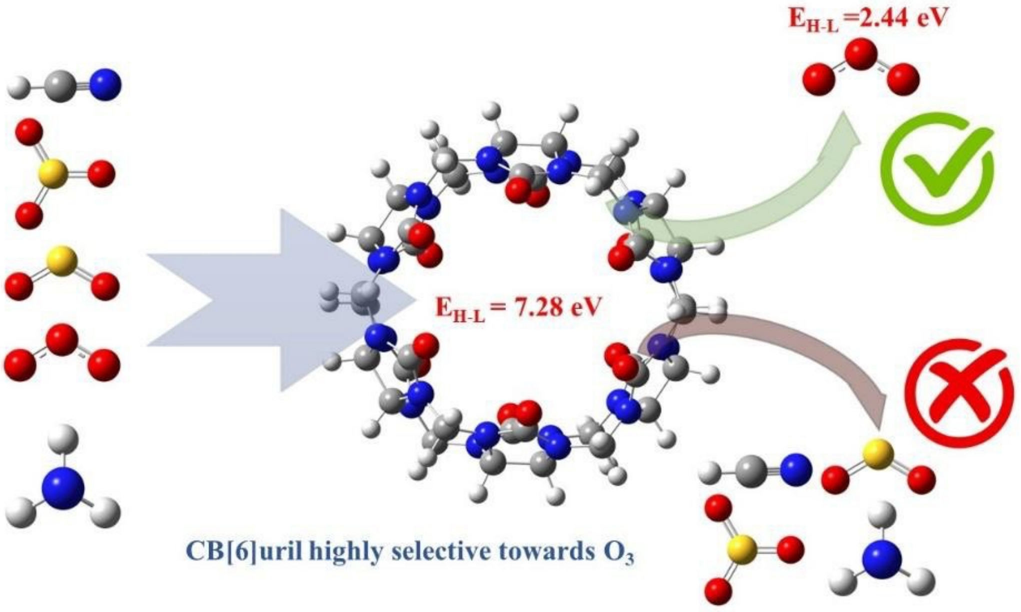

Selective adsorption of toxic air pollutants on the surface of cucurbit [6] uril.

Simulating Host–Guest Behavior of a Metal–Organic Cage in Solution

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P08

In the field of supramolecular chemistry, host–guest systems -where a molecular host encapsulates one or more guest species- have become increasingly prominent in recent years. This work presents a computational investigation into the host–guest behavior of a metal–organic cage with a rectangular architecture, constructed with iridium atoms positioned at each vertex.[1]

To explore these systems, quantum mechanical (QM) methods were applied to generate force field parameters using the MCPB protocol.[2] These parameters were then used to perform molecular dynamics (MD) simulations, to analyze the systems in solution under three distinct conditions: the empty cage, the cage with counterions, and the cage in complex with various guest molecules.

The results indicate that the type of counterion has little impact on the overall structure and dynamics. In all simulated scenarios, guest molecules remain encapsulated within the cage, although differences in their internal motion are noted. Encapsulation tends to reduce the guest's mobility, highlighting the stabilizing influence exerted by the cage environment.

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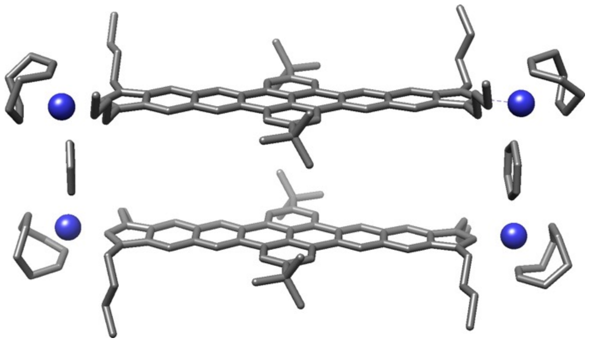
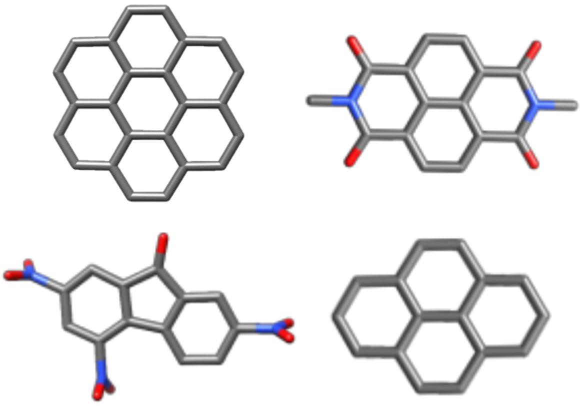
HOST



GUESTS



Asymmetric Hydrogenation of Ketones Using a Novel P*-Stereogenic Phosphinito-Quinoline-Based Iridium Pincer

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Secondary Phosphine Oxides (SPOs) have recently gained interest as ligands, presenting a tautomeric equilibrium between the pentavalent oxide form (SPO) and the trivalent phosphinous acid (PA).[1] Despite this, their deprotonated counterparts, O-anionic phosphinitos, remain understudied.[2]

In this project, we developed a bench-stable quinoline-based P*-stereogenic SPO that after complexation yields a unique O-anionic phosphinito iridium pincer. This unprecedented complex presented high activity and a high degree of stereo-control in the asymmetric hydrogenation of ketones. The transformation has proved robust, versatile and unraveled a new mechanism where the O-anionic phosphinito and an acidic activator like HFIP play a pivotal role. Moreover, the complex allows the unusual hydrogenation of ketones in acidic media and stands as the first example of asymmetric catalysis using an O-anionic phosphinito ligand.

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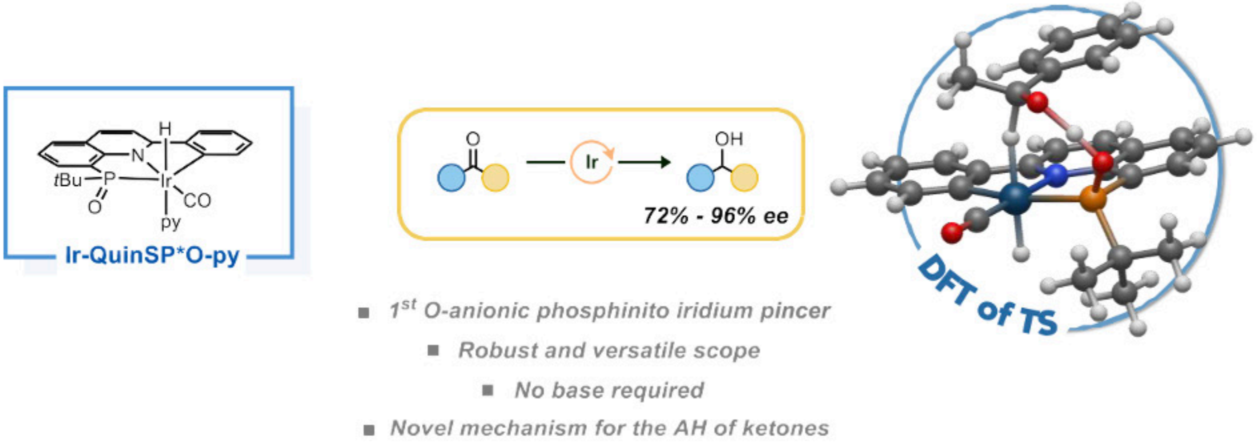

- 1st O-anionic phosphinito iridium pincer
- Robust and versatile scope
- No base required
- Novel mechanism for the AH of ketones

Molecular Encapsulation and Dynamic Behaviour in Metallocages

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P10

Metallocages are a type of self-assembled nanostructure with diverse geometries, including tetrahedral and cubic shapes.[1] These systems feature nanoscale cavities that enable selective encapsulation of small guest molecules. The tunable nature of these cavities allows for precise engineering of functions like molecular recognition, gas storage, drug delivery, and catalysis.[2].

Cationic metallocages leverage their inherent charge and cavity architecture to selectively stabilize guest molecules. Key structural determinants, such as cavity size and charge distribution, govern the efficiency and specificity of host-guest binding.[3] In this study, we integrate full DFT calculations with molecular dynamics (MD) simulations to unravel the underlying mechanisms of host-guest interactions at the atomic level.

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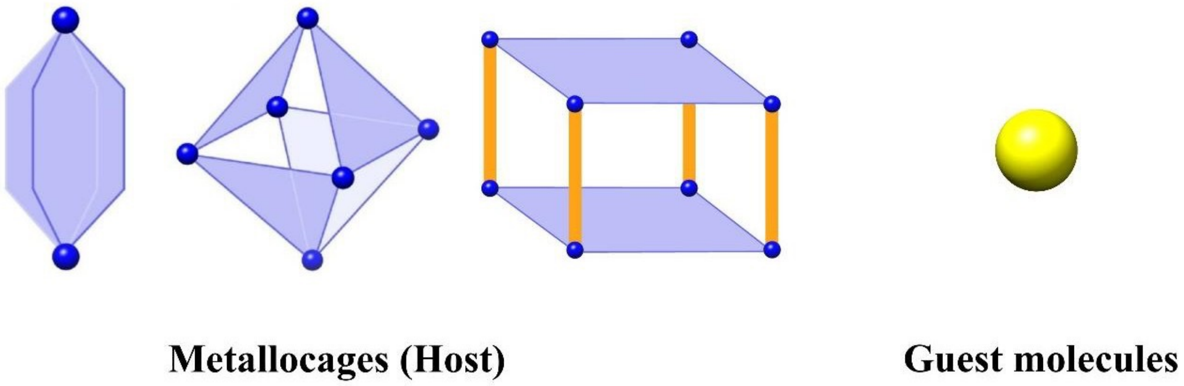

On the origin of stereoselectivity in asymmetric transfer hydrogenations catalyzed by chiral-at-iridium complexes

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P11

Secondary Phosphine Oxides (SPOs) have recently gained interest as ligands, presenting a tautomeric equilibrium between the pentavalent oxide form (SPO) and the trivalent phosphinous acid (PA).[1] Despite this, their deprotonated counterparts, O-anionic phosphinitos, remain understudied.[2]

Secondary phosphine oxides (SPOs) are well-known hydrogen-bonding non-innocent ligands in organometallic catalysis. This feature is usually reflected in key steps in reaction mechanisms, in which these ligands show an outstanding behavior.[1] Asymmetric catalysis based on chiral-only-at-metal organometallics (rather than on the chirality of coordinated lig- ands) is a blooming area of research thanks to the pioneering contributions of Prof. Meggers' group. In 2016, they presented a chiral-at-metal bis-cyclometalated iridium(III) complex for the asymmetric transfer hydrogenation of ketones, helped by a non-innocent hydrogen-bonding bulky pyrazole ligand.[2]

Recently, we reported on the catalytic activity of a family of chiral-at-metal iridium(III) SPO complexes in asymmetric (transfer) hydrogenation of ketones.[3] Herein, we will discuss comparatively those results with the catalytic behavior in hydrogenation reactions using moecular H_2. Eventually, we will try to unravel how steric hindrance determines the absolute configuration of the main catalytic product obtained, based on experimental results and DFT calculations.

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Acknoledments:

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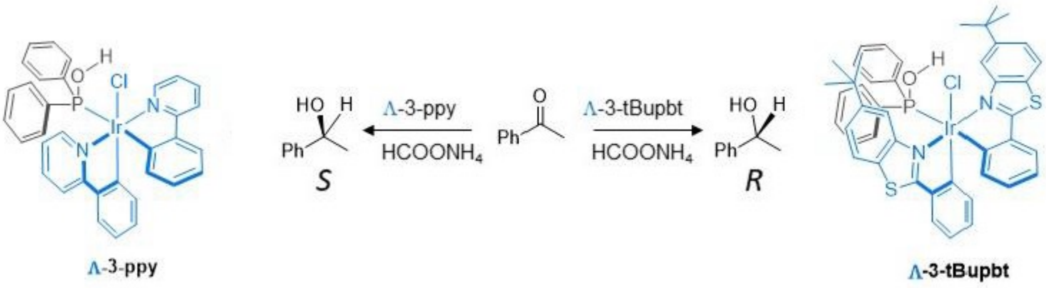

Stereoselectivity observed in the chiral-at-iridium catalyzed asymmetric transfer hydrogenation

On route to BN isosters of 2D and 3D cores

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P12

BN-isosterism is a molecular design principle in which a carbon–carbon unit is replaced by a boron–nitrogen fragment. Owing to the shared valence electron count of 8, both C–C and B– N derivative can be represented by analogous Lewis's resonance structures and often exhibit similar geometries. Also, this substitution transforms a low-polar C–C bond into a strongly polarized B–N bond, thereby altering the orbital energy landscape.[1] For this reason, planar aromatic B–N compounds have attracted significant attention in the field of organic optoelectronics. In contrast, the potential of BN-isosterism to expand the structural diversity of three-dimensional architectures based on sp^3-hybridized atoms remains largely unexplored. Here, we showcase synthetic tools recently developed in our laboratory for rapid and scalable preparation of BN-isosteres of various 2D and 3D organic cores. One such tool is the versatile use of triallylborane, $B(allyl)_3$ for quantitative B–N bond formation via propene elimination. Another is the highly efficient π-disruption of the B=N bond through the addition of a nucleophile/electrophile (Nu^-/E^+) combination.[2] The latest tool consists of an ortho-ipso annulative difunctionalization reaction based on Pd–Norbornene catalytic technology, which enables the expansion of the 2D core of the BN-naphthalene ring.[3] These methods now allow for the preparation of BN-isosteres of common polycyclic cores such as naphthalene, anthracene, and tetracene. In parallel, these and other strategies are being explored to access BN-isosteres of both known and unknown 3D structures, including polycycles and propellanes.[4]

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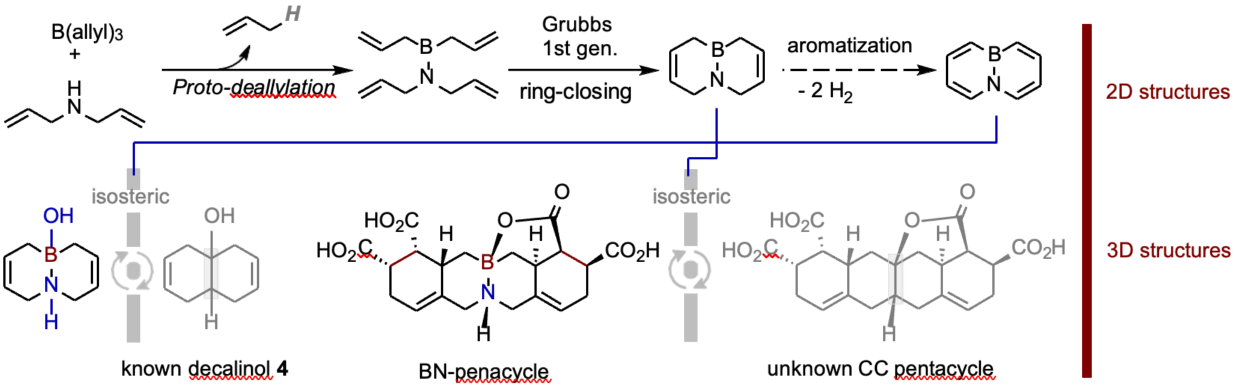

known decalinol **4**

BN-penacycle

unknown CC pentacycle

Computational study of a copper-catalyzed synthesis of fluoroalcohols from alkylboranes and ketones

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Fluoroalcohols are a class of organic compounds containing one or more fluorine atoms together with an alcohol group in their molecular structure.[1] These fluorinated species have a wide range of applications due to their unique properties and are used in medicine[2] and electronics.[3] Herein, we propose a new synthetic procedure, promoted by a copper(I) catalyst, for preparing fluoroalcohols from alkylboranes and symmetric ketones. The reaction has been computationally explored to propose a plausible mechanism, which allows identifying the rate-limiting step and quantitatively evaluating the electronic effects of each substrate on the overall reactivity. These DFT calculations suggest that the combination of electron-poor ketones with electron-rich alkylboranes produce the most efficient catalytic systems for preparing fluoroalcohols.

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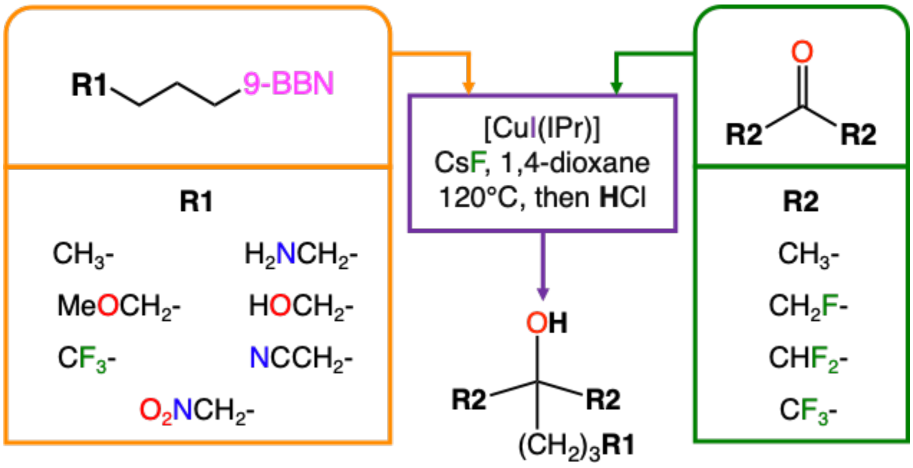

Dithienylethene-based photoswitchable phosphines for light-controlling catalytic activity

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P14

Photoswitchable catalysts that are capable of toggling between active and inactive states upon irradiation are of high interest, as they allow the optical control of catalytic reactions on demand.[1,2] The preparation of phosphines containing photoisomerisable backbones will likely enable light-controlled changes in their coordination behavior and, hence, variation of the catalytic activity of the corresponding complexes. With this aim, we have explored the use of dithienylethenes (DTEs) as light-responsive cores for preparing photoswitchable phosphines.

Dithienylethenes are well-known photoswitches that have already been applied to control chemical reactivity with light based on the geometrical and electronic changes that occur upon reversible open-closed photoisomerisation.[3] In particular, we are herein interested in exploiting the drastic variation in electronic communication that takes place between the external 5- and 5'-substituents of the DTE thiophene rings, which are not conjugated in the open isomer but become electronically connected after ring closing (Figure 1). Therefore, by introducing phosphine moieties in one of the thiophenes and electron-withdrawing groups in the other, a control of the phosphine's electronic properties upon DTE photoswitching is accomplished, which modulates its σ-donating ability.[4,5] As a result, different catalytic activities are measured for the transition metal complexes of these photoswitchable phosphine ligands[5]

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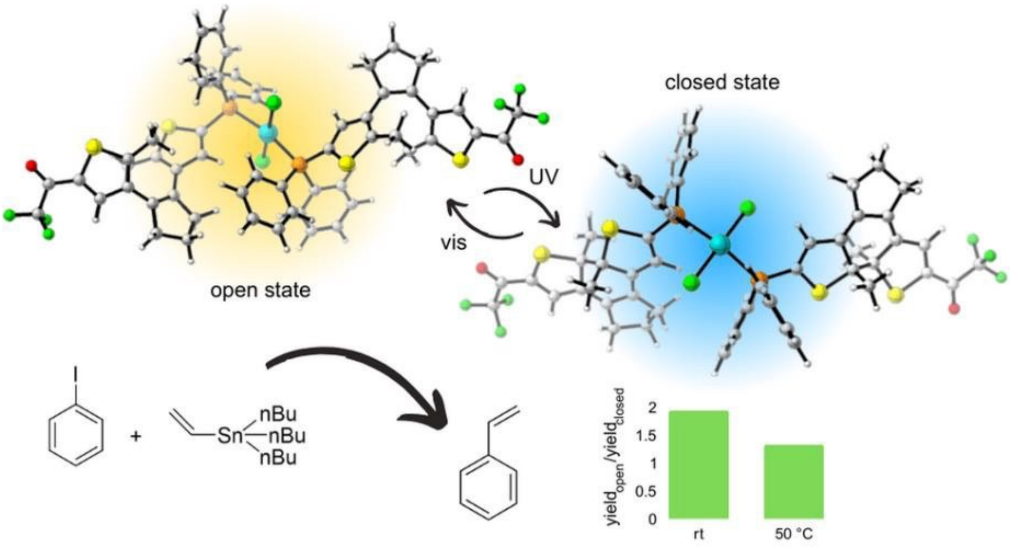

Computational analysis of the rocking movement of guest inside metallorectangle

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P15

Host-guest chemistry is a supramolecular subdiscipline focused on the design and study of molecular systems that selectively recognize, encapsulate, and release guest molecules through non-covalent interactions.[1-2]

The group of E. Peris has designed a Ir(I)-metallorectangle with a long and narrow cavity that enables the asymmetric encapsulation of polycyclic aromatic hydrocarbons (PAHs). Experimental evidence indicates that several PAHs are encapsulated near one side of the cavity, exhibiting shuttle-like motion from side to side.[3] However, one particular guest predominantly occupies the central region of the host and can rotate in place without any experimentally observable translational movement. This rotation relative to the host is referred to as a rocking motion.

In this work, we present a computational study aimed at characterizing this rocking motion using metadynamics simulations. Reconstruction of the free energy surface revealed two accessible mechanisms with comparable energy barriers.

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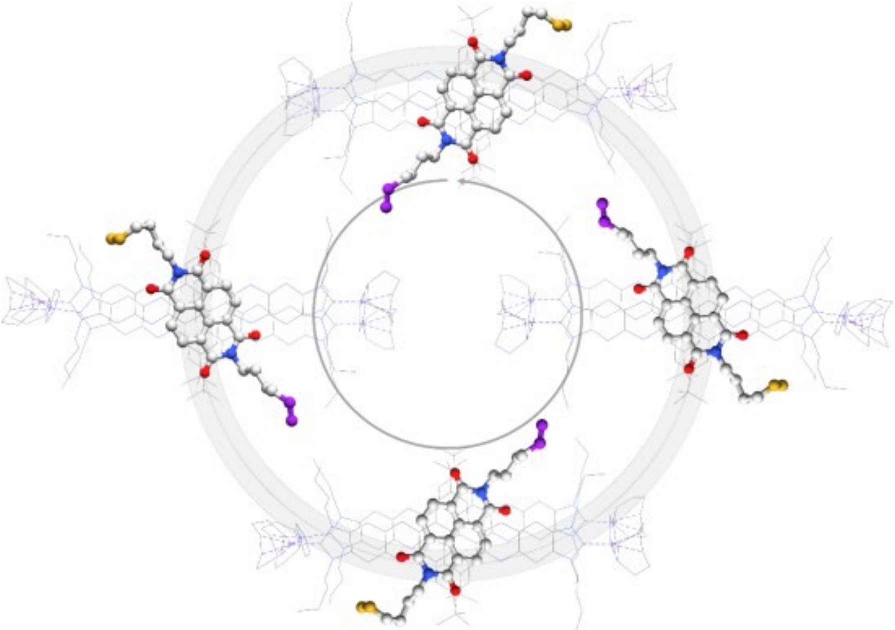

MD simulations in catalysis. Two cases: aqueous micellar organometallic catalysis and enzymatic reactions in dynamers environments

Sonsoles Martín-Santamaría[1*]; Alejandra Matamoros-Recio[1]; Joan Guzmán- Caldentey[1]; Ameerah Bibi Furjun[1]; Marc Hennebelle[1]; Ana Caballero[2]; Pedro J. Pérez[2]; Ruth Pérez[1]

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P16

Herein the first MD study of the dynamics of a catalytic organometallic system, in micellar media, is presented. The challenging methane catalytic functionalization into ethyl propionate through a silver-catalyzed process has been targeted as the case study. Computed simulations allow explaining the experimental results, indicating that micelles behave differently regarding the degree of accumulation and the local distribution of the reactants and their effect in the molecular collisions leading to net reaction (Figure 1).[1]

We also present the work in the optimization of Carbonic Anhydrase (CA) activity for CO_2 capture by direct addition of adaptive dynamers (dynamic polymers) into enzymatic reaction solutions. The MD simulations of CA in the dynamers environments are allowing us the characterization of dynamers adaptation to CA and changes in the 3D structure, active site and conformation in the modelled dynamers environments accounting for the different yields.

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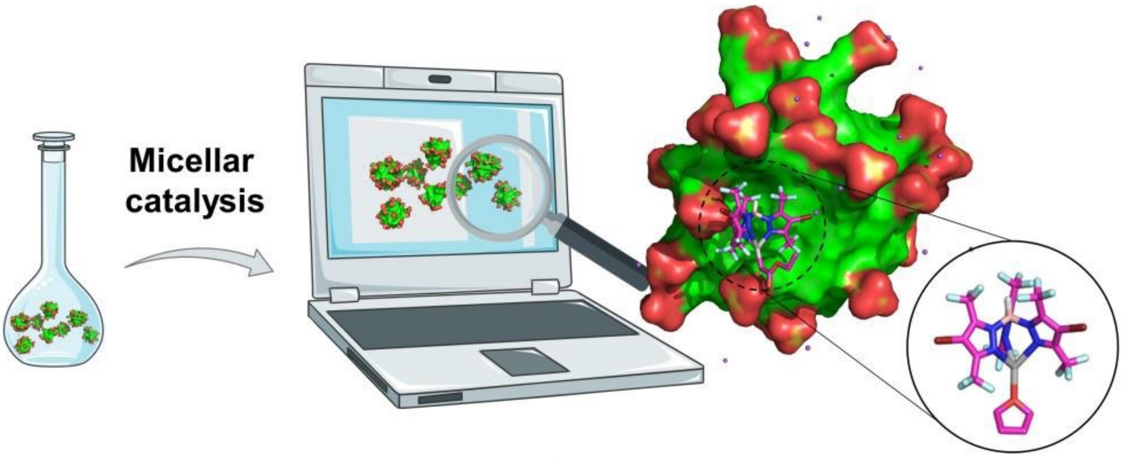

Figure 1

Understanding the activation mode in the synthesis of tetrasubstituted epoxides from ketones and α-Halo B/Si ylides: a computational perspective

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P17

Host-guest chemistry is a supramolecular subdiscipline focused on the design and study of molecular systems that selectively recognize, encapsulate, and release guest molecules through non-covalent interactions.[1-2]

Density Functional Theory (DFT) is an essential tool for mechanistic investigation, helping to uncover the complexities of chemical reactions. Our group focuses on achieving an

understanding of reaction mechanism [1-3], enabling us to predict and design new processes. In collaboration with the experimental group of Fernández [4], we explore a novel pathway for epoxide synthesis from iodo-pinacolato-borylmethyl derivatives. Their pioneering work introduced iodo-bis(pinacolboryl)methane [ICH(Bpin)2] and iodo- (pinacolboryl)(trimethylsilyl) methane [ICH(Bpin)(SiMe3)] as key intermediates. These compounds undergo deprotonation with a lithium salt to form a carbanion which can then lead to two different reactions: the boron Wittig reaction or epoxidation. Recent experimental

results show that the iodo-(pinacolboryl)(trimethylsilyl) methane [$ICH(Bpin)(SiMe_3)$] undergoes epoxidation exclusively, while iodo-bis(pinacolboryl)methane [$ICH(Bpin)_2$] favors

the Wittig reaction. This divergence is explored using DFT. We reproduce the experimental reaction and explain the role of the substituents.

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Unveiling the role of *Cis/Trans*-[RuCl$_2$(trpy(DMSO)] in Alcohol Coupling Reaction

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P18

Coupling reactions refer to the process in which two or more molecules combine to form a more complex compound. These reactions are commonly catalyzed by transition metals and have become increasingly important in green chemistry because they proceed with high atom economy, thus minimizing waste and reducing environmental impact [1]. This study examines a specific coupling reaction of borrowing hydrogen type, in which water is the only byproduct [2].

The reaction mechanism starts with oxidation of the substrates, followed by aldol coupling to yield an unsaturated ketone which is finally reduced to the coupled alcohol. The catalyst plays a role in the initial and final redox steps.

In this work, ruthenium complexes bearing polypyridyl and/or dmso ligands have been tested with the aim to evaluate the effect of structural and electronic parameters on the catalytic efficiency. Once tested, different catalytic activity was observed. Specifically, significant differences have been found as a function of the types of ligands present, and also between catalyst isomers. This difference has been attempted to be contrasted computationally in the case of complexes *cis*- and *trans*- [RuCl$_2$(trpy)(dmso)]. Additionally, the proposed reaction mechanism has been studied. DFT calculations at the BP86/Def2SVP level of theory have been performed, incorporating solvent effects (1,4-dioxane) using the SMD model.

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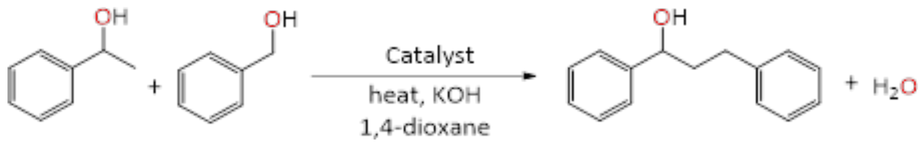

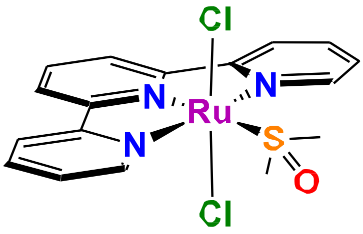

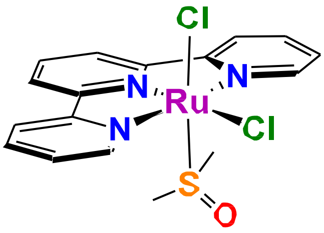

Effective Fragment Orbitals as a tool for wavefunction analysis

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P19

Classical chemical concepts remain extremely useful for describing, classifying, and predicting chemical processes.

In this work, we will show how the so-called effective fragment orbitals (EFOs) and their occupations can be a powerful tool for wavefunction analysis by providing deeper insight into certain heuristic chemical concepts. The EFOs are the generalization of Mayer's effective atomic orbitals to molecular fragments, and can be understood as the natural orbitals of atoms/fragments within a molecule.[1,2]

In our group, we have been using the EFOs and their occupations to assign oxidation states with the so-called EOS analysis. More recently, we have shown that the EFOs can be used to quantify the donor-acceptor capacities of ligands in complexes without the need for external references.[3] We will show that EFOs can be used to rationalize inductive and mesomeric effects in substituted benzenes, in alignment with Hammett parameters.[4]

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