

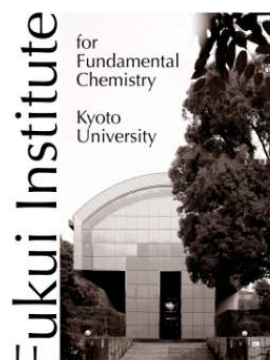


ICIQ-FIFC  
Spain-Japan Joint Symposium on

**Theoretical and  
Computational Chemistry  
of Complex Systems**

November 25-27, 2015  
ICIQ Auditorium, Tarragona

Sponsored By:



## **PRESENTATION**

We wish to welcome all participants to the "ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry of Complex Systems" held at the Institute of Chemical Research of Catalonia (ICIQ), in the new campus of the Rovira i Virgili University of Tarragona. This symposium, which is co-organized between the Fukui Institute for Fundamental Chemistry and ICIQ, will bring together researchers from both countries working in the general field of computational chemistry. The goal of the meeting is to exchange knowledge between the participating groups and strengthen the ties that may lead to future collaborations.

We would like to express our deepest gratitude to all participants for their interest, which has made this ICIQ-FIFC Symposium possible. We warmly welcome all of you to Tarragona, a beautiful city of Catalonia at the heart of the Costa Dourada, which was the capital of the Roman province Hispania Citerior Tarraconensis two millennia ago and enjoys some of the best preserved Roman ruins in Spain. Tarragona is a Mankind Heritage Site by UNESCO and we hope you get to enjoy the wonderful sights and experiences the city can offer.

This ICIQ-FIFC Symposium is made possible through the generous support from the Severo Ochoa Project and the Institute of Chemical Research of Catalonia.

We wish you all a wonderful time in Tarragona!

Keiji Morokuma  
Feliu Maseras  
Shigeyoshi Sakaki  
Agustí Lledós  
Koichi Yamashita

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Feliu Maseras  
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Universidad del País Vasco

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Institute for Molecular Science, Okazaki

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**Takeshi Yanai**

Institute for Molecular Science, Okazaki

**Kazunari Yoshizawa**

Kyushu University

## PROGRAMME

**Wednesday, 25th November**

*14:15 – 14:30: Opening Ceremony*

**14:30 – 15:15: Keiji Morokuma**

*Recent Progress in Theoretical Studies of Organometallic and Organic Catalytic Reactions*

**15:15 – 15:45: Agustí Lledós**

*Mechanistic Insights into Rhodium- and Iridium-Mediated Alkene Oxidation with O<sub>2</sub>*

**15:45 – 16:15: Miho Hatanaka**

*Theoretical Study of Asymmetric Carbon-carbon Bond Formations in Aqueous Media*

**16:15 – 16:45: Eliseo Ruiz**

*Room Temperature Magnetoresistance in Single-Molecule Devices*

*16:45 – 17:15: Coffee Break*

**17:15 – 18:00: Sonsoles Martín-Santamaría**

*Pattern Recognition Receptors: Computational Approaches to the Innate Immunity Mechanisms*

**18:00 – 18:30: Koichi Yamashita**

*Carrier Dynamics of Organic-Inorganic Metal Halide Perovskites*

**18:30 – 19:00: Miquel Torrent Sucarrat**

*Two-Spin State Reactivity of Fe-Containing Histone Demethylases*

## Thursday, 26th November

### 09:00 – 09:45: Mitsutaka Okumura

*DFT studies for the Characteristics and the Catalytic Activities of Au Cluster Catalysts*

### 09:45 – 10:15: Feliu Maseras

*Copper- and Rhodium-Catalyzed Oxidative Coupling: On the Role of the External Oxidant*

### 10:15 – 10:45: Satoshi Maeda

*Development of the Global Reaction Route Mapping (GRRM) Strategy toward Systematic Understanding of Organic and Photochemical Reactions*

*10:45 – 11:15: Coffee Break*

### 11:15 – 11:45: Josep M. Poblet

*Polyoxotungstates in Photocatalytic and Electrochemical Reactions*

### 11:45 – 12:15: Kazunari Yoshizawa

*Mechanism of Nitrogen Fixation Catalyzed by a Dinitrogen-Bridged Dimolybdenum Complex*

### 12:15 – 13:00: Carme Rovira

*How Does Nature Make Glycosidic Bonds. Ab initio QM/MM Metadynamics Investigations*

*13:00 – 14:30: Lunch*

### 14:30 – 15:15: Masahiro Ehara

*Unique Bond Activations and Reactions on Heterogeneous Catalysts*

### 15:15 – 15:45: Olalla Nieto Faza

*Mechanistic Study of Gold-catalyzed Reactions Using the Reaction Valley Approach*

### 15:45 – 16:15: Jun-ya Hasegawa

*Theoretical Study of CO<sub>2</sub> Fixation By a Bifunctional Porphyrin Catalyst*

### 16:15 – 16:45: Manuel Alcami

*Key Factors Governing Isomer Relative Stability of Fullerene Anions and Cations*

*16:45 – 19:00: Poster Session*

*21:00: ICIQ-FIFC Symposium Dinner*

## Friday, 27th November

### 09:00 – 09:45: Iñaki Tuñón

*Theoretical Description of Enzymatic Hydride Transfers. A Theoretical Analysis of Formate Dehydrogenase*

### 09:45 – 10:15: Shigeyoshi Sakaki

*Catalysis of Main Group Element Compound in Comparison with Transition Metal Complex from the Viewpoint of Theoretical Study*

### 10:15 – 10:45: Takeshi Yanai

*Advanced Multireference Theory Based on Density Matrix Renormalization Group: Theory and Applications*

*10:45 – 11:15: Coffee Break*

### 11:15 – 11:45: Israel Fernández

*Understanding and Controlling Molecular Reactivity*

### 11:45 – 12:15: Masataka Nagaoka

*Toward Controlling Complex Chemical Reactions in the “Molecular Aggregation States” – From Multiscale Simulation to Computational Molecular Technology*

### 12:15 – 13:00: Miquel Solà

*Molecular Electrides and Metallaelectrides*

*13:00 – 13:15: Closing Ceremony*

# **CONFERENCE ABSTRACTS (CA)**



## Conference Abstract 1

Keiji Morokuma

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### Recent Progress in Theoretical Studies of Organometallic and Organic Catalytic Reactions

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For theoretical studies of reactions of complex molecular systems, we have often been using the Global Reaction Route Mapping (GRRM) strategy for automatic exploration of reaction pathways.<sup>1</sup> The ADDF (anharmonic downward distortion following) and the AFIR (artificial force induced reaction) methods have been used for determination of energy minima and saddle points.

In the present talk, I will discuss our recent studies on the mechanism of organometallic and organic catalytic reactions. We have used the GRRM strategy to study organic multicomponent reactions such as the Passerini reaction involving isocyanide, carboxylic acid and aldehyde,<sup>2</sup> as well as the Biginelli reaction involving urea, benzaldehyde and ethyl acetoacetate.<sup>3</sup> These reactions turned out to be organocatalytic reactions with a component acting as a catalyst as well as a reactant. We also discuss the phase-transfer catalytic reaction involving quaternary ammonium catalysts<sup>4</sup> and biomolecular photo-dissociation reactions.<sup>5</sup> Several examples will be also shown in which the mechanism of organometallic reactions has been studied, including Iron(II)-catalyzed asymmetric Mukaiyama aldol reaction<sup>6</sup> and Rh and Pd catalyzed C-H activations.<sup>7,8</sup>

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1. S. Maeda, K. Ohno and K. Morokuma, *Phys. Chem. Chem. Phys.* **2013**, *15*, 3683-3701.
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8. J. Jiang, R. Ramozzi, and K. Morokuma, *Chem. Eur. J.* **2015**, *21*, 11158-11164.

## Conference Abstract 2

Agustí Lledós

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems | Abstract

### MECHANISTIC INSIGHTS INTO RHODIUM- AND IRIIDIUM-MEDIATED ALKENE OXIDATION WITH O<sub>2</sub>

Laia Vilella<sup>a</sup>, Max García-Melchor<sup>b</sup>, David Balcells<sup>c</sup>, Agustí Lledós<sup>a\*</sup>

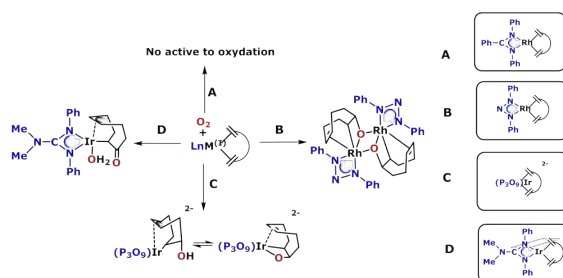
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The oxygenation of olefins is a powerful synthetic strategy to convert hydrocarbon feedstock into high added-value chemicals. Although molecular oxygen would be the most desirable oxidant agent in these reactions, its use as a source of oxygen atoms is challenging because its reactivity is not easily controlled.<sup>1</sup> In this regard, complexes of Rh and Ir were shown to promote C-O bond formation from alkanes by O<sub>2</sub>,<sup>2</sup> but similar compounds reacting with the same olefin (COD) give very different results (Scheme 1).<sup>3</sup>



Aimed to provide a detailed understanding of the Rh- and Ir-mediated O<sub>2</sub> to alkene O-transfer, we have started a theoretical study of its reaction mechanism. Detailed aspects regarding the intermediates, transition states and triplet-singlet state crossing points of the reactions depicted in Figure 1 have been calculated. The computational study has revealed that, after O<sub>2</sub> coordination, different pathways are possible. We found that the reaction outcome is governed by the relative stability of the peroxo and superoxo adducts formed after O<sub>2</sub> coordination.

#### References

1. L. Boisvert and K. I. Goldberg, *Acc. Chem. Res.*, 2012, **45**, 899.
2. B. de Bruin, P. H. M. Budzelaar and A. W. Gal, *Angew. Chem. Int. Ed.*, 2004, **43**, 4142.
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## Conference Abstract 3

Miho Hatanaka

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### Theoretical study of asymmetric carbon-carbon bond formations in aqueous media

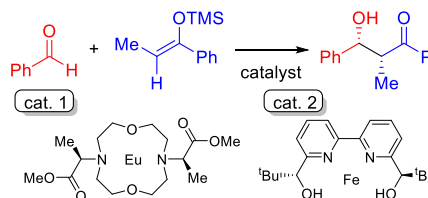
Miho Hatanaka\*

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Catalytic reactions in aqueous media have been one of the most important topics for green chemistry. Although conventional Lewis acid catalysts are inactive under hydrous condition, lanthanide trications ( $\text{Ln}^{3+}$ ) and several dicationic transition metals, such as Fe, Cu etc, are active. The first report of the water-tolerant Lewis acid catalyst was  $\text{Eu}^{3+}(\text{OTf})_3$  for the Mukaiyama Aldol reaction. Nowadays, a number of chiral water-tolerant Lewis acid catalysts have been reported and highly stereoselectivity has been achieved. Surprisingly, the chiral catalysts used under the hydrous conditions were different from those widely used under the anhydrous conditions. To understand the origin of stereoselectivity and the reason of difference between hydrous and anhydrous systems, the aqueous Mukaiyama Aldol reactions catalyzed by two chiral catalysts (cat. 1 and 2 shown in Scheme 1) were investigated.<sup>1,2</sup>

The aqueous Mukaiyama Aldol reactions catalyzed Lewis acid proceed *via* a step-wise mechanism, first formation of prereaction complex between the catalyst and benzaldehyde, followed by carbon-carbon bond formation, proton transfer and trimethyl silyl (TMS) dissociation. In the prereaction complexes including cat.1 and 2, the spaces around the aldehyde are large enough for the approach of the TMS enol ether both from *Re*-face and *Si*-face. Thus, to discuss the stereoselectivity, the transition states (TSs) of the stereo-determining carbon-carbon bond formation steps must be evaluated. To gather the TSs exhaustively the artificial force induced reaction (AFIR) method was applied. In this talk, the origin of the stereoselectivity of two catalytic systems will be discussed based on the TSs of the carbon-carbon bond formation step.



SCHEME 1. Asymmetric aqueous Mukaiyama Aldol reactions

#### References

1. M. Hatanaka, K. Morokuma, *ACS Catal.* **2015**, 5, 3731-3739.
2. W.M. Sameera, M. Hatanaka, T. Kitanosono, S. Kobayashi, K. Morokuma, *J. Am. Chem. Soc.* In press.

## Conference Abstract 4

Eliseo Ruiz

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### Room Temperature Magnetoresistance in Single-Molecule Devices

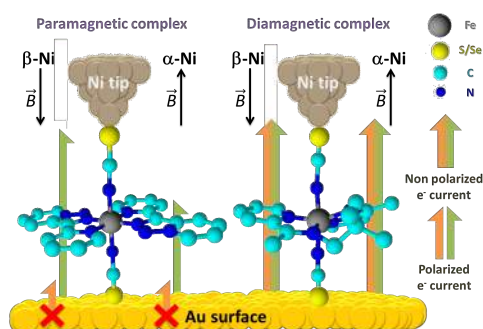
Eliseo Ruiz,<sup>a\*</sup> Albert C. Aragonès,<sup>b</sup> Daniel Aravena,<sup>c</sup> Jorge I. Cerdá,<sup>d</sup> José Antonio Real,<sup>e</sup> Josh Hihath,<sup>f</sup> Ismael Díez-Pérez<sup>b</sup>

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The novelty of our approach is to present a well-defined route map to reach single-molecule devices at room temperature by their deposition on heavy metal surfaces that have large spin-orbit contributions toward the creation of nanodevices, showing magnetoresistance effect as that reported by Fert and Grünberg in magnetic metal layers used in hard disk heads. Inside the device, mononuclear Fe<sup>II</sup> complexes deposited on a gold substrate are in contact with magnetic Ni STM tip. Our preliminary results provide a proof of concept strongly indicating that the STM conductance through the Fe<sup>II</sup> complex changes one order of magnitude with the direction of the Ni tip magnetic field (see Figure 1). Our study shows a theoretical analysis and the practical implementation through two-terminal devices using STM equipment to achieve the room temperature molecular-based spintronic nanodevices. Also, complexes with other transition metal atoms have been explored either doing the STM measurements or with computational studies.



## PATTERN RECOGNITION RECEPTORS: COMPUTATIONAL APPROACHES TO THE INNATE IMMUNITY MECHANISMS

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Pattern Recognition Receptors (PRRs) are specialized in the specific recognition of molecular patterns. In particular, Toll-like receptors (TLR, main actors in innate immunity) recognize Gram negative bacterial lipopolysaccharides (LPS),<sup>1</sup> and Galectins (important role in infection, inflammatory diseases and tumor progression) recognize beta-galactosides.<sup>2</sup> The molecular basis of the interaction and response, at atomic level, are still elusive. Our computational studies aim to understand the molecular details of ligand recognition (Figure 1) as a source of new compounds able to modulate the target behaviour with possible therapeutic applications.

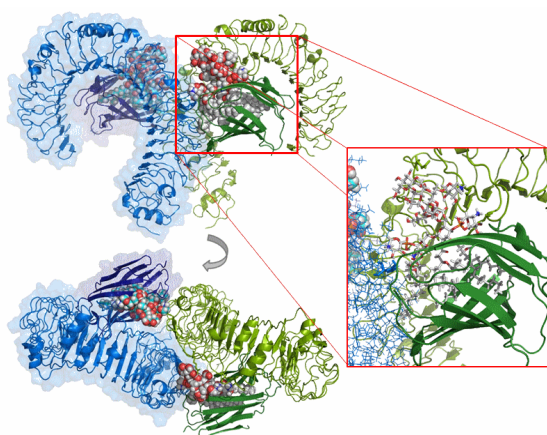


Figure 1. Computational molecular model for activation of the human TLR4/MD-2 complex by penta-acylated lipid A explaining the ability of hypoacylated *Burkholderia cenocepacia* LPS to promote proinflammatory responses.<sup>3</sup>

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# CARRIER DYNAMICS OF ORGANIC-INORGANIC METAL HALIDE PEROVSKITES

Koichi Yamashita

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Methylammonium (MA) lead iodide perovskite ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) plays an important role in light absorption and carrier transport in efficient organic-inorganic perovskite solar cells [1]. Spin-polarized DFT calculations have been performed with the GGA. Effective masses of photogenerated electrons and holes are estimated to be  $m_e^* = 0.23m_0$  and  $m_h^* = 0.29m_0$ , respectively, including spin-orbit coupling effects. This result is consistent with the long-range ambipolar transport property and with the larger diffusion constant for electrons compared with that for holes in the perovskite, which enable efficient photovoltaic conversion [2]. We also have focused our attention on the MA cation and studied the role it plays in the electronic/optical features of the perovskite [3]. An analysis of hot-carrier lifetimes from electron-phonon interaction in lead iodide perovskites using density-functional perturbation theory and many-body perturbation theory [4] shows that the holes in the perovskite have very long lifetimes in the valence band region situated 0.9eV below the top of the valence band. We propose a reduction of the relaxation paths in the small valence density of states as being the origin of the slow hot-hole cooling (see Fig.1 ) [5].

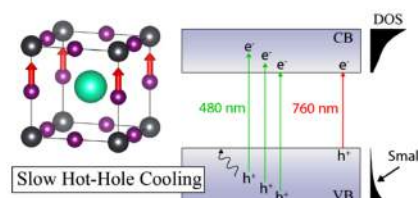


Fig.1 Intraband carrier relaxation of lead iodide perovskites. A reduction of the relaxation paths in the small valence DOS as being the origin of the slow hot-hole cooling. The 480-nm peak can be assigned to transitions from the VB states along the R-M path.

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## TWO-SPIN STATE REACTIVITY OF Fe-CONTAINING HISTONE DEMETHYLESES

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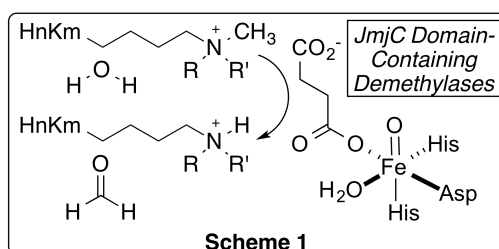
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Histone demethylases regulate the degree of methylation in lysine residues of histones. These enzymes play an essential role in epigenetics, namely heritable covalent changes in chromatin that do not modify the sequence of bases of DNA. Epigenetic phenomena are very relevant in oncology [1]. In particular, JmjD domain-containing demethylases (Scheme 1) are emerged as very promising therapeutic targets [2].



In this communication, we present our DFT results obtained for model systems that mimic the chief geometric and electronic features of the active site of JmjD domain-containing enzymes bound to model substrates. Different reaction mechanisms associated with different methylation patterns will be shown.

### References

1. J. W. Hojfeldt, K. Agger, K. Helin, K. *Nat. Rev. Drug. Discov.* **2013**, *12*, 917-930.
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## DFT studies for the characteristics and the catalytic activities of Au cluster catalysts

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Gold was commonly regarded as the noblest material for catalytic reactions. This view has changed drastically since gold nanoparticles (NP) supported on oxides such as TiO<sub>2</sub> were discovered to exhibit extraordinary catalytic activity for low-temperature CO oxidation<sup>1,2</sup> and other useful reactions<sup>3</sup>. Numerous experimental and theoretical efforts have been made to find the origin of catalytic activity of gold catalysts [3], especially the position of active sites. It is generally viewed that CO oxidation occurs along the perimeter of Au/oxide interface ('perimeter hypothesis')<sup>4</sup>. For the most basic case of Au/TiO<sub>2</sub>, this hypothesis has recently been confirmed by experiments showing the proportionality between the rate of oxidation and the length of perimeter<sup>5,6</sup>.

However, there are still unclear problems for the hypothesis. O<sub>2</sub> adsorption and CO oxidation on a Au/rutile TiO<sub>2</sub>(110) catalyst have been examined by DFT in order to elucidate the exact reaction sites on Au/TiO<sub>2</sub> catalysts. O<sub>2</sub> is found to adsorb on the five-fold coordinated Ti sites that are away from the perimeter as well as on those next to the perimeter. Both O<sub>2</sub> show similar reactivity toward a gaseous CO. CO oxidation still occurs predominantly at the perimeter because O<sub>2</sub> adsorption is strongest at the perimeter Ti site and because CO is activated on Au through back donation. Additionally, I would like to give theoretical investigation for the effect of residual chlorines, which originate from HAuCl<sub>4</sub>, in the preparation process for Au catalysts and other related results on this symposium.

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## Conference Abstract 9

Feliu Maseras

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

Copper and rhodium-catalyzed oxidative coupling: on the role of the external oxidant

Feliu Maseras

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Oxidative coupling is an appealing alternative to cross-coupling for the selective formation of new C-C bonds under mild conditions. It does not require the placement of a halide or other leaving group in the position to be activated, and it improves atom economy by reducing the formation of waste products. An obstacle to further development of such chemistry is the usual need of an external oxidant. If the two hydrogen atoms depart as protons, as is normally the case, the catalytic system will gain two electrons, which have to be removed prior to a new catalytic cycle. The role of the external oxidant is not fully understood.

In this communication, we extend our previous work on cross-coupling<sup>1</sup> to oxidative coupling by analyzing two different cases. The first of them is the role of the dioxygen oxidant in the classical Cu(I)-catalyzed Glaser-Hay coupling between terminal alkynes.<sup>2</sup> The second of them is the role of a Cu(II) oxidant in the Rh(III)-catalyzed coupling of benzoic acid with alkynes which was first reported in 2007 and has opened a new line of functionalization.<sup>3</sup> In both cases, calculation reproduces all available experimental data and provides new insight.

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## Development of the Global Reaction Route Mapping (GRRM) Strategy toward Systematic Understanding of Organic and Photochemical Reactions

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Finding transition states (TSs) is one of the most important tasks in theoretical studies on the mechanism of chemical reactions. By locating a TS, its structure can be visualized. Starting from the TS, the intrinsic reaction coordinate (IRC) can be calculated as a reaction path for the corresponding elementary step. Then, one can understand movements of atoms along the IRC. The reaction barrier can also be estimated from the energy profile along the IRC. Therefore, mechanisms of various chemical reactions have been elucidated by calculations of TSs and related IRC paths.

However, finding TSs is not always an easy task. This is because a good initial guess is required in standard geometry optimization techniques. Especially, locating all TSs relevant to complex mechanisms involving many reaction steps and/or flexible parts controlling reactivity and selectivity has been very difficult. Therefore, we have developed automated methods for systematic exploration of structures of TSs.

We have developed two automated reaction path search methods [1]. One is the anharmonic downward distortion following (ADDF) method, and the other is the artificial force induce reaction (AFIR) method. By using these tools, we have proposed different strategies of global reaction route mapping (GRRM) for various chemical processes. For example, ADDF has been applied to many gas-phase, thermal and photochemical reactions [2]. AFIR has been employed in elucidation of various organic and organometallic reactions [3]. AFIR has recently been extended for photoreactions involving nonadiabatic processes [4], toward theoretical understanding and design of photo-functional materials [5]. In this talk, our GRRM strategies especially those using AFIR will be introduced together with some representative applications.

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## Conference Abstract 11

Josep M. Poblet

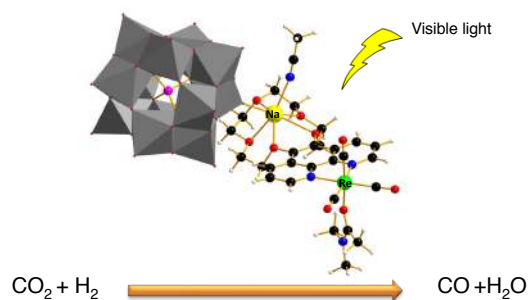
ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### POLYOXOTUNGSTATES IN PHOTOCATALYTIC AND ELECTROCHEMICAL REACTIONS

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Polyoxometalates are well-known as molecular electron reservoirs and as excellent electrocatalysts. In combination of a photosensitizer, polyoxoanions have been also used in photocatalytic reactions, where the polyoxometalate and the photosensitizer can be covalently bonded or not; for example, for production of  $H_2$ ,<sup>1</sup> water splitting,<sup>2</sup> or  $CO_2$  reduction.<sup>3</sup> In this communication, we will show that theoretical methods can be very useful in the understanding of reaction mechanisms of complex processes where a polyoxotungstate acts as catalyst.<sup>4</sup>



**Figure.** Anion  $\{Re^I(L)(CO)_3(DMA)-Na^I[PW_2^V W_{10}^{VI}O_{40}]^{5-}\}^{3-}$  has been used for the photoreduction of  $CO_2$ .<sup>3</sup>

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## Conference Abstract 12

Kazunari Yoshizawa

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### Mechanism of Nitrogen Fixation Catalyzed by a Dinitrogen-Bridged Dimolybdenum Complex

Kazunari Yoshizawa<sup>a\*</sup>, Hiromasa Tanaka<sup>a</sup>, and Yoshiaki Nishibayashi<sup>b</sup>

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It is vital to design effective nitrogen fixation systems that operate under mild conditions. We recently reported a successful example of the conversion of N<sub>2</sub> into NH<sub>3</sub> catalyzed by a dinitrogen-bridged dimolybdenum complex bearing a PNP-type pincer ligand [Mo(N<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(m-N<sub>2</sub>) **1**, where up to 23 equiv of NH<sub>3</sub> were produced based on the catalyst. In this catalytic system, [LutH]OTf (Lut = 2,6-lutidine; OTf = OSO<sub>2</sub>CF<sub>3</sub>) and cobaltocene were chosen as proton and electron donors. Here we have investigated a possible reaction pathway for the nitrogen fixation catalyzed by **1** using DFT calculations. Based on experimental findings, a mononuclear molybdenum nitride complex [Mo(≡N)(OTf)] was considered as a key intermediate. The first molecule of NH<sub>3</sub> should be formed on dinitrogen-bridged dimolybdenum complexes, and then two Mo cores are separated to afford the nitride complex. The dinitrogen-bridged Mo cores will be regenerated after formation of the second molecule of NH<sub>3</sub> via sequential protonation/reduction steps of the nitride complex. It should be noted that dinitrogen ligands in mononuclear Mo complexes cannot be protonated by LutH<sup>+</sup> and therefore **1** must be regenerated to start a new cycle of the N<sub>2</sub> conversion. Synergy of the two Mo cores at the first protonation of N<sub>2</sub> enable **1** to exhibit the catalytic ability.

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## Conference Abstract 13

Carme Rovira

ICIQ-FIFIC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### HOW DOES NATURE MAKE GLYCOSIDIC BONDS. *AB INITIO* QM/MM METADYNAMICS INVESTIGATIONS.

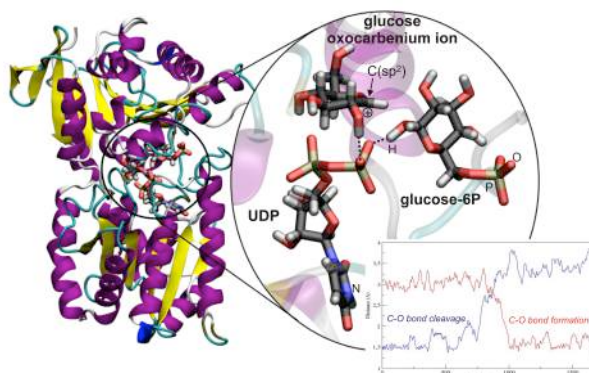
**Carme Rovira**

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One of the great scientific challenges of our time is to find new molecules as potential new drugs to fight disease. Carbohydrate-active enzymes are the focus of enormous interest due to the critically important roles that complex glycans play in health and disease, as well as the rekindled interest in enzymatic biomass conversion. Nature has created a multitude of ingenious methods to cleave and form glycosidic bonds in carbohydrates. Here we will summarize our work of the last few years on the prediction of sugar binding and catalytic mechanisms of these enzymes, using classical/*ab initio* (QM/MM) molecular dynamics and metadynamics methods.



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## Conference Abstract 14

Masahiro Ehara

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### Unique Bond Activations and Reactions on Heterogeneous Catalysts

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Heterogeneous and nanocluster catalysts have been focused because they perform wide varieties of catalytic reactions. In this talk, we overview our recent works on the bond activation or catalytic reaction of some heterogeneous and nanocluster (NC) catalysts.

Ag NC catalyst supported on  $\text{Al}_2\text{O}_3$  performs selective hydrogenation of  $-\text{NO}_2$  group. We have investigated the  $\text{H}_2$  activation by Ag NC supported on  $\text{Al}_2\text{O}_3(110)$  surface using the slab model DFT calculations [1]. The heterolytic cleavage of  $\text{H}_2$  at the silver-alumina interface, yielding  $\text{Ag}-\text{H}^{\delta-}$  and  $\text{O}-\text{H}^{\delta+}$ , is thermodynamically and kinetically preferred compared to other cases or sites showing that "dual perimeter site" is important for the catalytic activity. The interfacial cooperative mechanism between Ag cluster and Lewis acid-base pair site (bare Al-O site) is essentially relevant for the  $\text{H}_2$  activation over Ag-loaded  $\text{Al}_2\text{O}_3$  catalysts. The d-band center of the Ag atoms of Ag NC correlates with the dissociative adsorption energy.

We will also introduce unique C-Cl or C-Br bond activation on Au/Pd alloy nanocluster catalyst [2], photoassisted selective reduction of NO on  $\text{TiO}_2$ , and alcohol oxidation on  $\text{Nb}_2\text{O}_5$ .

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## Conference Abstract 15

Olalla Nieto Faza

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems | Abstract

### Mechanistic study of gold-catalyzed reactions using the Reaction Valley Approach

Olalla Nieto Faza<sup>a\*</sup>, Carlos Silva López,<sup>a</sup> Elfi Kraka<sup>b</sup>, Dieter Cremer<sup>b</sup>

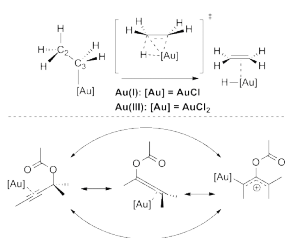
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The Unified Reaction Valley Approach (URVA) is a novel methodology which allows a detailed analysis of the mechanisms of a chemical reaction, starting from the first stages of the reaction and leading up to the product basin. It is based on the reaction path hamiltonian, an accurate path following algorithm, the description of the path in terms of path direction and path curvature, and the decomposition of these path properties into internal coordinate components.

In this work, we have applied URVA to explore the intricacies of two different gold-catalyzed mechanisms (see Figure). The one-step  $\beta$ -hydride elimination on an alkyl-gold complex provides a simple testing ground for the methodology. We have characterized the phases in the gold(I) and gold(III) mechanisms, explaining the origin of the reaction barriers and successfully proposing ways to improve the reactivity of the system. A second example, much more complex in terms of the number of reaction steps and internal coordinates, is related to the mechanisms involved in the propargyl carboxylate manifold, which is one of the most studied systems in gold catalysis. The insights offered by the URVA analysis for these mechanisms are expected to help in the prediction of reaction outcomes and selectivity.



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## Conference Abstract 16

Jun-ya Hasegawa

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

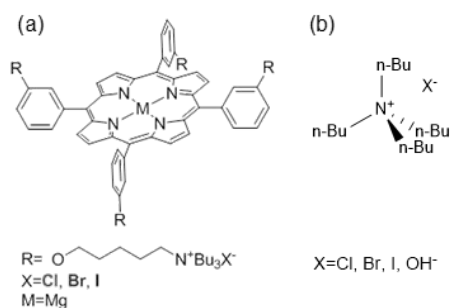
### THEORETICAL STUDY OF CO<sub>2</sub> FIXATION BY A BIFUNCTIONAL PORPHYRIN CATALYST

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A bifunctional porphyrin catalyst (Fig. 1a), which shows an excellent CO<sub>2</sub>-fixation capability, was developed by Ema et al in a previous study [1]. The catalyst couples CO<sub>2</sub> with epoxide and converted into cyclic carbonate. In the present study, we conducted density-functional theory (DFT) calculations to understand potential energy profile of the reaction cycle [2]. The result is also compared with those of tetrabutylammonium catalysts (Fig. 1b) [3]. We found that (i) the Mg moiety works for stabilizing the negative charge in an intermediate state. (ii) The alkyl chain allows the TBA unit to follow the negative charge migration during the reaction. (iii) The rate determining steps of the reaction by the TBA catalysts are ring-opening reaction of epoxide. (iv) The rate-limiting step in the porphyrin catalyst is a ring-closing step to form cyclic carbonate because the activation energy for the ring-opening reaction was reduced very efficiently by the catalyst.



**Figure 1.** Structure of (a) porphyrin catalysts and (b) tetrabutylammonium catalysts.

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## Key factors governing isomer relative stability of fullerene anions and cations

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Fullerene anions and cations play an important role in organic photo voltaics, material science and astrophysics. An unusual behaviour of charged fullerenes is that the isomer relative stability could be substantially different from that of their neutral counterparts [1]. The well-established stability rules for neutral fullerenes are no longer valid for many experimentally observed structures.

Some approximate rules, based on different physical arguments, such as maximum aromaticity [2], minimum electrostatic repulsion [3] or minimum strain [4] have been proposed for fullerene anions. However, these models often lead to conflicting predictions [5]. In this presentation, we propose a new simple and general scheme [6] that allows predicting and understanding the stability of charged fullerenes. Geometry optimizations or electronic structure calculations are not needed but just the knowledge of cage connectivity, allowing to explore the stability of a very large number of potential isomers.

The predictive power of the model has been checked, by considering all fullerene isomers from C<sub>28</sub> to C<sub>104</sub> with charges between +6 and -6. It correctly predicts the structures observed experimentally for endohedral metal fullerenes and also allows to identify the key factors determining fullerene stability. This new approach should allow to explore the stability of larger fullerenes and fullerene derivatives, where millions of isomers are possible.

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## Conference Abstract 18

Iñaki Tuñón

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### THEORETICAL DESCRIPTION OF ENZYMATIC HYDRIDE TRANSFERS. A THEORETICAL ANALYSIS OF FORMATE DEHYDROGENASE

Rafael García-Meseguer<sup>a</sup>, Damien Laage<sup>b</sup>, James T. Hynes<sup>b</sup> and Iñaki  
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Formate Dehydrogenase (FDH) is an enzyme that catalyzes the reaction between formate and NAD<sup>+</sup> cofactor to produce carbon dioxide and NADH. The chemical step is the hydride transfer from formate to the cofactor. This study is based in the implementation of a new environmental coordinate for QM/MM simulations defined as the relaxed energy gap between the states resulting from the hydride transfer between the donor and acceptor atoms. This coordinate allows the quantization of the motion not only for the transferred hydride but also of the secondary hydrogen atom bonded to the acceptor atom, which will take place concertedly. The transition state defined according to this coordinate shows a broad distribution of donor-acceptor distances where the hydride transfer can take place in different regimes [1]. At large distances, the energy barrier for the motion of the H-atom between the donor and the acceptor atoms will be high and the transfer essentially occurs via quantum tunneling. This is the weak-coupling or nonadiabatic limit. When the distance is reduced the barrier becomes lower and thinner, enhancing tunneling. Finally, at small values of donor-acceptor distances the barrier can be lowered below the energy of the vibrational ground state, reaching the adiabatic or strong-coupling limit. Rate constant and Kinetic Isotope Effects will be evaluated taking into account these different limits and the intermediate regime using an adequate expression for the transmission coefficient.

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## Catalysis of Main Group Element Compound in Comparison with Transition Metal Complex from the Viewpoint of Theoretical Study

Guixiang Zeng,<sup>a,b</sup> Nozomi Takagi,<sup>a,c</sup> Shigeyoshi Sakaki<sup>a\*</sup>

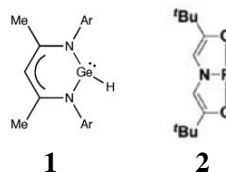
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Recently, the  $\sigma$ -bond activation reactions by heavy main-group element compounds have been experimentally reported and analysed by theoretical studies.<sup>1)</sup> Also, the insertion reaction of the C=O double bond of ketone and carbon dioxide into the Ge-H bond (**1**) has been reported experimentally.<sup>2)</sup> As well known, these reactions are involved as key elementary step in many catalytic reactions by transition-metal complexes. Considering these results, one can expect that heavy main-group element compounds can be used as catalyst instead of transition metal complexes. However, the reports of full catalytic cycle by main-group element compound have been very limited except for frustrated Lewis Pair (FLA). In this regard, recently reported transfer hydrogenation reaction of azobenzene with ammonia-borane catalysed by three-coordinate phosphorous compound (**2**) is of great interest.<sup>3)</sup>



In this talk, we wish to report our recent theoretically studies of the insertion reaction of C=O double bond into the Ge-H bond **1**<sup>4)</sup> and reaction mechanism of transfer hydrogenation catalysis by three-coordinate phosphorous compound **2**.<sup>5)</sup> In both studies, we tried to present theoretical prediction how to construct a full catalytic cycle by the Ge-H compound and how to improve the catalytic activity of the phosphorous compound.

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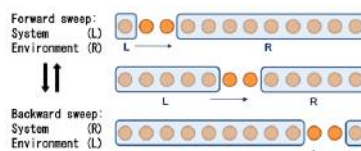
## Advanced multireference theory based on density matrix renormalization group: theory and applications

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The density matrix renormalization group (DMRG) method has been emerging as a new powerful tool to investigate multireference electronic structures for ab initio quantum chemistry calculations. The strength of the DMRG method arises in the applications where mean-field methods, such as density functional theory, are no longer reliable because of strong (or multireference) electron correlation effects. In my talk, we will describe recent methodological advances in quantum chemical DMRG and associated dynamical correlation methods [1-6], and demonstrate their applicability for chemical applications including  $\pi$ -conjugated organic systems [7,8] and multi-nuclear transition metal complexes [9,10].



DMRG algorithm

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## UNDERSTANDING AND CONTROLLING MOLECULAR REACTIVITY

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The recently introduced activation strain model (ASM) of reactivity has allowed us to gain more insight into the intimacies of different fundamental processes in chemistry.<sup>1</sup> In combination with the energy decomposition analysis (EDA) method,<sup>2</sup> we have nowadays a very useful tool to quantitatively understand the physical factors that govern the activation barriers of reactions within organic and organometallic chemistry.

In this lecture, we shall first present an illustrative example of the application of this methodology to a particular class of pericyclic reactions known as Double Group Transfer Reactions.<sup>3</sup> Then, the Diels-Alder reactivity of fullerenes and endohedral metallofullerenes will be analysed (Figure 1).<sup>4</sup> Finally, examples in organometallic chemistry will be described as well.<sup>5</sup>

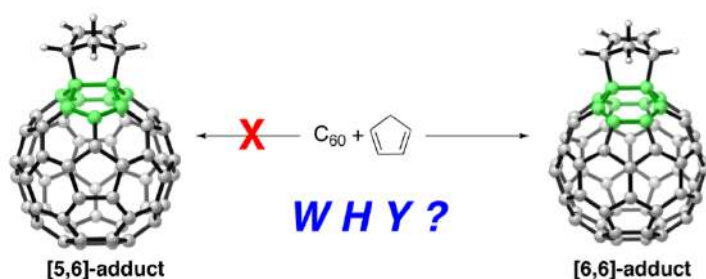


Figure 1

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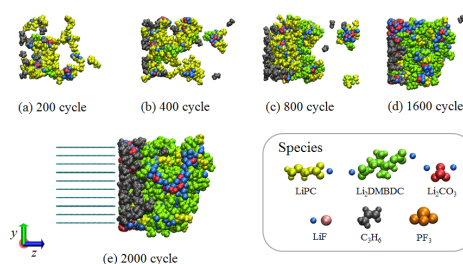
## Toward Controlling Complex Chemical Reactions in the "Molecular Aggregation States" -From Multiscale Simulation to Computational Molecular Technology-

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We demonstrate a new efficient hybrid MC/MD reaction method with a rare event-driving mechanism (Red Moon method) as a practical 'atomistic' molecular simulation of large-scale chemically reacting systems. Application of the method to (*R*)-2-chlorobutane molecules in *N,N*-dimethylformamide (DMF) molecules starting in the optical pure state (100% e.e.) was shown to successfully provide such an atomistic state with ~0% e.e., the expected purity of (*R*)- to (*S*)-enantiomers of the racemic mixture in chemical equilibrium<sup>1</sup>.



**Figure 1** Typical snapshots of the concentration change of reductive products of the SEI film with the MC/MD cycles in the EC-based electrolytes.<sup>2a</sup>

This hybrid MC/MD reaction method is promising for various application studies in complex chemically reacting systems, e.g., the formation process of solid electrolyte interphase (SEI) film (Figure 1) in Li-ion or Na-ion batteries (LIB or NIB)<sup>2</sup> and the nanostructure analysis of interfacially polymerized membrane on the mixing ratio of constituent monomers<sup>3</sup>. In particular, it was understood that the SEI film formation is strongly sensitive to the small structural difference of electrolyte molecules at the microscopic level<sup>2</sup>.

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## Conference Abstract 23

Miquel Solà

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### MOLECULAR ELECTRIDES AND METALLAELECTRIDES

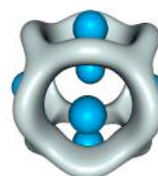
Miquel Solà<sup>a\*</sup>, Verònica Postils<sup>a</sup>, Ouissam El-Bakouri<sup>a</sup>, Marc Garcia-Borràs<sup>a</sup>, Ferran Feixas<sup>a</sup>, Josep M. Luis<sup>a</sup> and Eduard Matito<sup>b</sup>

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Electrides are unique ionic compounds where the anionic part is constituted only by isolated electrons. These new type of compounds were postulated and synthesized first by Dye [1]. They have interesting physicochemical properties that make them suitable for certain technological applications. Thus far, only *solid-state* electrides have been reported. Electrides were shown to exhibit large non-linear optical properties (NLOP) [2], non-nuclear attractors (NNA) of the electron density, and electron localization function (ELF) basins. However, several molecules show some of these properties without the presence of an isolated electron. Therefore, none of these properties alone are sufficient to characterize electrides. In this work, we provide an unambiguous computational means to distinguish *molecular* electrides from similar species [3]. We analyze seven species that were previously considered molecular electrides on the basis of large NLOPs and frontier orbitals with large density values in the position where one would expect the isolated electron of the electride. We show that some of them are actually not electrides [3]. Finally, we present two examples ( $O_h Li_6^+$  with  $S=3/2$  and  $Be_6$  with  $S=2$ ) of a new type of *molecular* electrides named metallaelectrides. They are characterized by having more NNA than atoms and all (or most of) the valence electron density located in the NNA regions. These species can be considered molecular models for the study of the metallic bond [4].



**Figure 1.** The ELF isosurface of 0.8 for  $O_h Be_6$  with  $S=2$ .

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# **POSTER ABSTRACTS (PA)**



## Poster Abstract 1

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems | Abstract

### ELECTRONIC STRUCTURE OF IRON CARBENES AND THEIR REACTIVITY WITH ALKENES: ALKENE CYCLOPROPANATION vs. ALKENE METATHESIS

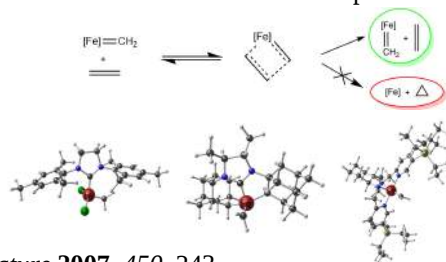
Égil Sá,<sup>a,b\*</sup> Xavier Solans-Monfort,<sup>a</sup> Luís Rodrigues Santiago,<sup>a</sup> Mariona Sodupe<sup>a</sup>

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The olefin metathesis reaction is one of the most efficient C=C double bond forming reactions. Mo, W and Ru based molecular catalyst have been synthesized with outstanding activities and selectivity.<sup>[1]</sup> However, cheap and eco-friendly catalysts are desired. One option would be to design iron-based olefin metathesis catalysts, since iron is inexpensive and has a low toxicity.<sup>[2]</sup> Unfortunately, the up-to-date existing iron carbenes undertake alkene cyclopropanation instead of metathesis.<sup>[3]</sup> In this contribution, we use a DFT approach to study the electronic structure and reactivity of several existing as well as *in silico* designed iron carbenes. We analyze the factors that make alkene cyclopropanation more feasible than alkene metathesis with the aim of determining the nature of the ligand, coordination sphere and oxidation state of iron that could lead to a potential olefin metathesis catalyst (Figure 1).



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## Poster Abstract 2

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### A DFT Mechanistic Study on Cooperative Rh-Cu catalysis. The Oxidative Cross-Coupling between Benzoic Acid and Alkynes

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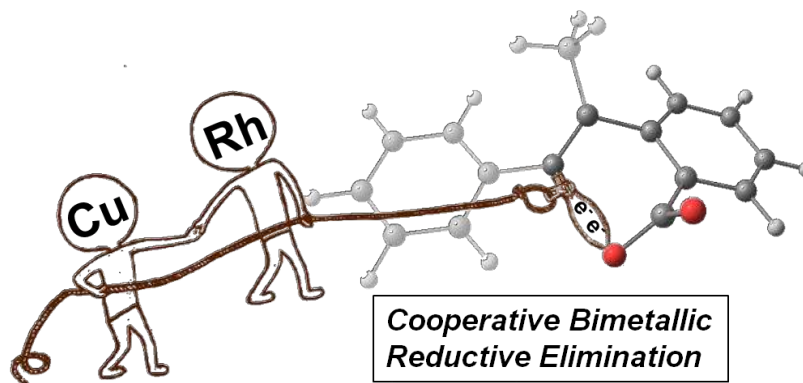
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Oxidative coupling reactions have been developed in the last years as a clean and efficient alternative to the classic cross-coupling procedures due to their atom economy, easily C-H bond functionalizations and, in the ideal case, the possibility of using molecular oxygen as final oxidant, producing only water as waste product. Although many reactions have been discovered in the recent years, the mechanistic understanding of these reactions is still a challenge, and should help for the design of new reactions in a rational way.

Herein, we present a theoretical study (DFT methodology) on the mechanism of the coupling between alkynes and benzoic acids [1,2], with a special focus on the key role of copper acetate in the chemoselectivity of the reaction, favoring the formation of the isocoumarin derivative. We discovered a cooperative effect between metals, rhodium and copper, in the catalytic cycle.



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## Poster Abstract 3

ICIQ-FIFIC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### ASSESSING THE IMPORTANCE OF PROTON TRANSFER REACTIONS IN DNA

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As already noted by Watson and Crick by 1953, the correct replication of DNA rests on the assumption that the original genetic sequence of the adenine-thymine (AT) and guanine-cytosine (GC) base pairs is fully preserved during the process [1]. However, protons along the interbase hydrogen-bond network are not static entities but they can be exchanged through proton transfer (PT) reactions. The resulting non-canonical A\*T\* and G\*C\* structures are the so-called rare tautomers (see Figure 1). In Watson and Crick's words: "*It would be of interest to know the precise difference in free energy between the various tautomeric forms under physiological conditions*". Unfortunately, rare tautomeric forms are very difficult to detect [2], so no direct and accurate free energy measure has been discerned. In contrast, theoretical chemistry could provide an accurate quantification of PT reactions in DNA and their biological consequences [3].

My poster overviews the literature as well as part of our current work devoted to assess the importance of rare tautomers as promoters of mutations in DNA.

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## Poster Abstract 4

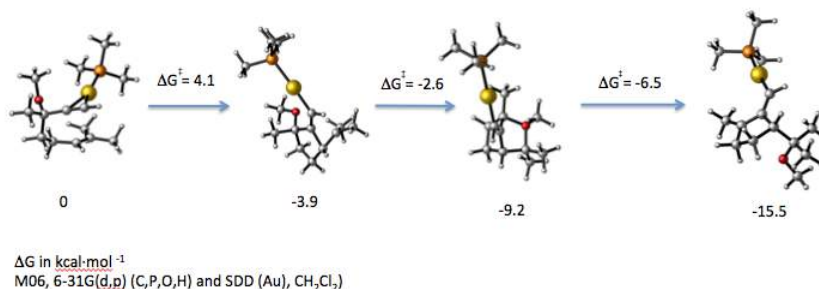
ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems | Abstract

### COMPUTATIONAL STUDIES ON THE GOLD(I)-CATALYZED 1,5-MIGRATION OF ALKOXY GROUPS

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In 2009, our group reported the formation of gold(I)-carbenes through a new type of intramolecular 1,5-migration of propargylic alkoxy groups.<sup>1</sup> Different natural occurring sesquiterpenes have been prepared via intra-<sup>2</sup> or intermolecular<sup>3</sup> cyclopropanation of these cyclopropyl gold(I) carbene intermediates. Herein, we present a detailed examination of gold(I) catalyzed skeletal rearrangements of different model 1,6-enynes prone to undergo intramolecular 1,5-migration in the absence of external nucleophiles for a deeper understanding of these transformations. DFT calculations indicate that an exocyclic rearrangement is more favored than the corresponding endocyclic process. However, the nature of the propargylic alkoxy group and the substitution pattern in the alkene moiety play a crucial role for the formation of 1,5-migration product (fig 1.) vs the *single-cleavage rearrangement* product.



**Fig 1.** Free energy reaction profile for the formation of 1,5 migration product

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## Poster Abstract 5

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

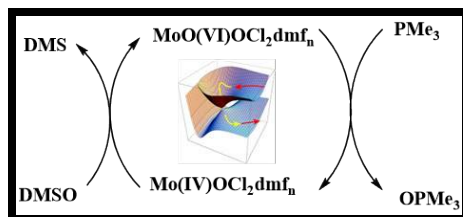
### Molybdenum catalyzed Oxygen Atom Transfer Reaction

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The mechanisms of catalyzed oxygen atom transfer (OAT) reactions are interesting in biological and industrial processes, and also from an academic point of view. Different metals (Pd, V, Cr, Fe, Re) can mediate these transformations, among which molybdenum is specially interesting due to its low cost, abundance and stability of its compounds.

We have carried out a detailed study of the transfer of an oxygen atom from DMSO to phosphine catalyzed by  $\text{MoO}_2\text{Cl}_2(\text{dmf})_n$   $n=0-2$ , described by Sanz et al<sup>1</sup>. In this work, we devote special attention to the possibility of spin interconversion as well as to the metal coordination sphere and how it can modulate the reactivity, in terms of reaction barriers, multiplicity and intermediates.



**Figure.** Computed catalytic cycles for the oxygen atom transfer between DMSO and  $\text{PMe}_3$ .

We have confirmed that the  $\text{MoO}_2^{2+}$  core is capable of catalysing the OAT process illustrated in the **Figure** above independently of the number of solvent molecules (dmf) present in the coordination sphere.

We have also found that the coordination sphere of Mo determines the multiplicity of the reaction intermediates (the lower the coordination number, the more the triplet state is favored) and that the reaction barriers are also slightly reduced as  $n$  decreases.

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## Poster Abstract 6

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

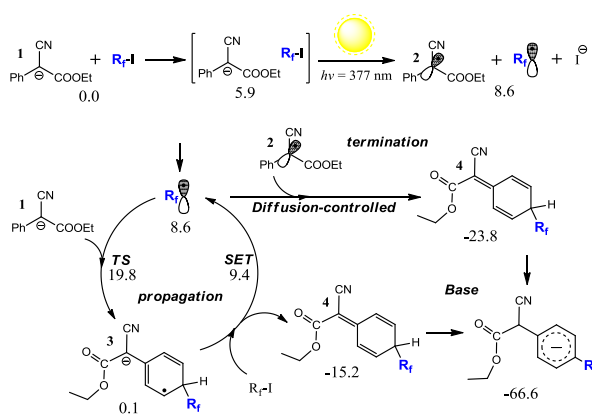
### COMBINED DFT STUDY AND KINETIC MODELS ON THE MECHANISM OF PHOTOINITIATED AROMATIC PERFLUOROALKYLATIONS

Fernandez-Alvarez Victor M.<sup>a,\*</sup>, Nappi Manuel<sup>a</sup>, Melchiorre Paolo<sup>a</sup>, Maseras Feliu<sup>a</sup>

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The photochemical aromatic perfluoroalkylation of  $\alpha$ -cyano arylacetates was investigated using DFT calculations.<sup>1</sup> Our theoretical approach confirmed that the process is driven by the photochemical activity of electron donor-acceptor (EDA) complexes, formed in situ by the interaction of transiently generated enolates and perfluoroalkyl iodides. The resulting mechanistic framework rationalizes the quantum yield above 1, 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 is shown to be critical. This approach can lead the way to future quantum-mechanical investigations of visible light-driven photochemical processes.<sup>2</sup>



General scheme for the reaction. Energies in  $\text{kcal.mol}^{-1}$ .

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## Poster Abstract 7

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### INFLUENCE OF THE SPIN STATE IN THE AROMATICITY OF FULLERENES AND ENDOHEDRAL METALLOFULLERENES

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Nowadays, it is assumed that fullerenes have an ambiguous aromatic character with some properties that supports the aromatic view of these systems and others that do not.<sup>1</sup> In this work we demonstrate that increasing the spin of the fullerene cage, the aromatic character of the five-membered rings increases substantially. This aromaticity increase can be explained by the 4N Baird aromaticity rule for the lowest-lying triplet excited states. The intensification of the aromatic character of fullerenes when going to higher spin states has implications in the molecular structure and reactivity of fullerenes and endohedral metallofullerenes.

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## Poster Abstract 8

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

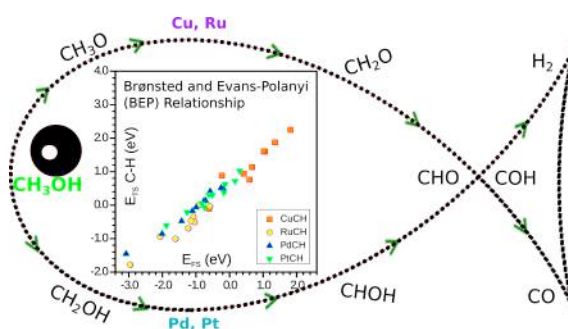
### Density functional theory comparison of methanol decomposition and reverse reactions on Cu, Pt, Pd and Ru metal surfaces

Qiang Li<sup>a)</sup>, Rodrigo García-Muelas<sup>\*</sup> and Núria López<sup>a)</sup>

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Methanol decomposition and synthesis on transition metals, usually concentrating in a particular set of reactions in the main reaction path, have been widely investigated by both theoretical and experimental studies[1,2,3]. In this work[4], we present an extensive density functional theory study that considers the all potential elementary steps for four closed-packed surfaces including Cu, Ru, Pt and Pd that shows the different behaviours and alternative routes through which the decomposition can take place by theoretical methods including dispersion or hydrogen bond contributions changing the first step in Pt and Ru from methylenic to alcohol H activation. In addition, reverse reaction networks which can be inspected for the formation of methanol from CO and hydrogen have also been considered. By using Brønsted-Evans-Polanyi (BEP) relationships[5], the compilation of the results with comparable computational set-ups presents a detailed database that can be added to the thermodynamics and kinetics for other reactions, such as methanation, with which they share a common list of reactions

or employed when analysing larger alcohols as those derived from biomass.



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## Poster Abstract 9

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### Exploring Potential Energy Surfaces of Complex Molecular Systems using Zermelo's Navigation Variational Model

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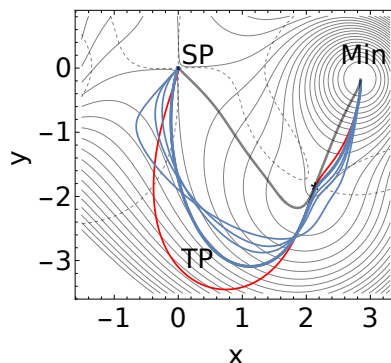
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Abstract text:

We propose an optimal navigation in a Potential Energy Surface (PES) where the objective is to find the fastest path between an initial Minimum point of this PES and a final Transition State. The optimal navigation model is based in the Zermelo's variational navigation problem.



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## Poster Abstract 10

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### **AB INITIO KINETIC MONTE CARLO STUDY OF TEMPERATURE-PROGRAMMED DESORPTION SPECTRA OF RuO<sub>2</sub>(110)**

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Ruthenium dioxide is a versatile catalyst with numerous industrial applications. We use *ab initio* Kinetic Monte Carlo approach to study the interaction of RuO<sub>2</sub>(110) surface with oxygen and water, which are common participants in many chemical reactions. Our implementation of the method reproduces temperature-programmed desorption spectra of the material, which may be directly compared against experimental data. As the resulting spectra are quite sensitive to the surface energetic predicted by Density Functional Theory (DFT), our approach may be used to benchmark accuracy of DFT calculations.

#### **References**

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## Poster Abstract 11

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### COPPER-CATALYZED REARRANGEMENT OF O-PROPARGYL OXIMES: A MECHANISTIC STUDY

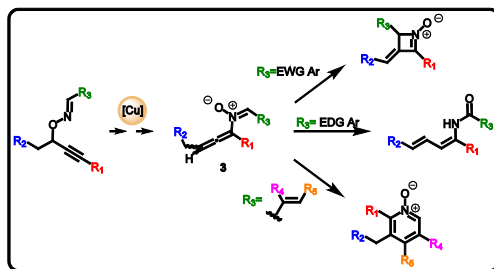
Marta González Comesaña<sup>a\*</sup>, Olalla Nieto Faza<sup>b</sup>, María Magdalena Cid<sup>a</sup>  
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The Cu-mediated rearrangement of *O*-propargyl oximes features a mechanistic manifold yielding different compounds. Strategic modification of the parent oxime moiety ( $R_3$ ) allows the selection of a preferred mechanistic route. Thus, *O*-propargyl arylaldoximes lead to azete oxides when they possess an EWG,<sup>1</sup> or amidodienes if they have an EDG<sup>2</sup> and  $\alpha,\beta$ -unsaturated aldoximes including a vinyl group afford pyridine N-oxides<sup>3</sup>.



Herein, we report a mechanistic study that explains 1- the dependence between the electronic nature of the substituent at  $R_3$ , and the product obtained in the rearrangement of *O*-propargyl arylaldoximes, 2- the different behaviour of this reaction with  $\alpha,\beta$ -unsaturated aldoximes; and 3- which is the role of the Cu-catalyst in these rearrangements.

All the reaction pathways have a common intermediate, allenylnitron 3, from which the mechanism is divided in three branches. The nature of  $R_3$  decides which of these branches is more favourable and therefore which is the final product.

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## Unravelling the mechanism of water oxidation catalysed by novel tacn-based ruthenium complexes

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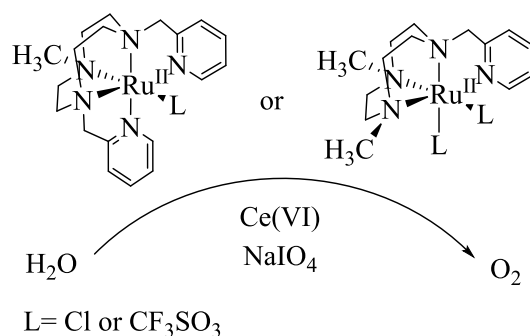
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Mechanistic understanding of the metal-catalysed water-oxidation (WO) on a molecular scale is essential for its development. Since water is abundant and its oxidation produces O<sub>2</sub> as by-product, light-driven WO is the most attractive source of electrons to be used in a multi-ton scale. However, WO has been identified as the bottleneck, because it requires a rapid stepwise building up of very high redox potentials only bearable by few chemical species and, thus, difficult to control against side oxidative damage. Despite of all these chemical challenges, WO is absolutely required because it is a fundamental transformation for the development of artificial photosynthetic systems.

Furthermore, ligands based on 1,4,7-triazacyclononane (tacn) are very robust and they have been proved to stabilise metals in high oxidation states<sup>1</sup>. Therefore, such ligands constitute an excellent platform for the development and study of oxidation catalysts based on either first or second row transition metals.

Herein, a novel family of Ru<sup>II</sup> complexes based on the triazacyclononane moiety has been synthesised and fully characterized. More concretely, the catalytic activity of novel tetradentate [Ru<sup>II</sup>Cl(dmsO)(Py<sup>Me2</sup>tacn)]Cl and pentadentate [Ru<sup>II</sup>Cl(Py<sub>2</sub><sup>Me</sup>tacn)]Cl complexes has been studied as water oxidation catalysts. In addition, the WO mechanism has been elucidated in the basis of different studies such as kinetics, isotopic labelling, trapping of the intermediates and computational studies.<sup>2</sup>



**Scheme 1.** New ruthenium complexes for the mechanistic investigation of WO to O<sub>2</sub>.

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## Poster Abstract 13

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

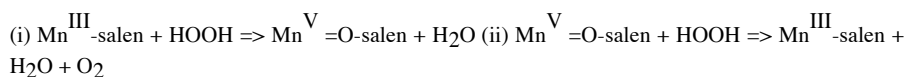
### Catalase activity of Mn<sup>III</sup> complexes

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Abstract text: The study of oxidative stress and the close relationship this has with ageing means there is much interest in the effects of antioxidant complexes, which often contain manganese. Although experimental data in biological studies have shown very positive effects in prolonging the lifespan of mice,<sup>1</sup> there is much uncertainty about what is the origin of these effects and how they could be improved. Interestingly, very few chemical investigations have been performed on this subject,<sup>2,3</sup> and even less using computational chemistry. Therefore, we studied the mechanism of a catalase reaction of a manganese-salen complex that proved beneficial at the biological level, using advanced methods of computational chemistry.<sup>4</sup> The catalase mechanism contains two phases, a first one in which a Mn<sup>III</sup>-salen complex captures an oxygen from a hydrogen-peroxide to form a high-valent Mn<sup>V</sup>-oxo and water; and a second phase where the Mn<sup>V</sup>-oxo complex converts a second hydrogen-peroxide into water and oxygen:



Besides a detailed description of all the different reaction pathways present in the mechanism and the important role of the spin state,<sup>5</sup> we have found new results and concepts that open the possibility of improving the efficiency and feasibility of the antioxidant complex. This is especially relevant for the initial part of the mechanism, where the manganese complex has to capture the hydrogen-peroxide in order to activate it. Two important aspects for the description of the reaction mechanism is the ability of the computational method to correctly describe the spin-state and the weak interactions, for which S12g performs excellently.<sup>4</sup>

Part of this work was supported by COST Action CM1305 (ECOSTBio) and I+D MINECO project SPINENZYMECAT (CTQ2014-59212-P).

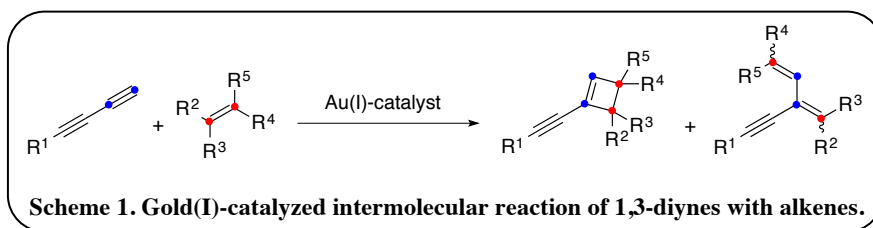
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## GOLD(I)-CATALYZED INTERMOLECULAR REACTION OF 1,3-DIYNES WITH ALKENES

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Although significant advances in homogeneous gold catalysis,<sup>1</sup> intermolecular reactions between alkynes and alkenes are a challenge as diverse competing pathways could lead to undesired oligomers and other byproducts.<sup>2</sup> In the gold(I)-catalyzed intermolecular [2+2] cycloaddition of alkynes and alkenes,<sup>3</sup> cyclobutenes are formed as the major or exclusive products. Only in the case of *ortho*-substituted ethynylbenzenes, 1,3-dienes are also generated. To further explore the scope of this cycloaddition, we decided to study the gold(I)-catalyzed reaction of 1,3-diynes with alkenes. We discovered by means of experimental and computational approaches that depending on the substitution pattern of the alkene both cyclobutenes and 1,3-dienes were obtained.



Scheme 1. Gold(I)-catalyzed intermolecular reaction of 1,3-diynes with alkenes.

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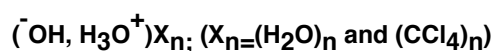
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## Poster Abstract 15

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### Theoretical Studies Of The Effect Of Solvents On The Neutral Complexes



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#### Abstract

The optimised structures were obtained up to  $(\bar{\text{O}}\text{H}, \text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$  and  $(\bar{\text{O}}\text{H}, \text{H}_3\text{O}^+)(\text{CCl}_4)_n$ ,  $n=0,1$  and 4, with an approach by ab initio calculations, using three methods: Hatree-Fock, MP2[1] and DFT / B3LYP with the 6-31 + G \*\*[2]. It is found that  $\text{H}_3\text{O}^+$  and  $\bar{\text{O}}\text{H}$  are indeed the central unit in all the lowest energy structures we found. Results has allowed us to determine the configurations of coordinates which represent the neutral complex  $(\bar{\text{O}}\text{H}, \text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$ . In the comparative study of the hydrogen bond distance of a monomer to monomer donor acceptor complex in different neutral complexes, we also found that the distance O ... H successively increases with the number of water molecules added to the neutral complex  $(\bar{\text{O}}\text{H}, \text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$ . The study of the acidity or alkalinity of the medium for the system  $(\bar{\text{O}}\text{H}, \text{H}_3\text{O}^+)$  in two different regions, one aqueous and one organic has allowed to show the sensitivity of the medium (pH) of the solute  $(\bar{\text{O}}\text{H}, \text{H}_3\text{O}^+)$ . In an acid medium and in the presence of  $(\text{CCl}_4)_n$  for  $n$  ranging from 0 to 4.

We also discuss the effect of non-polar aprotic solvents  $(\text{CCl}_4)_n$  aprotic polar  $(\text{H}_2\text{O})_n$ . The influence of the solute on the solvent water concludes that the solute is very sensitive to environments.

**Keywords:** ab initio, hydrogen bonding, lon complex neutral molecules, solvent .

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### DFT study of molybdenum oxides as selective catalysts to biomass conversion

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Formaldehyde, one of the top chemicals with more than 6 M Tons produced yearly, is industrially obtained by catalytic methanol oxidation in the Formox<sup>TM</sup> process.[1] The catalyst of this process is composed mainly by two phases, MoO<sub>3</sub> and Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>. [2] The active phase of the catalyst and the reasons for the selectivity observed are still unknown. By means of DFT we illustrate the reaction network that drives the selective conversion of methanol to formaldehyde on the molybdenum oxide phase to explain the activity and selectivity of the process and determinate the role of Mo and Fe phases.[3]

In addition, molybdenum oxides are promising catalysts to a selective bond cleavage in the catalytic conversion of biomass derived compounds. It has been experimentally shown that reduced MoO<sub>3</sub> can drive the selective hydrodeoxygenation (HDO) of oxygenated compounds into unsaturated hydrocarbons.[4,5] A DFT study of the route to the selective glycerol conversion to propylene on oxygen defective MoO<sub>3</sub> has been performed to illustrate the selective C-O bond cleavage over C-C bonds and pave the way to a better understanding of these HDO processes.

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## On the role of tetrel bonding interactions in the design of Pb (II) MOFs: A computational approach

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A proper understanding and intelligent utilization of the noncovalent forces is essential to achieve progress in fields such as supramolecular chemistry,<sup>1</sup> molecular recognition and materials science.<sup>2</sup> In this context,  $\sigma$ -hole interactions involving tetrel, pnictogen, chalcogen and halogen atoms are being recognized by the scientific community as powerful tools in supramolecular chemistry, crystal engineering and biochemistry. They refer to the interaction between group IV<sup>3</sup> to VII bearing compounds (donor) and nucleophiles (acceptor). In this study, three Pb (II) solid materials were obtained from Pb(SCN)<sub>2</sub> and a bis-pyridyl hydrazone ligand. In all three the lead center is placed sterically optimal for participation in tetrel bonding, involving thiocyanate sulphur and nitrogen atoms. DFT calculations showed these contacts to be tetrel bonds of considerable energy (6.5-10.5 kcal/mol). Additionally, a CSD survey showed that similar contacts often appear in crystals of Pb (II) complexes with regular geometries, highlighting the role of noncovalent tetrel bonding interactions in the supramolecular chemistry of Pb (II).<sup>4</sup>

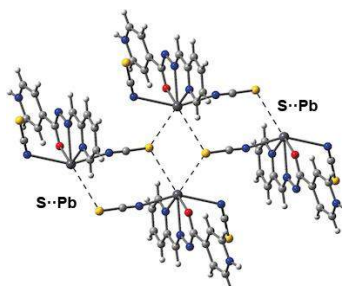


Fig.1 Self-assembly dimers exhibiting tetrel bonding interactions

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## Poster Abstract 18

ICIQ-FICF Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems | Abstract

### COMPUTATIONAL STUDY OF REACTION MECHANISM OF GLYCOLS DEOXYDEHYDRATION WITH A VANADIUM CATALYST

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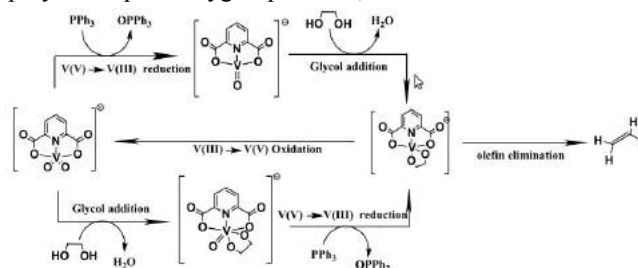
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The valorization of biomass processing waste materials, such glycerol obtained as a byproduct of biodiesel synthesis or another polyols obtained from fermentation of agroforestry waste, is an objective of both economic and ecological interest. In our research group aim to establish the mechanism by which vanadium and molybdenum catalysts in high oxidation state reduce these polyols to poor oxygen products, which are more suitable to be used like raw

materials in the chemical industry.

A longer term goal is to improve these process and design new more efficient and selective catalysts.



Scheme1- A general vision of different pathways which the reaction proposed can follow

In this work we use DFT to study the reaction of deoxydehydration of glycols with a vanadium (V) complex ( $\text{Bu}_4\text{N}[(2,6\text{-pyridinecarboxylate})\text{VO}_2]$ ) described by Chapman et. al.<sup>[1]</sup> In this reaction the catalytic core of dioxovanadium containing rigid tridentate dipicolinate ligand transfers an oxygen from ethylene glycol to an external reducing agent (phosphine). Ethylene is obtained as a product. Several reaction pathways have been explored in which the oxidation and glycol coordination occur in different order. The last step (olefin elimination) occurs through an homolytic cleavage of the C-O bond which is followed by the formation of a V-C bond and finishes with the olefin elimination through a [2+2] process. In this mechanism we also explore the role of external water molecules in the glycol coordination step, which seems relevant leading in some cases to the stabilization of key transition states.

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## Poster Abstract 19

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems | Abstract

### Effect of the hydrogen bonds on the reactivity of alcohols on noble metal surfaces

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Abstract:

There are some apparent contradictions between experimental and theoretical results corresponding to the first stage of methanol dehydrogenation on Pd(111), Pt(111), and Ru(0001). While Density Functional Theory predicts that the first dehydrogenation occurs in the C–H bond to form hydroxymethyl,<sup>1,2</sup> because the activation energy for this C–H bond breaking is lower than the O–H bond breaking, as shown in Figure 1. However, Temperature Programmed Desorption experiments indicate that the first dehydrogenation step is the O–H bond breaking.<sup>3</sup> We show that the presence of spectator methanol molecules lowers the activation barrier for the O–H bond breaking and changes the preferred reaction path, solving the apparent discrepancy between DFT predictions and experiments.<sup>2</sup>

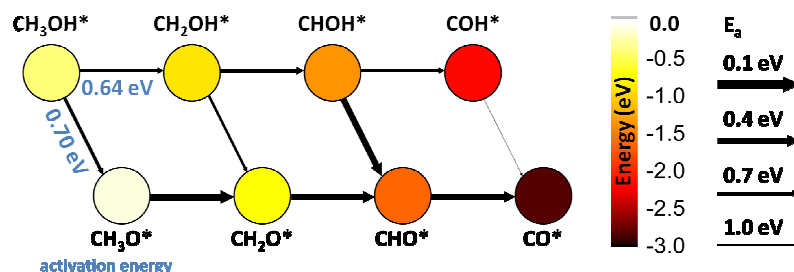


Figure 1. Reaction scheme for methanol dehydrogenation on Pt(111). Arrows thickness are defined by the activation energy. The color scale shows the potential energy for the intermediates.

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## Poster Abstract 20

ICIQ-FIFC Spain-Japan Joint Symposium on Theoretical and Computational Chemistry for Complex Systems I Abstract

### Dynamic Properties of Water Encapsulated in Keplerate Nanocapsules

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During the last decade, the chemistry of polyoxometalates (POMs) enabled growing impressive new giant molecular metal oxide nanostructures. In some cases, the shape of the POM framework is such that it forms inner cavities, which are usually filled with other molecular species. These two characteristics are found in the family of Keplerates.<sup>1</sup> One of the largest members of this family is Mo132.<sup>2</sup> This structure can be understood as a porous capsule with a cavity where a large quantity of water molecules or other species can be confined. It's well known<sup>3</sup> the effect that confinement in nanocapsules induces in the structure of water molecules and its dependence on the size of the cavity. Our research group holds a longstanding experience in the theoretical study of the physico-chemical properties of this type of capsules.<sup>4,5,6,7</sup> In this work, we will present our progress in the analysis of structural and dynamical properties of water molecules encapsulated inside the Keplerates. We start determining computationally the molecular structure of these species with standard DFT methods, to determine the charge and the dispersive potentials of the atoms and then simulate the behavior of the capsule in an aqueous environment, by means of MD simulations. We will focus our attention to the transitions of water under confinement in the capsules, as well as the changes in the properties of the confined medium induced by the change in the structure and hydrophilicity-hydrophobicity of the ligands decorating the inner wall of the cavity.<sup>7</sup>

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