

Girona Seminar 2018

Predictive Catalysis: Transition-Metal Reactivity by Design

April 3-6th, 2018



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Predictive Catalysis: Transition-Metal Reactivity by Design

Girona, April 3-6, 2018

Sponsors

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Predictive Catalysis: Transition-Metal Reactivity by Design

Girona, April 3-6, 2018

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Predictive Catalysis: Transition-Metal Reactivity by Design

Girona, April 3-6, 2018

Venue

The Girona Seminar 18 will be held at Centre Cultural la Mercè, located in the old town/old quarter/Barri Vell of the city of Girona. All lectures and coffee-breaks will take place in this historic building, in particular in the Auditorium/Hall of La Mercè and the cloisters. The lunches will be served close to the venue of the conferences. Getting to Centre Cultural la Mercè is well hidden even for those people that live in Girona and so Plaça Catalunya is a good starting point, since it is only 200 m away from it. Most of the well-known hotels of Girona, especially those located in the city center of Girona, are within walking distance from where the congress takes place. Hotels further away from Centre Cultural la Mercè are connected to the city center by bus. The Girona Seminar 18 Conference Dinner will take place at restaurant AC Palau de Bellavista, at the Pujada Polvorins n°1, Girona.





Predictive Catalysis: Transition-Metal Reactivity by Design

Girona, April 3-6, 2018

Program

YOUNG RESEARCHERS SYMPOSIUM

April 3th, 2018

	Session I Session Chairs: Giorgio Olivo, Anton Stasvuk
12.00-12.15	Sun Xiaobo (VU Univ. Amsterdam) "Teaching Fe to behave like Pd in catalytic bond activation based on the activation strain model"
12.15-12.30	Eila Serrano (Univ. Girona) "Computational insights into epoxide hydrolase asymmetric hydrations of epoxides"
12.30-12.45	Carla Casadevall (ICIQ Tarragona) "Isolation and characterization of an elusive n₂-[Ru ^Ⅳ - OO] ²⁺ intermediate after the O-O bond formation in Ru catalysed WO: the missing link"
12.45-13.00	Carlos Fuertes (Univ. Girona) "Selective separation of fullerenes and endohedral metallofullerenes mediated by supramolecular nanocapsules"
13.00-13.15	Coffee break
	Session II Session Chairs: Giorgio Olivo, Anton Stasyuk
13.15-13.30	Jesús Luque (Univ. Girona) "Mechanism study of 2,2'-bipiridine-6,6-dicarboxylate Ru"
13.30-13.45	Irene Casademont (UPV/EHU Donostia) "Disclosing six-porphyrin nanoring's aromaticity catalyst as a water oxidation catalyst"
13.45-14.00	Zsolt Benedek (Univ. Budapest) "Rational design of tetradentate transition metal ligands for atmospheric pressure ammonia synthesis"
14.00-14.15	Francesca Milocco (Univ. Groningen) "Electronics and structural properties of iron complexes with formazanate ligands"
1/ 15-15 30	Lunch

YOUNG RESEARCHERS SYMPOSIUM

April 3th, 2018

	Session III Session Chairs: Michaela Milan, Ferran Feixas
15.30-15.45	Jessica de Ruiter (Leiden Univ.) "Explorations of water oxidation within an explicitly solvated environment"
15.45-16.00	Angel Mudarra (ICIQ Tarragona) "Getting insight into the Rh-Cu bimetallic cooperation: a new case of cooperative reductive elimination"
16.00-16.15	Veronica Papa (Leibniz Inst. Rostock) "Homogeneous cobalt catalysed amides to amines hydrogenation"
16.15-16.30	Albert Artigas (Univ. Girona) "Synthesis of open-cage fullerene derivatives by rhodium(I)- catalyzed [2+2+2] cycloaddition of C ₆₀ and diynes"
16.30-16.45	Coffee break
	Session IV Session Chairs: Michaela Milan, Ferran Feixas
16.45-17.00	Marco Dalla Tiezza (Univ. Padova) "Rational design of half-sandwich group 9 catalysts for [2+2+2] alkynes cycloadditions"
17.00-17.15	Ranajit Mondol (Univ. Groningen) "Reactivity of 2-electron reduced formazanate boron compounds with electrophiles: facile N-H/N-C bond homolysis due to formation of stable ligand radicals"
17.15-17.30	Marta Lovisari (Trinity Coll. Dublin) "IMAM ligands for low-coordinate late transition metal complexes"
17.30-17.45	Marco Bugnola (Weizmann Inst.) "Aerobic electrochemical oxygenation of hydrocarbons"
17.45-18.00	Young Researchers Prizes
18.30-20.00 20.00-22.00	Visit Girona (City tour) GirSem18 Welcome Reception

April 4th, 2018

Session I		
Session Chairs: Christine McKenzie		
	09.15-09.30	Opening
KL	09.30-10.00	Eva Hevia (Keynote) Towards a paradigm shift in main group polar organometallic chemistry
СТ	10.00-10.20	Mònica Rodríguez Carbene insertion to C₅₂2-H-bonds catalyzed by a nonheme iron complex
СТ	10.20-10.40	Erik Andris Spin-state-dependent generation and spectroscopy of terminal iron(v) nitrides
PL	10.40-11.20	Lawrence Que Jr. (Plenary) In pursuit of the elusive Fe(V)=O oxidant in bio-inspired nonheme iron-catalyzed oxidations
	11.30-12.00	Coffee break
	11.30-12.00	Coffee break Session II
	11.30-12.00	Coffee break Session II Session Chairs: Max García-Melchor
KL	11.30-12.00	Coffee break Session II Session Chairs: Max García-Melchor Mi Hee Lim (Keynote) Chemical tools and tactics to study multiple facets in Alzheimer's disease
KL CT	11.30-12.00 12.00-12.30 12.30-12.50	Coffee break Session II Session Chairs: Max García-Melchor Mi Hee Lim (Keynote) Chemical tools and tactics to study multiple facets in Alzheimer's disease Marc-Etienne Moret Side-bound C=O and C=N bonds as cooperative ligands in nickel catalysis
KL CT CT	11.30-12.00 12.00-12.30 12.30-12.50 12.50-13.10	Coffee break Session II Session Chairs: Max García-Melchor Mi Hee Lim (Keynote) Chemical tools and tactics to study multiple facets in Alzheimer's disease Marc-Etienne Moret Side-bound C=O and C=N bonds as cooperative ligands in nickel catalysis Maren Podewitz Reaction mechanism of olefin metathesis with a novel molybdenum catalyst
KL CT CT PL	11.30-12.00 12.00-12.30 12.30-12.50 12.50-13.10 13.10-13.50	Coffee break Session II Session Chairs: Max García-Melchor Mi Hee Lim (Keynote) Chemical tools and tactics to study multiple facets in Alzheimer's disease Marc-Etienne Moret Side-bound C=O and C=N bonds as cooperative ligands in nickel catalysis Maren Podewitz Reaction mechanism of olefin metathesis with a novel molybdenum catalyst Christopher Cramer (Plenary) Catalysts for the synthesis of sustainable polymers: mechanistic analysis and design

April 4th, 2018

Session III Session Chairs: Elena Fernández		
KL	16.00-16.30	Robert Paton (Keynote) Theory-led design of new ligands for asymmetric catalysis
CT	16.30-16.50	Wesley Browne Catching transient intermediates
CT	16.50-17.10	Javier Iglesias Recapitulating allostery in tryptophan synthase enzyme by means of computational techniques
PL	17.10-17.50	Christina White (Plenary) Molecular Surgery via C-H Oxidation
	18.00-20.00	Poster Session

April 5th, 2018

Session IV		
Session Chairs: Vera Krewald		
KL	09.30-10.00	Julio Lloret-Fillol (Keynote) Light-driven reductions using well-defined coordination complexes
CT	10.00-10.20	Sara Kyne Computational studies of visible light photoredox catalytic reactions
CT	10.20-10.40	Lluís Blancafort What controls photocatalytic water oxidation on TiO ₂ ?
PL	10.40-11.20	Laura Gagliardi (Plenary) Rationalizing the reactivity of bimetallic molecular catalysts for CO ₂ hydrogenation
	11.30-12.00	Coffee break
		Session V Session Chairs: Doron Pappo
KL	12.00-12.30	Kallol Ray (Keynote) Small molecule activation at transition metal centers: structure-function correlations
СТ	12.30-12.50	Marine Desage-El Murr Redox dialogue between ligands and metal for unconventional reactivities
СТ	12.50-13.10	Aidan McDonald Tuning the reactivity of high-valent nickel oxidants for hydrocarbon oxidation
PL	13.10-13.50	Polly Arnold (Plenary) Small molecule activation and catalysis with F-block organometallics; (any) two metals are better than one
	14.00-16.00	Lunch
	16.00-23.55	Excursions

GIRONA SEMINAR April 6th, 2018

Session VI Session Chairs: Alicia Casitas		
KL	09.30-10.00	Mariola Tortosa (Keynote) Synthesis of versatile synthetic intermediates through copper catalysis
СТ	10.00-10.20	Arkaitz Correa Base metal catalysts in C-H functionalization
СТ	10.20-10.40	Gregorio Guisado Mesoionic carbenes (MICS) based metal complexes: synthesis, reactivity and catalytic applications
PL	10.40-11.20	Ben Feringa (Plenary) Exploring catalytic space
	11.30-12.00	Coffee break
		Session VII
		Session Chairs: Johannes Klein
KL	12.00-12.30	Leslie Murray (Keynote) Metals, macrocycles, and small molecules: a tale of bond breaking and formation
СТ	12.30-12.50	Corinna Hess First row transition metal MABIQ complexes as (photo)catalysts for small molecule chemistry
СТ	12.50-13.10	Agustí Lledó A deep cavitand receptor functionalized with Fe(II) and Mn(II) aminopyridine complexes for bioinspired oxidation catalysis
PL	13.10-13.50	Sharon Hammes-Schiffer (Plenary) Proton-coupled electron transfer in catalysis and energy conversion
	14.00-16.00	Lunch

April 6th, 2018

		Session VIII Session Chairs: Adoración Quiroga
KL	16.00-16.30	Paola Belanzoni (Keynote) Catalysis by gold(I) complexes: ligand and anion effects
CT	16.30-16.50	Ignacio Funes Understanding the active role of the oxidant in the oxidative coupling of benzoic acid and alkyne
СТ	16.50-17.10	Jéssica Rodríguez Au(I)/Au(III) catalyzed arylation of C₅p2-H-bonds
PL	17.10-17.50	Shunichi Fukuzumi (Plenary) Production and usage of liquid solar fuels
	17.50-18.30	Closing and Award Ceremony
	20.30-23.55	Conference dinner



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Talks

YOUNG RESEARCHERS SYMPOSIUM

TEACHING FE TO BEHAVE LIKE PD IN CATALYTIC BOND ACTIVATION BASED ON THE ACTIVATION STRAIN MODEL

Xiaobo Sun,*[a] Marcus V. J. Rocha,[a] Jordi Poater, [a] F. Matthias Bickelhaupt [a,c]

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Abstract: A systematic approach for first-principle catalyst design is presented in which potential energy surface is obtained, followed by the activation strain analysis to study the steric and electronic effect separately and determine which is the key factor to influence the energy barrier. If the steric effect dictates the catalytic activity, the angle or other structural parameters can be frozen in the model reaction analysis to achieve the optimum structure. This can be achieved, for example, by using a bridging ligand. If the electronic effect is the focus of the tuning, which is indicated by the interaction energy term in the activation strain model^[1,2], the problem can be tackled by adjusting the metal electronic structure to enhance the catalyst-substrate interaction via the choice of ligands with different electron-donating and accepting capability. Thus, based on this approach, we tried to develop a new type of iron-based catalysts that mimic the behavior of palladium catalysts in cross- coupling reactions. Firstly, we have investigated the activity of the model catalyst complexes Fe(CO)₄ toward CH₃X (with X = H, CI, CH₃) C-X oxidative addition, including different charges and spin states. Secondly, such different reactivity between Fe(CO)₄ and Pd in activating these model reactions are compared and reasons can be explained by electronic-structure and activation strain analysis. Finally, by applying the aforementioned approach the behavior of palladium can be mimic by iron complex. Our long-term purpose is to find ways to replace palladium for bond activation and crosscoupling reactions.

Activation Strain Model (ASM)



L. P. Wolters, F. M. Bickelhaupt, *WIRES Comput. Mol. Sci.* 2015, 5, 324
 I. Fernandez, F. M. Bickelhaupt, *Chem. Soc. Rev.* 2014, 43, 4953

COMPUTATIONAL INSIGHTS INTO EPOXIDE HYDROLASE ASYMMETRIC HYDRATIONS OF EPOXIDES

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Among optically active chiral compounds, enantiopure epoxides are recognized as high valuable synthons in organic synthesis for the manufacturing of pharmaceuticals, agrochemicals and fine chemicals. Producing such compounds in high stereo- and regioselectivities with reasonable yields is still a major challenge using conventional strategies. Epoxide hydrolases (EHs) have caught the pharmaceutical industry attention as they have shown promising features for the preparation of enantiopure epoxides and diols during the selective hydrolysis of epoxides racemic mixtures. Indeed, EHs exhibit different enantiopreferences depending on the substrate epoxide structure and its substituents. For instance, in EH from *Bacillus megaterium* (BmEH)^[1] a switch in its (*R*)-selectivity towards aryl glycidyl ethers (PGE) is observed when a nitro group is included at the *orto position* (*o*-NO₂) of the PGE substrate.^[2] The factors that are governing the stereo- and regioselectivities of the process remain unknown, despite different mechanistic studies put forward to get insights into those fine details of the catalytic reaction.^[3-4] In this study, we evaluate through conventional nanosecond time-scale Molecular Dynamics (MD) simulations the enzyme conformational dynamics, and active site preorganization. We also explore the enzyme active site channels, and its binding affinities towards different aromatic epoxides substrates and their corresponding products. Quantum Mechanics (QM) calculations are also applied to study the reaction mechanism and the effect of the substrate substituents.^[5]

Our results provide valuable insights into the mechanism and the origins of selectivity in BmEH that pave the way to the proper rational design of synthetically useful EHs for the hydrolysis of racemic epoxides.

¹⁾ X.-D. Kong, S. Yuan, L. Li, S. Chen, J.-H. Xu and J. Zhou, Proc. Natl. Acad. Sci. U. S. A., 2014, 111, 15717–15722

²⁾ J. Zhao, Y.-Y. Chu, A.-T. Li, X. Ju, X.-D. Kong, J. Pan, Y. Tang and J.-H. Xu, Adv. Synth. Catal., 2011, 353, 1510–1518.

B. A. Amrein, P. Bauer, F. Duarte, A. J. Carlsson, A. Naworyta, S. L. Mowbray, M. Widersten and S. C. L. Kamerlin, ACS Catal., 2015, 5, 5702-5713

⁴⁾ M. E. S. Lind and F. Himo, ACS Catal., **2016**, 8145-8155

⁵⁾ E. Serrano-Hervás, M. Garcia-Borràs and S. Osuna, Org. Biomol. Chem., 2017, 15, 8827-8835

ISOLATION AND CHARACTERIZATION OF AN ELUSIVE h2-[RU^{IV}- OO]²⁺ INTERMEDIATE AFTER THE O-O BOND FORMATION IN RU CATALYSED WO: THE MISSING LINK

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The application of artificial photosynthesis to store solar energy into chemical bonds is one of the major challenges of our society.^[1] Since water is abundant and its oxidation produces O₂ as by- product, it is the most attractive source of electrons to be used in large scale. However, WO has been identified as the bottleneck, because it requires very high redox potentials only bearable by few species. Therefore, to design more efficient and robust WOC it is necessary to understand the intermediates involved in either the activation of water and the O-O bond formation.

Figure 1. Generation of the intermediates involved in the WO catalytic cycle and the peroxo species formed after the O-O.



We recently reported a catalytic and mechanistic study of a Ru-WOC based on an aminopyridyl ligand,^[2] which pointed towards a high valent [Ru^V=O]³⁺ as the active species responsible for the O-O bond formation. DFT studies showed that after the O-O bond formation a [Ru^{III}-OOH]²⁺ is formed, yielding a closed shell h2-[Ru^{IV}-OO]²⁺ intermediate after a PCET, which would finally release O₂. There has been a extended discussion about the electronic and coordination nature of such postulated peroxo species.^[3] Herein we report the isolation and characterization of this elusive h²-[Ru^{IV}-OO]²⁺ intermediate under catalytic conditions: the missing link after the O-O formation that has nor been reported so far. Characterization of the isolated h²-[Ru^{IV}-OO]²⁺ intermediate by means of X-ray, EXAFS, NMR, IR, HRMS and DFT shows a closed-shell heptacoordinated structure with a side-on coordination of the peroxo moiety.

1) a) N. Lewis, D. G. Nocera, PNAS. 2006, 103, 15729; T. Moore et. al., Acc. Chem. Res. 2009, 42, 1890; b) C.

- Casadevall, A. Call, Z. Codolà, F. Acuña-Parés, J. Lloret-Fillol, An. Quím., 2016, 112 (3), 133.
- 2) C. Casadevall, Z. Codolà, M. Costas, J. Lloret-Fillol, Chem. Eur. J. 2016, 22, 10111.
- 3) J. J. Concepcion et. al., J. Am. Chem. Soc. 2010, 132, 1545; E. Garand et. al., Angew. Chem. Int. Ed. 2016, 55, 4079.

SELECTIVE SEPARATION OF FULLERENES AND ENDOHEDRAL METALLOFULLERENES MEDIATED BY SUPRAMOLECULAR NANOCAPSULES

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From the early stages of fullerene research, it was shown that fulerenes were in general able to host atoms and even small molecules in their interior.^[1] Generally, fullerenes and Endohedral Metallofullerenes (EMFs), which are produced as a soot, need to be purified by a multistage high-performance liquid chromatography (HPLC).^[2] However, this conventional purification process may not be used for the effective purification of milligrams quantity of fullerenes or EMFs. To overcome these difficulties, large efforts have been geared toward the design of an efficient alternative strategy to obtain highly pure fullerenes ^[3] and EMFs ^[4]. In this context, a three-dimensional tetragonal prismatic molecular receptor (4·(BArF)₈) has been reported as a suitable tool for fullerenes soot purification.^[5] The nanocapsule was prepared by coordination-driven self-assembly reaction of two tetracarboxylate Zn^{II}-porphyrin and four Pd^{II}-based molecular clips. The exceptional behavior of (4·(BArF)₈) encouraged us to consider this system as an effective tool towards the design a strategy for EMFs soot purification. Moreover, the better features showed by Cu(II) instead of Pd(II) related with the metal-ligand bond lability, prompt us to design a novel Cu(II) based molecular receptor for fullerenes and EMFs soot purification, in analogy to 4·(BArF)₈.



References

1) J. R. Heath et al., J. Am. Chem. Soc. 1985, 107, 7779 - 7780.

- 2) H.Shinohara et al., Rep. Prog. Phys. 2000, 63, 843.
- 3) C. García-Simón et al, Chem. Soc. Rev. 2016, 45, 40-62.
- 4) N. Chaur et al, Angew. Chem. Int. Ed. 2009, 48, 7514-7538.
- 5) C. García-Simón et al, Nat.Commun. 2004, 5, 5557.

MECHANISM STUDY OF 2,2'-BIPIRIDINE-6,6-DICARBOXYLATE RU CATALYSTAS A WATER OXIDATION CATALYST

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In situ production of H₂ has been a hot topic^[1] for some time now and catalysts that are able to perform this task are currently being researched,^[2] such as our Ru catalyst. The full mechanism of 2,2'-bipyridine-6,6'-dicarboxylate Ru catalyst for water oxidation catalysis (WOC)^[3] using DFT calculations. The rate determining step is found at the dimer formation while the bond cleavage for the O₂ liberation process is barrier-less. Water appears not to be involved in the cleavage process. Taking into account the recent results by Concepcion's group^[4] related to the same catalyst, where the Ru-O-Ru metallic core was proposed to be involved instead of the typical Ru- O-O-Ru one, coming from the direct interaction between the oxygens of two Ru=O moieties we report the mechanism including the possible open carboxylate and closed carboxylate structures (see Figure 1). The computational results confirm that the most common path (closed carboxylate) is strongly preferred, and consequently, the formation of such Ru-O-Ru moiety is impeded.



Figure 1. Closed and open carboxylate structures of our mechanism. Axial ligands omitted for clarity.

1) Morris, J.; Radu, M. Int. J. Hydrog. Energy 2010, 35, 7021-7023.

2) Kang, R.; Chen, K.; Yao, J.; Shaik, S.; Chen, H. Inorg. Chem. 2014, 53, 7130-7136.

3) Duan, L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L. Nat. Chem. 2012, 4,418-423.

4) Concepcion, J. J.; Zhong, D. K.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. Chem. Commun. 2015, 51, 4105-4108.

DISCLOSING SIX-POHYRIN NANORING'S AROMATICITY

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Porphyrin nanorings are interesting compounds because they offer an end-free π -conjugated system with remarkable properties such as photophysical and guest-encapsulating.^[1] Aromaticity is a multifold property^[2] that is useful to understand the electronic structure of such belt-shaped π -systems. Herein we focused in FLU, HOMA and AV1245^[3] to provide an electronic structure assessment of these hoop structures.

In this project, the aromaticity of a six-porphyrin nanoring in four different oxidation states (neutral, tetracationic, hexacationic and dodecationic species)^[4] has been studied. Aromaticity indices reveal the local and global changes of aromaticity among the different studied species of the nanoring as well as the role of the connectors between the porphyrins.



Figure 1. HOMO of the neutral six-porphyrin nanoring.

[1] P. Liu et al. Angew. Chem. Int. Ed. 2016, 55, 8358.

[2] A. R. Katritzky et al. J. Am. Chem. Soc. **1989**, 111, 7.

[3] E. Matito, Phys. Chem. Chem. Phys. 2016, 18, 11839.

[4] M. D. Peeks et al. *Nature*. **2017**, *541*, 200.

RATIONAL DESIGN OF TETRADENTATE TRANSITION METAL LIGANDS FOR ATMOSPHERIC PRESSURE AMMONIA SYNTHESIS

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Ammonia (NH₃) is one of the most important compounds produced in industry. NH₃ production adds up to approximately 140 million tons per year. Still, the production in its present form is not efficient. Converting N₂ to NH₃ via the Haber-Bosch process accounts for about 3% of the world's greenhouse gas emission and more than 1% of the world's annual energy consumption due to the high pressure and temperature (150-300 atm, 400-500°C). In order to produce ammonia in a more environment-friendly and energy efficient way, one should find a method that could operate at room temperature and atmospheric pressure.

Interestingly, microorganisms in nature can fix dinitrogen and produce ammonia at ambient conditions. Thus, it would be reasonable to mimic the active site of nitrogenase enzymes and design artificial catalysts that could be competitive alternatives to the Haber-Bosch process.

In this work we investigate recently synthesized biomimetic catalysts¹⁻³ with DFT methods to understand their catalytic activity. These complexes contain a central metal atom surrounded by tetradentate trisphosphino scorpionate ligands (Figure 1). In recent years numerous similar complexes have been successfully synthesized that reduce dinitrogen into ammonia in the presence of proton and electron sources at atmospheric pressure. Since the experimental characterization of the intermediates is challenging, the exact steps of the catalytic cycle are not clear yet. By studying the Gibbs free enthalpy profile, we determine the exact reaction paths of these catalysts and identify the critical steps. Our results indicate that the reduction of N₂ most likely proceeds via the so-called hybrid pathway (-N₂ \rightarrow -NNH₂ \rightarrow -NH₂NH₂ \rightarrow 2 NH₃) and that the thermodynamical driving force disappears in the last steps of the cycle (-NH₂NH₂ \rightarrow 2 NH₃). These observations enable the rational re-design of the obtained profile.

The exploration of the catalytic mechanism requires careful examination of the spin states of all intermediates as the molecular spin quantum number of the experimentally characterized structures ranges from 0 to 2. Thus, we computed all (theoretically) possible spin states of a given intermediate in order to find the thermodynamically most stable species. This process was preceded by extensive test calculations based on experimental data (e.g. Mössbauer spectra) to confirm the reliability of the chosen density functional.



Figure 1. Reduction of dinitrogen to ammonia by EPPP scorpionate complexes at atmospheric pressure.

[.] 1) J. Rittle., J.C. Peters, J. Am. Chem. Soc., 2016, 138, 4243-4248.

²⁾ T. Del Castillo, N. Thompson, J. C. Peters, J. Am. Chem. Soc. 2016, 138, 5341-5350.

³⁾ M. Chalkley, T. Del Castillo, B. Matson, J. Roddy, J. C. Peters, ACS Central Science, 2017, 3, 217-223.

ELECTRONIC AND STRUCTURAL PROPERTIES OF IRON COMPLEXES WITH FORMAZANATE LIGANDS

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Complexes that show spin-crossover are well known for 6-coordinate, octahedral geometries. Due to a much weaker ligand field in 4-coordinate complexes, these (with very few exceptions)^[1] lead to high spin-states only. Here, we present 4-coordinate iron(II) complexes with formazanate ligands (L₂Fe), some of which show spin-crossover. The strong π -acceptor properties of these ligands leads to an unusual d-orbital splitting pattern that stabilizes the low-spin (S = 0) state in these compounds.^[2] We investigated the effect of steric and electronic changes in the ligand framework and a range of spectroscopic, magnetic and computational techniques is used to understand the origin of spin-crossover in these compounds. The redox behavior of the bis(formazanate) iron complexes has also been studied by cyclic voltammetry and isolation and characterization of the reduced compounds (Fe(I), S = 1/2) have been carried out.

Furthermore, the reactivity of isocyanide with L_2Fe leads to the formation of an octahedral diamagnetic complex. Moreover, attempted oxidative addition of alkyl halides to the Fe(I) complex [L_2Fe]⁻ allows the isolation of a high-spin mono(formazanate) iron complex, for which a rational synthesis was developed.



Figure1. Iron formazanate complexes.

- 1) a) J. J. Scepaniak, T. D. Harris, C. S. Vogel, J. Sutter, K. Meyer, J. M. Smith, J. Am. Chem. Soc. 2011, 133, 3824; (b) A. C. Bowman, C.
- Milsmann, E. Bill, Z. R. Turner, E. Lobkovsky, S. DeBeer, K. Wieghardt, P. J. Chirik, J. Am. Chem. Soc. 2011, 133, 17353.
- 2) R. Travieso-Puente, J. O. P. Broekman, M.-C. Chang, S. Demeshko, F. Meyer, E. Otten, J. Am. Chem. Soc. 2016, 138, 5503.

EXPLORATIONS OF WATER OXIDATION WITHIN AN EXPLICITLY SOLVATED ENVIRONMENT

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Water oxidation catalysis is a crucial process in any device designed to convert solar energy into storable chemical energy. The search for efficient and stable homogenous water oxidation catalysts remains a scientific challenge, especially when considering those based on abundant transition metals. Computational methods based on quantum chemical calculations do allow for significant insights into the relevant catalytic mechanisms, however it is becoming increasingly clear that explicit solvent molecules are needed to obtain realistic descriptions of these catalytic mechanisms. Here we analyse and evaluate, based on ab-initio molecular dynamics, the effects of a changing solvent environment on the water oxidation mechanism of a mononuclear ruthenium based water oxidation catalyst. Moreover, proton and electron acceptors are included within the simulation box to more closely represent experimental conditions. This allows for a more detailed description of proton-coupled electron transfer processes.

References:

- 1) J.M. de Ruiter and F. Buda. Phys. Chem. Chem. Phys. 2017, 19, 4208-4215
- 2) J.M. de Ruiter et al. ACS Catal. 2016, 6, 7340-7349
- 3) A. Monti et al. J. Phys. Chem. C 2016, 120, 23074–23082.

GETTING INSIGHT INTO THE Rh-Cu BIMETALLIC COOPERATION: A NEW CASE OF COOPERATIVE REDUCTIVE ELIMINATION

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The C-H activation in cross-coupling reactions have appeared as a green alternative that allows the formation of new C-C bond in a non-pre-functionalized position. In a non-neutral redox catalytic system, after reductive elimination, an oxidant is required. Different transition metals have been reported to be effective in these transformations but only with some selective oxidative partners. Recently, in our group, a perfect cooperation between Rh and Cu has been reported.^[1] Interestingly, the reductive elimination does not take place from a single metal but from a Rh-Cu intermediate. Herein, we study computationally another example of bimetallic Rh and Cu system.^[2] Many evidences point out the cooperation of both of them in the reductive elimination step.



- (1) I. Funes-Ardoiz, F. Maseras, Angew. Chem. Int. Ed. 2016, 55, 2764
- (2) Y. F. Wang, K. K. Toh, J. Y. Lee, S. Chiba, Angew. Chem. Int. Ed. 2011, 50, 5927

HOMOGENEOUS COBALT CATALYSED AMIDES TO AMINES HYDROGENATION

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Amines constitute an important class of compounds with wide application in major industrial fields, such as in agrochemical and pharmaceutica ^[1] For the synthesis of structurally complex compounds and natural products containing amine moieties, a route foresees the reduction of the amide to corresponding amine. Unfortunately, amides constitute one of the least reactive derivatives among all classes of carbonyl and traditionally, their reduction is performed using an excess of reducing agents producing stoichiometric amounts of waste-products.^[2]

Thus, catalytic hydrogenation using molecular hydrogen is of high interest as it offers an atom- economic and wastefree methodology. ^[3]

Depending on the type of homogeneous catalyst, the hydrogenation of amides (Scheme 1, path A and B) can follow two distinct pathways: path A, which foresees the C-O bond cleavage to afford the more desired higher amine or, alternatively, the catalyst can promote the C-N bond breaking (path B), that leads to the formation of corresponding alcohol and amine; in the last decade, significant improvements in amide hydrogenation using homogeneous Ir and Ru-based catalysts have been achieved. ^[4]

In this work, we have developed a three components catalytic system constituted by Co(N(Tf)₂)₂ as metallic precursor, 1,1,1-tris{bis(4-methoxyphenyl)phosphinomethyl}ethan as ligand and a Lewis acid as external additive, that is able to hydrogenate a wide range of amides; the presence of Lewis acid additive improves yields and selectivity of the higher desired amines.



- 1) Amines: Synthesis, Properties and Applications; S.A. Lawrence, Ed.; Cambridge University: Cambridge, 2006.
- a) H. C. Brown, S. Narasimhan and Y. M. Choi, Synthesis-Stuttgart, **1981**, 441-442; b) J. March, Advanced Organic Chenistry, 4th edn., Wiley, New york, **1992**; c) S. Werkmeister, K. Junge and M. Beller, *Organic Process Research & Development*, **2014**, 18, 289-302.
- 3) A. M. Smith, R. Whyman, Chem. Rev. 2014, 114, 5477.

4) a) A. A. Núñez Magro, G. R. Eastham and D. J. Cole-Hamilton, *Chem. Commun.* 2007, 3154-3156; b) D. L. Dodds, J. Klankermayer, S. Brosinski, W. Leitner and D. J. Cole-Hamilton, *Chem. Commun.*, 2012, 48, 12249-12262; c) J. Coetzee, D. L. Dodds, J. Klankermayer, S. Brosinski, W. Leitner, A. M. Z. Slawin and D. J. Cole-Hamilton, *Chem. Eur. J.*, 2013, 19, 11039-11050; d) J. R. Cabrero-Antonino, E. Alberico, K. Junge, H. Junge and M. Beller, *Chem. Sci.*, 2016, 7, 3432-3442; e) M. L. Yuan, J. H. Xie and Q. L. Zhou, *Chemcatchem*, 2016, 8, 3036-3040; f) M. L. Yuan, J. H. Xie, S. F. Zhu and Q. L. Zhou, *ACS Catal.*, 2016, 6, 3665-3669.

SYNTHESIS OF OPEN-CAGE FULLERENE DERIVATIVES BY RHODIUM(I)-CATALYZED [2+2+2] CYCLOADDITION OF C₆₀ AND DIYNES

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Since the discovery of C_{60} in 1985 [1], fullerenes have attracted the attention of chemists due to their unique structure, properties and reactivity, along with their potential applications in a variety of fields ranging from materials science to biomedicine [2–5]. Many functionalized fullerene derivatives resulting from the structural modification of the fullerene cage have been reported over the last 30 years. Specifically, fullerene derivatives resulting from cycloaddition reactions involving [6,6] junctions of C_{60} have been reported [6]. The preparation of cyclohexadiene-fused C_{60} derivatives can be achieved by [2+2+2] cycloaddition reactions of C_{60} with alkynes [7–9]. These compounds have been found to be important intermediates in the synthesis of so-called open-cage fullerenes [10]. Here, we report the first example of [2+2+2] cycloaddition involving C_{60} and dignes under catalytic conditions promoted by a rhodium(I) catalyst, which leads to the formation of a series of open-cage bisfulleroids. The products obtained can be subjected to oxidative cleavage when exposed to light and O_2 . Additionally, further derivatisation by Suzuki-Miyaura cross-coupling reaction has also been achieved. The mechanism of the process has been studied by means of DFT calculations [11].



- [1] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. Nature 1985, 318, 162.
- [2] Langa, F.; Nierengarten, J. F. Fullerenes: principles and applications. 1st ed., Royal Society of Chemistry, Cambridge, 2011.
- [3] Yan, W.; Seifermann, S. M.; Pierrat, P.; Bräse, S. Org. Biomol. Chem. 2015, 13, 25.

[4] Bagchi, D.; Bagchi, M.; Moriyama, H.; Shahidi, F. Bio-nanotechnology: a revolution in food, biomedical, and health sciences. 1st ed., Wiley-Blackwell, Chichester, 2013.

[5] Cataldo, F.; Da Ros, T. Medicinal chemistry and pharmacological potential of fullerenes and carbon nanotubes; 1st ed., Springer, Dordrecht, 2008.

- [6] Hirsch, A.; Brettreich, M. Fullerenes: chemistry and reactions. 1st ed., Wiley-VCH, Weinheim, 2005.
- [7] Hsiao, T.-Y.; Santhosh, K. C.; Liou, K.-F.; Cheng, C.-H J. Am. Chem Soc. 1998, 120, 12232.
- [8] Liou, K.-F.; Cheng, C.-H. J. Chem. Soc. Chem. Commun. 1995, 1603.
- [9] Inoue, H.; Yamaguchi, H.; Suzuki, T.; Akasaka, T.; Murata, S. Synlett 2000, 1178.
- [10] Vougioukalakis, G. C.; Roubelakis, M. M.; Orfanopoulos, M. Chem. Soc. Rev. 2010, 39, 817.

[11] Artigas, A.; Lledó, A.; Pla-Quintana, A.; Roglans, A.; Solà, M. Chem. Eur. J. 2017, 21, 5067

RATIONAL DESIGN OF HALF-SANDWICH GROUP 9 CATALYSTS FOR [2+2+2] ALKYNES CYCLOADDITIONS

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Nowadays, modern computational facilities allow us to predict reactivity in *silico* and tackle molecular systems that are otherwise difficult to rationalize. In this work, state-of-the-art relativistic density functional (DFT) methodologies are employed to design catalytic fragments for the [2+2+2] alkynes/alkynes-nitriles cycloaddition to benzene/pyridine. The very good selectivity and the possibility to maintain a solvent-free environment make this type of reactions very attractive and justify the continuing investigations.¹ The catalyst's structure is Cp'M, where Cp' is the cyclopentadienyl ligand (Cp) or a more extended aromatic/heteroaromatic moiety, and M is a group 9 metal (Co, Rh, Ir). The singlet potential energy surface of the process is explored by locating all intermediates/transition states and the catalysts' performance is calculated in terms of turnover frequency (TOF), by implementing the equations of the energy span model.^{2,3} The different bonding mode of the substrate to the catalyst, and, vicariously, the nature of Cp'-M coordination, is investigated using the activation strain model (ASA) and energy decomposition analysis (EDA) in order to follow the metal displacement (slippage) and connect structural information with the energy.⁴ Commonly, the highly symmetric coordination of the metal to the aromatic ligand is never achieved, but the distortions during the cycle can be larger or smaller under different conditions (different metal center, changes in the aromatic ligand, presence of an additional ancillary ligand, etc.) and this fluxionality is found to significantly influence the overall efficiency.



References:

- (1) Tanaka, K. *Transition-metal-mediated aromatic ring construction*; Wiley: Hoboken, New Jersey, 2013. (2) Kozuch, S.; Shaik, S. *Acc. Chem. Res.* **2011**, *44* (2), 101–110.
- Orian, L.; Wolters, L. P.; Bickelhaupt, F. M. Chem. Eur. J. 2013, 19 (40), 13337–13347. (4)
 Bickelhaupt, F. M.; Houk, K. N. Angew. Chem. Int. Ed. 2017, 56 (34), 10070–10086.

REACTIVITY OF 2-ELECTRON REDUCED FORMAZANATE BORON COMPOUNDS WITH ELECTROPHILES: FACILE N-H/N-C BOND HOMOLYSIS DUE TO FORMATION OF STABLE LIGAND RADICALS

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The majority of synthetic molecular catalysts change their oxidation state by changing the formal oxidation state of the central metal atom. In contrast, Nature often uses metalloenzymes in which there is a redox-active organic moieties which accumulate redox equivalents that can subsequently be used by the metalloenzyme to perform challenging multi-electron transformations.^[1] Inspired by these enzymatic systems, there is increasing interest in the chemistry of synthetic catalysts with redox-active ligands.^[2] Herein, we have explored the reactivity of a boron complex with redox-active formazanate ligand, LBPh₂ (L = PhNNC(*p*-*tol*)NNPh). Two-electron reduction of this main group complex generates the stable dianion [LBPh₂]², which is susceptible to electrophilic attack by BnBr and H₂O and yields products that derive from ligand benzylation and protonation, respectively (scheme 1). The resulting complexes are anionic boron analogues of leucoverdazyls. N-C and N-H bond homolysis of these compounds was studied by exchange NMR spectroscopy and kinetic experiments. The weak N-C and N-H bonds in these systems derive from the stability of the resulting borataverdazyl radical, in which the unpaired electron is delocalized over the four nitrogen atoms in the ligand backbone. We thus show the ability of this system to store [2e-/E⁺] on the organic ligand and convert it to E⁺ radicals, reactivity that has implications in energy storage applications such as hydrogen evolution.



Scheme 1. Synthesis of compounds ^{Bn}3⁻ and ^H3⁻.

References

- 1) J. W. Whittaker, Chem. Rev. 2003, 103, 2347.
- 2) W. I. Dzik, J. I. van der Vlugt, J. N. H. Reek, B. de Bruin Angew. Chem. Int. Ed. 2011, 50, 3356.

IMAM LIGANDS FOR LOW-COORDINATE LATE TRANSITION METAL COMPLEXES

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The design of new catalysts for the functionalization of inert C-H bonds is a compelling goal to be able to take advantage of hydrocarbon-based feedstock in a more selective, cost-effective and environmentally friendly way.^[1] The synthesis of biomimetic complexes inspired by active oxidant species involved in enzymatic catalytic cycles, notably metal-oxo intermediates, is one important route of investigation to overcome this limit.^[2] Late transition metal-oxo complexes (groups 9, 10, 11) are postulated to be potentially stronger oxidants than early-transition ones, but they have so far been elusive due to electronic structural requirements.^[3] One possible strategy to override this "Oxo Wall"^[1] is to synthesize low-coordinate precursors in square planar, tetrahedral or trigonal planar geometries. Bulky β -diketiminate ligands are widely investigated in order to access metal complexes with low coordination numbers and have been used to synthesize trigonal planar mononuclear Ni(II)^[4] and Cu(II) superoxo and bis(μ -oxo) complexes.^[5] Herein we propose a novel IMAM (IMinoAMido) ligands family (1) to access low-coordinate precursors and bearing an anionic donor to stabilize the high-valent late transition metal-oxo species. The new compounds were fully characterized through IR, NMR, HRMS, and their coordination properties with Fe, Ni, Co and Cu (2) were explored.





References:

- 1) Labinger, J.A., Bercaw, J.E., Nature 2002, 417, 507
- 2) Que, L. Jr., Tolman, W.B., Nature 2008, 455, 333
- 3) Winkler, J.R, Gray, H.B., Struct. Bond. 2012, 142, 17
- 4) Holland, P.L., Cundari, T.R., Perez, L.L., Eckert, N.A., Lachicotte, R.J., J. Am. Chem. Soc. 2002, 124, 14416
- 5) Spencer, D. J. E, Aboelella N.W., Reynolds, A. M., Holland, P. L., Tolman, W. B., J. Am. Chem. Soc. 2002, 124, 10, 2108

AEROBIC ELECTROCHEMICAL OXYGENATION OF HYDROCARBONS

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Activation of molecular oxygen is one of the holy grails in catalysis. Without a catalyst, the reaction between O₂ and an organic substrate has a high activation barrier and it proceeds via a free radical mechanism bringing to complete oxidation.^[1] Nature inspires us with fascinating copper and iron metalloenzymes that utilize air at room temperature, paradoxically under reducing conditions. The mechanism of these enzymes has been widely investigated both in vivo or using complexes that mimic their active sites.^[2-9] Surprisingly, reduction via electrolysis of these enzymes or similar biomimetic catalysts has been only sparingly reported and do not lead to alkane oxidation.^[10-13] In our work an iron-tungsten porous capsule was used as catalyst to hydroxylate light alkanes and cleave C=C bonds in alkenes at room temperature. The first step of the catalysis is the reduction of the metal center via electrolysis, followed by O₂ activation and hydrocarbon oxidation. The experimental results as well as relevant mechanistic studies will be reported.



Figure. A polyhedral (left) and stick (middle) presentation of the iron-tungsten capsule, { $Fe^{III_{30}} W^{VI}_{72}$ }. Iron-green, tungsten-black, oxygen-red. Not shown are the 25 disordered sulfate/bisulfate ligands coordinated to W and Fe within the capsule that supply a protic environment and NH₄⁺ cations on the outside of the capsule. The pore into the capsule is pointed to by the arrowed line, which is shown in more detail on the right.

- 1) F. R. Mayo, Acc. Chem. Res. 1968, 1, 193-201.
- 2) D. A. Quist, D. E. Diaz, J. J. Liu, K.D. Karlin, J. Biol. Inorg. Chem. 2017, 22, 253
- 3) S. Hong, Y. M. Lee, K. Ray, W. Nam, Coord. Chem. Rev. 2017, 334, 25
- 4) X. Engelmann, I. Monte-Perez, K. Ray, Angew. Chem. Int. Ed. 2016, 55, 7632
- 5) L. Que, W. B. Tolman, *Nature* **2008** 455, 333
- 6) F. Nastri, M. Chino, O. Maglio, A. Bhagi-Damodaran, Y. Lu, A. Lombardi, Chem. Soc. Rev.2016, 45, 5020
- 7) X. Huang, J. T. J. Groves, *Biol. Inorg. Chem.* **2017**, 22, 185
- 8) A. Trehoux, J.-P. Mahy, F. Avenier, Coord. Chem. Rev.2016, 322, 142
- 9) K.-B.Cho, H. Hirao, S. Shaik, W. Nam, Chem. Soc. Rev. 2016, 45, 1197
- 10) A. K. Udit, M. G. Hill, H. B. Gray, J. Inorg. Biochem. 2006,100, 519
- 11) T. Michida, C. Saiki, C. Yamasaki, Y. Yamaoka, Chem. Pharm. Bull. 2005, 53, 151
- 12) S. E. Creager, S. A. Raybuck, R. W. Murray, J. Am. Chem. Soc. 1986,108, 4225
- 13) C. P. Horwitz, S. E. Creager, R. W. Murray, Inorg. Chem. 1990, 29, 1006



Predictive Catalysis: Transition-Metal Reactivity by Design

Girona, April 3-6, 2018

Talks

TOWARDS A PARADIGM SHIFT IN MAIN GROUP POLAR ORGANOMETALLIC CHEMISTRY

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Organolithium compounds (*e.g.*, alkyls, aryls and amides) have been and remain pivotal to the development of synthetic chemistry.^[1] Staple reagents in academic laboratories and chemical industries worldwide, their extensive utilization reflects their high reactivity and selectivity (notably in directed *ortho*-metallation). However, in many cases this high reactivity can also compromise their functional group tolerance, imposing the use of severely restrictive protocols (*e.g.*, moisture- and oxygen-free organic solvents, inert atmospheres, extremely low temperatures *etc.*) and frequently the lithiated organic intermediates can be unstable and decompose.

This presentation will explore alternative organometallic strategies to overcome some of these major drawbacks faced by standard organolithium reagents. This includes the use of bimetallic combinations for deprotonative metallation reactions, which operating in tandem enable the trapping of sensitive anions such as metallated diazines^[2] or fluoroarenes (see Scheme).^[3] Furthermore, the promising use of non-conventional solvent systems such as Deep Eutectic Solvents (DESs) in organolithium chemistry will also be discussed,^[4] edging closer towards developing greener and air and moisture compatible methodologies.



References

- 1) Mongin, F.; Harrison-Marchand, A.; Chem. Rev. 2013, 113, 7563.
- 2) Uzelac, M.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E.; Angew. Chem. Int. Ed. 2016, 55, 1314.
- (a) McLellan, R.; Uzelac, M.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E.; Angew. Chem. Int. Ed. 2017, 56, 9566. (b) Maddock, L. C. H.; Nixon, T.; Kennedy, A. R.; Probert, M. R.; Clegg W.; Hevia, E.; Angew. Chem. Int. Ed. 2018, 57, 187.
- (a) Vidal, C.; Garcia-Alvarez, J.; Hernan-Gomez, A.; Kennedy, A. R.; Hevia, E.; Angew. Chem. Int. Ed. 2014, 53, 5969. (b) Vidal, C.; Garcia-Alvarez, J.; Hernan-Gomez, A.; Kennedy, A. R.; Hevia, E.; Angew. Chem. Int. Ed. 2016, 55, 16145. (c) Rodriguez-Alvarez, M. J.; Garcia-Alvarez, J.; Uzelac, M.; Fairley, M.; O'Hara, C. T.; Hevia, E.; Chem. Eur. J. 2018, 24, 1720.
CARBENE INSERTION TO C_{SP}²-H BONDS CATALYZED BY A NON-HEME IRON COMPLEX

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The functionalization of non-activated C-H bonds is a reaction of high interest since it becomes a starting point for the synthesis of value-added compounds. Among all transformations, metal-catalyzed carbene transfer reaction from diazocompounds to inert C-H bonds is a promising methodology to generate new C-C bonds. [1] Until now, copper and rhodium complexes have been found to be the most efficient metals to perform this transformation. However, the iron-catalyzed carbene transfer reactions have been less explored and they are mainly based on porphyrinic ligands. [2]

Although benzene is an important structure present in most of the pharmaceuticals, its use in carbene insertion reaction using commercially available diazoesters has not been extensively explored due to the existence of a competing reaction, called Buchner reaction, which generates a cycloheptatriene as side product, yielding a mixture of products at the end of the reaction. [3]

Herein, we present the functionalization of different arenes catalyzed by an Fell complex bearing tetradentate aminopyridine-based ligand, through the insertion of ethyl diazoacetate into C-H bonds. The high selectivity towards Csp2-H bonds and the absence of neither cycloheptatriene product nor carbene dimers provides an efficient transformation catalyzed by a non-precious metal complex. In addition, experimental and theoretical studies have been carried out to disclose the mechanism of the reaction. [4]



[1] (a) M. P. Doyle, R. Duffy, M. Ratnikov, *Chem. Rev.* 2010, 110, 704. (b) M. M. Díaz-Requejo, P. J. *Pérez, Chem. Rev.* 2008, 108, 3379.

[2] Y. Li, J. Huang, Z. Zhou, C. Che, J. Am. Chem. Soc. 2002, 124, 13185.

[3] (a) E. Büchner, T. Curtius, Ber. Dtsch. Chem. Ges. 1885, 18, 2371. (b) M. R. Fructos, T. R. Belderrain, P. de Fremont, N. M.

Scott, S. P. Nolan, M.M. Díaz-Raquejo, P. J. Pérez, Angew. Chem. Int. Ed. 2005, 44, 5284.

[4] A. Conde, G. Sabenya, M. Rodríguez, V. Postils, J. M. Luis, M. M. Díaz-Requejo, M. Costas, P. J. Pérez, Angew. Chem. Int. Ed. 2016, 22, 6530.

SPIN-STATE-DEPENDENT GENERATION AND SPECTROSCOPY OF TERMINAL IRON(V) NITRIDES

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Study of terminal iron(V) nitrides with tetragonal ligand symmetry is a daunting task due to their extreme reactivity and instability above cryogenic temperatures.^[1] We have overcome those obstacles by studying them in the gas phase. We examined, how the nitrides can be formed by iron(III) azide photodissociation.^[2] By studying the wavelength and temperature dependence of the photodissociation reaction of various azides, we demonstrated that the the photodissociation outcome depends on the spin state of the iron azide, as previously suggested.^[3] After establishing the crucial role of the spin state in the photodissociation process, we characterized the resulting iron(V) nitrides by gas-phase IR spectroscopy.^[4] We assigned the weak Fe=N stretching vibrations of the iron nitrides using combination of isotopic labelling experiments and DFT/CASPT2 calculations. We identified, how the Fe=N band intensity can be diminished by coupling with by ligand vibrations, which precludes its measurement by conventional spectroscopic techiques.



- 1) J. M. Smith, D. Subedi, Dalton Trans. 2012, 41, 1423.
- 2) E. Andris, R. Navrátil, J. Jašík, G. Sabenya, M. Costas, J. Roithová, Angew. Chem. Int. Ed. 2017, 56, 14057.
- 3) Y.-F. Song, J. F. Berry, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, Inorg. Chem. 2007, 46, 2208.
- 4) E. Andris, R. Navrátil, J. Jašík, G. Sabenya, M. Costas, J. Roithová, manuscript in preparation.

IN PURSUIT OF THE ELUSIVE FE(V)=O OXIDANT IN BIO-INSPIRED NONHEME IRON-CATALYZED OXIDATIONS

Lawrence Que Jr. (with the help of many friends)

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It has been 20 years since we initiated efforts to mimic the oxidation chemistry of nonheme iron enzymes and discovered the first example of a nonheme iron complex, $[[Fe^{II}(TPA)(NCMe)_2]^{2+}$, to be capable of using H₂O₂ as oxidant to catalyze the stereospecific hydroxylation of alkanes and the epoxidation and cis-dihydroxylation of olefins. Other Fe^{II}(N4) catalysts have since been identified and developed by a number of groups. The observation that at least some ¹⁸O from labeled water could be incorporated into the oxidation products led us to postulate a water-assisted mechanism involving an (N4)Fe^v(O)(OH) oxidant, strong evidence for which was obtained by Costas and Cronin using cryospray mass spectrometry. However, no experimental insight into the electronic structure of this elusive species could be obtained until more recently. The discovery of White that carboxylic acid additives modulated the chemistry of these catalysts opened new doors for catalyst development and applications in synthetic organic chemistry, as well as for obtaining mechanistic insight. Talsi used EPR to identify a number of fleeting S = 1/2 species that could represent the elusive $Fe^{V}(O)$ oxidant. The most intriguing of these was an EPR signal with fairly low g-anisotropy at g = 2.07, 2.01, 1.95, which accounted for <5% of the Fe in the samples but decayed at a rate dependent on substrate concentration. Serrano-Plana, Company and Costas recently discovered a related Fe^{II}(N4) catalyst capable of producing this g = 2.07 species in 40-50% yield, corresponding to an intermediate exhibiting the fastest rate for cyclohexane hydroxylation determined to date. Our spectroscopic and computational studies on this intermediate reveal a unique electronic structure that is predominantly $Fe^{V}(O)(O_2CR)$ in character with some contributions from its $Fe^{III}(OOC(O)R)$ and $Fe^{IV}(O)(\bullet OC(O)R)$ electromers mixed in. These details will be elaborated upon in my talk.

CHEMICAL TOOLS AND TACTICS TO STUDY MULTIPLE FACETS IN ALZEHIMER'S DISEASE

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Alzheimer's disease (AD), associated with degeneration of neurons and synapses in the brain, leads to motor impairment and eventual fatality. Neurodegeneration could be related to various interconnected features, including (i) plaque formation from amyloid- β (A β) peptide fragments, (ii) metal ion dyshomeostasis and miscompartmentalization, as well as (iii) inflammation and increased oxidative stress due to overproduction of reactive oxygen species (ROS). The inter-relations between some of these pathological factors have been investigated. Metals are found entangled in the A β plaque and likely contribute to A β neurotoxicity and oxidative stress. ROS have been shown to increase the rate of A β plaque formation. Our understanding of the correlation between these elements and AD neuropathogenesis has been very limited, however. There is currently no cure for AD; therapies are focused on symptomatic relief targeting the decrease in the levels of acetylcholine, only one of the multiple factors causing the disease.^[1-5] To find a cure for AD, we require a better understanding of the relationship between the various causative factors of this devastating disease. Towards this goal, we need suitable chemical tools and tactics capable of targeting and regulating its multiple underlying factors simultaneously.^[2-4] Herein, our rational design and preparation of our chemical tools will be discussed with our investigations of their interactions and reactivities with targets *in vitro* as well as their efficacy *in vivo*.^[6-11]

- 1) A. S. DeToma et al., Chem. Soc. Rev. 2012, 41, 608.
- 2) M. G. Savelieff et al., ACS Chem. Biol. 2013, 8, 856.
- 3) M. G. Savelieff et al., Acc. Chem. Res. 2014, 47, 2475-2482.
- 4) J. S. Derrick, M. H. Lim, *ChemBioChem* **2015**, *16*, 887.
- 5) H. J. Lee et al., Chem. Soc. Rev. 2014, 43, 6672.
- 6) J.-S. Choi et al., Proc. Natl. Acad. Sci. USA 2010, 107, 21990.
- 7) M. W. Beck et al., Chem. Sci. 2015, 6, 1879.
- 8) S. Lee et al., J. Am. Chem. Soc. 2014, 136, 299.
- 9) J. S. Derrick et al., J. Am. Chem. Soc. 2015, 137, 14785.
- 10) M. W. Beck, J. S. Derrick et al., Nat. Commun. 2016, 7, 13115.
- 11) J. S. Derrick et al., J. Am. Chem. Soc. 2017, 139, 2234.

SIDE-BOUND C=O AND C=N BONDS AS COOPERATIVE LIGANDS IN NICKEL CATALYSIS

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The development of greener and cheaper chemical processes motivates a widespread investigation of complexes of first-row transition metals as potential homogeneous catalysts to replace or, better, improve on traditional systems that are widely based on noble metals.^[1] Progress in this area has been intimately related to the development of tailored ligands, such as cooperative ligands that actively participate in chemical reactions.^[2]



In this contribution, we investigate the use of side-bound C=O and C=N π -ligands^[3,4,5] tethered by phosphine side-arms as cooperative ligands in base-metal catalysis. In particular, a hemilabile P(CO)P ligands afford selective Ni(0) alkyne cyclotrimerization catalysts (top), and Ni(0) complexes of P(CN)P ligands activate Ph₂SiH₂ over the C=N bond and function as olefin hydrosilylation catalysts (bottom). Insights into the mechanism of these transformations are provided by both experiment and computations.

References:

- 1) Bullock, R. M., Ed. Catalysis Without Precious Metals; Wiley-VCH: Weinheim, 2010
- 2) van der Vlugt, J. I. Eur. J. Inorg. Chem. 2011, 363
- 3) Verhoeven, D. G. A.; Moret, M.-E. Dalton Trans. 2016, 45 (40), 15762–15778.
- 4) Saes, B. W. H.; Verhoeven, D. G. A.; Lutz, M.; Klein Gebbink, R. J. M.; Moret, M.-E. Organometallics 2015, 34, 2710–2713.
- 5) J. Hou, W. -H. Sun, S. Zhang, H. Ma, Y. Deng, X. Lu, Organometallics, 2006, 25, 236-244.

REACTION MECHANISM OF OLEFIN METATHESIS WITH A NOVEL MOLYBDENUM CATALYST

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Synthesis of highly functionalized polymers is an ultimate goal in chemistry because it allows for design of materials with tailored properties. Molybdenum catalysts (e.g. of the Schrock type) have successfully been used for polymerization of olefins but these catalysts are very sensitive to functional groups at the monomers. However recently, an *N*-heterocyclic carbene Mo-alkylidene catalyst has been reported that does tolerate functional groups and polymerizes olefins with hydroxyl or carbonyl functionalities.¹

Density functional theory investigations were used in combination with experimental studies to unravel the reaction mechanism of this new catalyst generation and to explore the origin of its functional group tolerance. Regioselectivity of the polymerization was studied at the example of bicyclo[2.2.1]hept-5-en-2-carbaldehyd monomer. Energetics of the polymerization reaction as well as of the deactivation reaction are presented and regioselectivity of the polymer formation is explained. Compared to Schrock type catalysts, this novel Mo-alkylidene catalyst shows significantly reduced reactivity towards carbonyl coordination.²

References

1) M. R. Buchmeiser, S. Sen, J. Unold, W. Fey, Angew. Chem Int. Ed. 2014, 53, 9384.

2) Manuscript in preparation

CATALYSTS FOR THE SYNTHESIS OF SUSTAINABLE POLYMERS: MECHANISTIC ANALYSIS AND DESIGN

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At the University of Minnesota, the NSF-funded Center for Sustainable Polymers pursues basic polymer science research aimed at developing new, practical chemistries, polymers, processes, and technologies that embrace sustainability. We carry out our research stressing the principles of green chemistry to help protect the environment and ensure that future generations will be able to meet their societal needs. Theoretical modeling can play an especially critical role in the design cycle of catalysts for the preparation (or degradation) of monomers and polymers in a sustainable fashion, because theory offers in-depth insights into mechanistic details associated with productive and off-cycle reaction pathways, and permits in silico testing of nextgeneration systems having improved characteristics. In combination with collaborating experimental groups, we have been particularly active in pursuing catalysts that (i) generate α -olefins from alkanoic acids,^[1] (ii) copolymerize anhydrides and epoxides to prepare designed polyesters,^[2] (iii) copolymerize epoxides and carbon dioxide to prepare designed polycarbonates,^[3] and (iv) permit redox-switchable homopolymerization of mixed monomers so as to generate block copolymers in a controlled fashion.^[4] Selected examples that highlight contributions from theory will be presented.

^{1) (}a) Ortuño, M. A.; Dereli, B.; Cramer, C. J. "Mechanism of Pd-Catalyzed Decarbonylation of Biomass-Derived Hydrocinnamic Acid to Styrene Following Activation as an Anhydride" Inorg. Chem. 2016, 55, 4124 (doi:10.1021/acs.inorgchem.5b02664); (b) John, A.; Miranda, M. O.; Ding, K.; Dereli, B.; Ortuño, M. A.; LaPointe, A. M.; Coates, G. W.; Cramer, C. J.; Tolman, W. B. "Earth-Abundant Metal Catalysts for the Dehydrodecarbonylation of Carboxylic Acids to Olefins" Organometallics 2016, 35, 2391 (doi:10.1021/acs.organomet.6b00415); (c) John, A.; Dereli, B.; Ortuño, M. A.; Johnson, H. E.; Hillmyer, M. A.; Cramer, C. J.; Tolman, W. B. "Selective Decarbonylation of Fatty Acid Esters to Linear a-Olefins" Organometallics 2017, 36, 2956 (doi:10.1021/acs.organomet.7b00411).

²⁾ Fieser, M. E.; Sanford, M. J.; Mitchell, L. A.; Dunbar, C. R.; Mandal, M.; Van Zee, N. J.; Urness, D. M.; Cramer, C. J.; Coates, G. W.; Tolman, W. B. "Mechanistic Insights into the Alternating Copolymerization of Epoxides and Cyclic Anhydrides Using a (Salph)AICI and Iminium Salt Catalytic System" J. Am. Chem. Soc. 2017, 139, 15222 (doi:10.1021/jacs.7b09079).

³⁾ Qu, S.; Coates, G. W.; Cramer, C. J. to be published.

⁴⁾ Ortuño, M. A.; Dereli, B.; Delle Chiaie, K. R.; Biernesser, A. B.; Byers, J. A.; Cramer, C. J. to be published.

THEORY-LED DESIGN OF NEW LIGANDS FOR ASYMMETRIC CATALYSIS

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Despite the widespread adoption of computational tools across chemistry, the design of asymmetric catalytic reactions is not yet routine. In this talk I discuss some of the inherent challenges involved in the quantitative prediction of stereoselectivities, and our ongoing approaches to overcome them.^[1] We present approaches for the design of new phosphoramidite ligands for asymmetric transition metal catalysis. Alternative approaches, based on a full mechanistic study of competing pathways^[2] or on the development of quantitative structure-enantioselectivity relationships will be compared.^[3]

- (a) Johnston, C. P.; Kothari, A.; Sergeieva, T.; Okovytyy, S. I.; Jackson, K. E.; Paton, R. S.; Smith, M. D. Nature Chem. 2015, 7, 171; (b) Duarte, F.; Paton, R. S. J. Am. Chem. Soc. 2017, 139, 8886 (see also JACS spotlight 2017, 139, 8383).
- (a) Straker, R.; Peng, Q.; Mekareeya, A.; Paton, R. S.; Anderson, E. A. *Nat. Commun.* 2016, 7, 10109; (b) Pupo, G.; Ibba, F.; Ascough, D. M. H.; Vicini, A. C.; Ricci, P.; Christensen, K.; Morphy, J. R.; Brown, J. M.; Paton, R. S.; Gouverneur, V. 2017, *in review.*
- (a) Ardkhean, R.; Roth, P. M. C.; Maksymowicz, R. M.; Curran, A.; Peng, Q.; Paton, R. S.; Fletcher, S. P. ACS Catal. 2017, 7, 6729; (b) Ardkhean, R.; Mortimore, M.; Paton, R.S.; Fletcher, S. P.Chem. Sci. 2018, 10.1039/C7SC05304E

CATCHING TRANSIENT INTERMEDIATES

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The search for new and better reactivity has driven the development of 1st row transition metal catalysis over the last several decades, not least in the field of oxidation catalysis. Our group has focused on manganese and iron based catalysts for both fine chemical and bulk applications, and more recently on Ni(II) based catalysts,^[1] employing environmentally benign oxidants. A key challenge faced in catalyst development and in optimisation is to move from catalyst discovery to catalysis design. However, design requires understanding of the fundamental mechanisms that underpin the catalysis observed and the interplay of all reaction components. In this contribution I will focus on our efforts to track the formation and decay of transient intermediates and establish their relevance to the catalytic activity observed. In particular the challenges presented by mass transport and sampling rate in obtaining useful kinetic information. References should be numbered sequentially and highlighted in the text^[1] as superscript between square brackets.^[2]

1) S. K. Padamati, D. Angelone, A. Draksharapu, G. Primi, D. J. Martin, M. Tromp, M. Swart, W. R. Browne, J. Am. Chem. Soc. 2017, 139, 8718.

RECAPITULATING ALLOSTERY IN TRYPTOPHAN SYNTHASE ENZYME BY MEANS OF COMPUTATIONAL TECHNIQUES.

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Multimeric enzyme complexes, which perform many desirable chemical transformations, are often allosterically regulated by their protein partners, being the catalytic activity of isolated subunits seriously diminished.^[1,2] Stand-alone enzyme subunits, however, are desirable for biosynthetic applications as lower metabolic loads on the host cell are needed, and the efforts to engineer activity, substrate specificity, etc. are drastically simplified. Tryptophan synthase (TrpS) is a heterodimeric complex that catalyzes the condensation of indole and L-Serine to form L-Tryptophan. Structural studies based on X-ray crystallography identified several key conformational states exhibiting open and closed conformations in both subunits.^[1] For this enzyme, an allosteric network between the alpha-subunit (TrpA) and the beta-subunit (TrpB) keeps the proper conformational states along the catalytic itinerary, and allows indole diffusion from TrpA to TrpB through an internal tunnel. In an insightful work, Prof. Arnold and coworkers reactivated isolated TrpB subunits through directed evolution raising the catalytic efficiency to the level of the TrpS complex, by a stabilization of a closed/active conformation.^[3] The presence of several activating mutations outside any allosteric site raised, however, the question of how distal mutations are able to recapitulate the allosteric regulation induced by TrpA remains to be answered. In this work, molecular dynamics simulations together with metadynamics calculations^[4] were applied to map the effects of the introduced mutations, providing a detailed description of the enzyme most stable conformational states. This knowledge contributes to our current understanding on the effect of distal mutations on the protein conformational landscape, and how allosteric regulation can be recovered in isolated subunits.

- 4) Laio, A & Parrinello, M. Proc. Natl. Acad. of Sci. USA 2002, 99, 12562-12566.
- 5) Maria-Solano, M.; Iglesias-Fernández, J.; Osuna, S. *submitted for publication* **2017**.

¹⁾ Dunn. M. F. Arch. Biochem. Biophys. 2012, 519, 154-166.

²⁾ Kennedy, J.; Auclair, K.; Kendrew, S. G.; Park, C.; Vederas, J. C.; Hutchinson, C. R. Science 1999, 284, 1368-1372.

³⁾ Buller, A. R.; Brinkmann-Chen, S.; Rommey, D. K.; Herger, M.; Murciano-Calles, J.; Arnold, F. H. Proc. Natl. Acad. of Sci. USA 2015, 112, 14599-14606.

MOLECULAR SURGERY VIA C—H OXIDATION

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Site-selective, catalytic C—H oxidation reactions for broad use in organic synthesis will be discussed. Catalysts have been developed that enable atomistic changes in complex molecules transforming C(sp3)—H bonds to C(sp3)—O, C(sp3)—N, and C(sp3)—C under preparative conditions with predictable and catalyst-controlled site-selectivities- without the requirement for directing groups. The reactions and quantitative models developed to understand and predict site-selectivities for aliphatic C—H hydroxylations will be discussed. Collectively this understanding has provided fundamental insights into the physical organic properties of C—H bonds that govern their differential reactivity in complex molecules. These reactivity principles have been demonstrated in other C(sp3)—H reactions. The generality of these reactions have led to strategic advances synthesis, most notably the concept of late-stage C—H functionalization.

Keynote Lecture 4 KL 4

LIGHT-DRIVEN REDUCTIONS USING WELL-DEFINED COORDINATION COMPLEXES.

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One of the most appealing research areas is the mechanistic understanding of multi-electron multi-proton processes, which is a central part in the activation of small molecules such as CO₂ and H₂O. In this line, we have discovered that well-defined cobalt coordination complexes based on the tacn moiety are highly efficient homogeneous catalysts for reduction of water,^[1-2] organic substrates^[3] and CO₂. Interestingly, the low valent cobalt intermediate also promote the highly-challenging visible-light reductive radical cyclizations reactions from unactivated chloroalkanes, which open new avenues in photoredox catalysis. In the presentation we will discuss the synergy between experiments and theory to gain insights into intermediates and the operative mechanisms.



[1] Call A., Codolà Z., Acuña-Parés F., Lloret-Fillol J., Chem. Eur. J. 2014, 20, 6171-6183.

[3] Call, A., Casadevall, C., Acuña-Pares, F., Casitas Montero, A., Lloret Fillol, J., Chem. Sci. 2017, 8, 4739-4749.

^[2] A. Call, F. Franco, N. Kandoth, S. Fernández, M. González-Béjar, J. Pérez-Prieto, J.M. Luis, J. Lloret-Fillol Chem. Sci. 2018, DOI: 10.1039/C7SC04328G.

COMPUTATIONAL STUDIES OF VISIBLE LIGHT PHOTOREDOX CATALYTIC REACTIONS

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Radical chemistry is a powerful and versatile tool for synthetic chemistry. Single electron transfer processes offer complimentary reactivity to two-electron or polar reactions, due to the open shell reactive species that undergo chemical reaction through otherwise difficult to access pathways. The use of radical chemistry in synthesis has become more prevalent in part due to an improved appreciation of the usefulness of photochemistry, which has led to the area of photoredox catalysis. Visible light mediated photoredox catalysis has given rise to a wide variety of synthetic processes including late stage functionalization, carbon-carbon and carbon-heteroatom bond formation reactions.^[1] Photocatalyzed radical reactions also benefit from generally occurring under mild conditions such as ambient temperature, low catalyst loading, and also exhibiting good functional group tolerance.

Density functional theory (DFT) is a widely used computational method that supports the understanding of a diverse array of synthetic processes. Whilst computational methods have been used to study a variety of catalytic processes, use in visible light promoted reactions remains relatively uncommon.^[2] This theoretical study provides insight into the mechanism of transition metal catalyzed photoredox oxidation reactions such as that described in the Figure.



Figure. Photoredox oxidation reactions

Elucidating the reaction mechanism is important to the design and execution of new synthetic reactions and will assist in deepening the understanding of catalyst reactivity. Of particular importance to this project is to better understand both the chemo- and regio-selectivity of photoredox oxidation reactions.

References

¹⁾ M. H. Shaw, J. Twilton, D. W. C. MacMillan, J. Org. Chem. 2016, 81, 6898

²⁾ T. B. Demisse, J. H. Hansen, Dalton Trans. 2016, 45, 10878

WHAT CONTROLS PHOTOCATALYTIC WATER OXIDATION ON TiO₂?

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In the photocatalytic oxidation of water by TiO₂, excitation of the semiconductor generates a hole-electron pair that oxidizes and deprotonates adsorbed water molecules, leading to generation of oxygen. This process, also known as the oxygen evolution reaction (OER), is one of the main bottlenecks that prevents the use of water photoelectrolysis on TiO₂ for fuel generation, since it has a low efficiency. To determine the reasons behind this, we have studied the mechanism with theoretical methods.^[1] Our approach considers the reactivity of the hole and electron as a correlated exciton pair. We center on the first step, where hydroxy radicals are generated after a coupled proton and electron transfer (PCET) step:

 $H_2O@TiO_2 + h\nu \longrightarrow HO@TiO_2 + H^+ + e^-$

Our calculations show that the reaction is exothermic and almost barrierless. This is in contrast to previous studies which blame the low efficiency on the energy barriers for the PCET. In our model, the low efficiency is due to the high probability of charge recombination, which regenerates the reactant. In turn, the charge recombination is associated to crossings between electronic states with different charge configurations.





RATIONALIZING THE REACTIVITY OF BIMETALLIC MOLECULAR CATALYSTS FOR CO₂ HYDROGENATION

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We have recently reported the heterobimetallic nickel-gallium complex,[1] NiGaL (where L represents the tris(phosphinoamido)amine ligand, $[N(o-(NCH_2Pi-Pr_2) C_6H_4)_3]^{3-})$, which is the most active Ni-based molecular catalyst for CO₂ hydrogenation to date. Understanding the reaction mechanism of this catalytic system and identifying the factors that govern its catalytic activity are important toward designing even more efficient base metal catalysts. I will present the results of a computational study of possible reaction pathways for CO₂ hydrogenation catalyzed by NiGaL. The most favorable pathway for formate production has four elementary steps: (1) H₂ binding to the Ni center, (2) deprotonation of the H₂ adduct, (3) hydride transfer to CO₂ to form formate adduct, and (4) formate release to regenerate NiGaL. The reaction mechanism identified by the calculations agrees well with several key experimental observations. For hydride transfer to CO₂, the free energy of activation was found to depend linearly on the thermodynamic hydricity for a series of bimetallic HM₁M₂L⁻ complexes. This linear relationship provides a simple and efficient strategy for screening other bimetallic catalysts by predicting the free energies of activation for the hydridetransfer step based on experimental or computed thermodynamic hydricity data, rather than by calculating the entire reaction mechanism. The predicted trends and structure-activity relationships arising from these computational calculations provide tools for the rational design of more efficient catalysts for CO₂ hydrogenation and other hydride transfer processes for which reactive M-H species are generated in the presence of a Lewis base.

[1] Ryan C. Cammarota; Vollmer, M. V.; Xie, J.; Ye, J.; Linehan, J. C.; Burgess, S. A.; Appel, A. M.; Gagliardi, L.; Lu, C. C. *J. Am. Chem. Soc.* **2017**, *139* (40), 14244–14250.



Recipes for Designing Bimetallic Molecular Catalysts for CO₂ Hydrogenation

SMALL MOLECULE ACTIVATION AT TRANSITION METAL CENTERS: STRUCTURE-FUNCTION CORRELATIONS

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Small molecule activation constitutes one of the main frontiers of inorganic and organometallic chemistry, with much effort directed towards the development of new processes for the selective and sustainable transformation of abundant small molecules such as dioxygen (O2), water (H2O), hydrogen peroxide (H2O2) or protons (H+) into highvalue chemical feedstocks and energy resources. Because nature mostly uses metal ions to activate these relatively inert molecules and modulate their reactivity, much inspiration for the field has come from bioinorganic chemistry. This talk will focus on some of the recent highlights from our group on homogenously catalyzed bioinspired activation of small molecules, as well as stoichiometric reactions that further our understanding towards such ends. It will cover many aspects of small molecule activation including: organometallic chemistry, spectroscopy, synthesis, and detailed mechanistic studies involving trapping of reactive intermediates. The demonstrated examples will help to emphasize the continuous effort of our group in uncovering the structure-reactivity relationships of biomimetic model complexes, which may allow vital insights into the prerequisites necessary for the design of efficient catalysts for the selective functionalization of unactivated C-H bonds, O2/H2O/H2O2 activations, or H+ reductions by using cheap and readily available first-row transition metals under ambient conditions.



REDOX DIALOGUE BETWEEN LIGANDS AND METAL FOR UNCONVENTIONAL REACTIVITIES

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Metalloenzymes are Nature's ultimate catalytic tools. Not only do they display extreme selectivity coupled with efficiency, they also seem to be performing an endless list of chemical reactions. In order to achieve multielectronic transformations with first-row transition metals, which are the basis of the biochemical catalytic toolkit, metalloenzymes often rely on ligand radical species which participate by donating/accepting electrons or by forming and/or breaking substrate bonds. For this redox specificity, these ligands have been classified as **redox** or "**non-innocent ligands**" (**NILs**). Although challenging and elusive, bio-inspired catalysis must still be a goal for today's chemist, especially in the dawn of the foreseen shortage of precious metals resources. While redox non-innocence in biological settings has long been familiar to bioinorganic chemists, the use in a broader context of "synthetic" NILs as surrogates of the original biological radicals is only lately

emerging as a catalytic tool of its own.^[1]

We are interested in understanding and harnessing alternative mechanisms enabled by the redox-activity of the ligands.[2] This approach led us to study a formal umpolung of CF3,[2a] copper- and nickel-catalyzed trifluoromethylation[2b,c] and C–N bond formation through redox Nickel reacts with radicals Nickel Ports Wickel radicals Nickel Press here radicals Nickel reacts with radicals Nickel reacts with radicals Nickel generates radicals

ligand stabilization of masked high valent metallic oxidation states.[2d]

O. R. Luca, R. H. Crabtree, *Chem. Soc. Rev.* 2013, *42*, 1440; b) V. K. K.Praneeth, M. R. Ringenberg, T. R. Ward, *Angew. Chem., Int. Ed.* 2012, *51*, 10228; c) J. I. van der Vlugt, *Eur. J. Inorg. Chem.* 2012, 363; d) P. J. Chirik, K. Wieghardt, *Science*, 2010, 327, 794.

a) J. Jacquet, E. Salanouve, M. Orio, H. Vezin, S. Blanchard, E. Derat, M. Desage-El Murr, L. Fensterbank, *Chem. Commun.* 2014, *50*, 10394; b) J. Jacquet, S. Blanchard, E. Derat, M. Desage-El Murr, L. Fensterbank, *Chem. Sci.* 2016, *7*, 2030; c) J. Jacquet, K. Cheaib, Y. Ren, H. Vezin, M. Orio, S. Blanchard, L. Fensterbank, M. Desage-El Murr, *Chem. – Eur. J.* 2017, *23*, 15030; d) J. Jacquet, P. Chaumont, G. Gontard, M. Orio, H. Vezin, S. Blanchard, M. Desage-El Murr, L. Fensterbank, *Angew. Chem. Int. Ed.* 2016, *55*, 10712.

TUNING THE REACTIVITY OF HIGH-VALENT NICKEL OXIDANTS FOR HYDROCARBON OXIDATION

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High-valent terminal metal-oxygen adducts are hypothesized to be the potent oxidising reactants in late transition metal oxidation catalysis. In particular, examples of high-valent terminal nickel-oxygen adducts are sparse, meaning there is a dearth in the understanding of such oxidants. Herein we describe the preparation of a family of high-valent Ni oxidants. Electronic absorption, electronic paramagnetic resonance, and X-ray absorption spectroscopies, and density functional theory calculations have been used to probe the electronic and structural properties of these compounds. Structure function relationships in a series of complexes have been elucidated, providing us with critical insight into the reactivity properties of high-valent nickel oxidants.¹⁻³

¹ P. Pirovano, E. R. Farquhar, M. Swart, A. J. Fitzpatrick, G. G. Morgan, A. R. McDonald, *Chem. Eur. J.*, **2015**, *21*, 3785-3790;

² P. Pirovano, E. R. Farquhar, M. Swart and A. R. McDonald, J. Am. Chem. Soc., 2016, 138, 14362-14370.

³ P. Mondal, P. Pirovano, A. Das, E. Farquhar, A. R. McDonald, submitted 2017

SMALL MOLECULE ACTIVATION AND CATALYSIS WITH F-BLOCK ORGANOMETALLICS; (ANY) TWO METALS ARE BETTER THAN ONE

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The subtleties of structure and bonding in compounds of the rare earths (Group 3 and the lanthanides) and uranium, the heaviest naturally occurring element, are still poorly-understood. However, their complexes can exhibit high and tuneable Lewis acidity and reduction capability, and rapid ligand exchange reactions. Organometallic compounds of the lanthanides and actinides have shown many interesting small molecule activation reactions, including hydrocarbon C-H bond cleavage. Interest in their activity as catalysts is increasing since the recognition that many rare earths are at least as abundant as iodine, and many are cheap and less toxic than iron.

We will show new f-block organometallics that are capable of the reductive activation and functionalisation of CO, CO₂, N₂, and arenes, even using simple bulky ligands that have been previously overlooked. The dominance of singleelectron redox reactivity is a potential drawback they share with the 3d metal catalysts. We will present some dinuclear fblock complexes supported by new platform ligands, and their multiple-electron redox chemistry and catalysis.^[1]



References

- 1) a) Reviews: P. L. Arnold, Z. R. Turner, *Nature Chem. Rev.* 2017, *1*, 17. P.L. Arnold, M.W. McMullon, F.E. Kühn, J. Rieb, *Angew. Chem., Int. Ed.* 2015, 54, 82.
 - b) J. A. L. Wells, M. L. Seymour, M. Suvova, P. L. Arnold, Dalton Trans. 2016, 45, 16026.
 - c) P. L. Arnold, Z. R. Turner, R. Bellabarba, R. B. Tooze, Chem. Sci., 2011, 2, 77.
 - d) S. M. Mansell, N. Kaltsoyannis, P. L. Arnold, J. Am. Chem. Soc., 2011, 133, 9036.
 - e) P. L. Arnold, S. M. Mansell, D. McKay, L. Maron, Nature Chem., 2012, 4, 668.

Keynote Lecture 6 KL 6

SYNTHESIS OF VERSATILE SYNTHETIC INTERMEDIATES THROUGH COPPER CATALYSIS

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Metal catalysis is a powerful tool for the creation of stereocenters in organic molecules. Both, the use of a chiral catalyst or a chiral starting material, are valuable and complementary approaches to accomplish this goal. In our group, we have recently developed copper-catalyzed enantioselective and stereospecific transformations, in the context of carbon-boron bond formation and carbon-nitrogen bond cleavage. These methods have allow us to prepare a broad variety of useful synthetic intermediates such as 1,4-diols,^[1] trisubstituted alkenes,^[2] propargylic derivatives^[3] and functionalized small rings.^[4] Some of these transformations will be presented in this talk.



Acknowledgments: We thank the European Research Council (ERC-337776) and MINECO (CTQ2016-78779-R) for financial support.

- 3) Guisan-Ceinos, M.; Martin-Heras V.; Tortosa M. J. Am. Chem. Soc. 2017, 139, 8448.
- 4) Parra, A.; Amenós, L.; Guisan-Ceinos M.; López, A.; Garcia-Ruano, J. L.; Tortosa, M J. Am. Chem. Soc. 2014, 136, 15833.
- 5) Guisan-Ceinos, M.; Parra, A.; Martin-Heras V.; Tortosa M. Angew. Chem. Int. Ed. 2016, 55, 6969.

¹⁾ Tortosa M. Angew. Chem. Int. Ed. 2011, 50, 3950.

²⁾ Alfaro, R.; Parra, A.; Alemán, J.; García Ruano, J. L.; Tortosa, M. J. Am. Chem. Soc. 2012, 134, 15165.

BASE METAL CATALYSTS IN C-H FUNCTIONALIZATION

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Direct functionalization of molecules containing C(sp³)–H and C(sp²)–H bonds stands out today as a highly relevant area in modern organic chemistry.^[1] Despite the advances realized, the majority of the methodologies rely on the use of expensive precious metal catalysts and hence the implementation of abundant first-row transition metals represents a challenging task of utmost synthetic importance in the field of sustainable development.^[2] Our primary goal is not to simply replace existing catalysts but to discover new reaction chemistry that takes advantage of the unique electronic properties of inexpensive metals such as iron^[3] and cobalt.^[4] In this communication we will describe our latest developments in the conversion of feedstock substrates such as cyclic ethers into medicinally significant compounds upon iron- and cobalt-catalyzed oxidative couplings.^[5]



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- [3] (a) Shang, R.; Ilies, L.; Nakamura, E. Chem. Rev. 2017, 117, 9086. (b) Lv, L.; Li, Z. Top. Curr. Chem. 2016, 374, 225.
- [4] (a) Wang, S.; Chen, S.-Y.; Yu, X.-Q. Chem. Commun. 2017, 53, 3165. (b) Moselage, M.; Li, J.; Ackermann, L. ACS Catal. 2016, 6, 498.
- [5] (a) San Segundo, M.; Guerrero, I.; Correa, A. Org. Lett. 2017, 19, 5288. (b) Correa, A.; Fiser, B.; Gómez-Bengoa, E. Chem. Commun. 2015, 51, 13365.

 ^{[1] (}a) Zhu, R.-Y.; Farmer, M. E.; Chen, Y.-Q.; Yu, J.-Q. Angew. Chem. Int. Ed. 2016, 55, 10578. (b) Rouquet, G.; Chatani, N. Angew. Chem. Int. Ed. 2013, 52, 11726.

 ^{[2] (}a) Tzouras, N. V.; Stamatopoulos, I. K.; Papastavrou, A. T.; Liori, A. A.; Vougioukalakis, V. C. Coord. Chem. Rev. 2017, 343, 25. (b) Sanderson, K. Nature 2011, 469, 18. (b) Sheldon, R. A. Chem. Soc. Rev. 2012, 41, 1437.

MESOIONIC CARBENES (MICS) BASED METAL COMPLEXES: SYNTHESIS, REACTIVITY AND CATALYTIC APPLICATIONS

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Since the first reported example of metal complexes bearing 1,2,3-triazol-5-ylidene ligands and subsequent isolation,^{[1][2]} mesoionic carbene ligands (MICs) have received considerable attention due to their ready availability and the stronger σ -electron donating character when compared to classical NHC.^[3]

In this contribution, the synthesis, reactivity and catalytic applications of 1,2,3-triazol-5-ylidene based metal complexes will be presented. In particular, a CNC-pincer ligand stands out as a convenient scaffold that allows isolation of very reactive late transition metals complexes. ^{[4],[5]} and a selective catalysts for one-pot alkyne dimerization-hydrothiolation tandem reactions. ^{[6],[7]}

- 1) P. Mathew, A. Neels, and M. Albrecht, J. Am. Chem. Soc. 2008, 130, 13534
- 2) G. Guisado-Barrios, J. Bouffard, B. Donnadieu, and G. Bertrand, Angew. Chem. Int. Ed. 2010, 49, 4759
- 3) K. F. Donnelly, A. Petronihlo and M. Albrecht, Chem. Commun., 2013, 49, 1145
- 4) D. I. Bezuidenhout, G. Kleinhans, G. Guisado-Barrios, D. C. Liles, G. Ung and G. Bertrand, Chem. Commun., 2014, 50, 2431
- 5) G. Kleinhans, M. Hansmann, G. Guisado-Barrios, D.C. Liles, G. Bertrand and D. I. Bezuidenhout, J. Am. Chem. Soc. 2016, 138, 15873
- 6) G. Kleinhans, G. Guisado-Barrios, D. C. Liles, G. Bertrand and, D. Bezuidenhout, Chem. Commun., 2016, 52, 3504
- 7) I. Strydom, G. Guisado-Barrios, I. Fernández, D. C. Liles, E. Peris and D. I. Bezuidenhout, Chem. Eur. J. 2017, 23, 1393

EXPLORING CATALYTIC SPACE

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Organometallic reagents and transition metal catalysts are continuously at the frontier in the search for novel reactivity and synthetic methodology. Controlling chemo- and stereo-selectivity and low E-factor methods offer major challenges while novel approaches toward dynamic functions controlled by catalysis and transformations in aqueous media emerge. In this lecture various approaches to address these challenges will be discussed. Specific topics will be catalytic enantioselective allylation, Murahashi-Feringa cross coupling with organolithium reagents, sustainable low-E-factor transformations and adaptive catalysts.

METALS, MACROCYCLES, AND SMALL MOLECULES: A TALE OF BOND BREAKING AND FORMATION

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Metal-ion redox cooperativity is an underlying presupposed principal for the activation of small molecules by multimetallic cofactors in proteins and by metal surfaces. To delineate the principles that govern this cooperativity requires organic ligands to template specific metal binding sites and enforce metal-metal separations. In particular, there is a limited understanding of the reactivity of metal clusters coordinated by weak-field ligands, which is typical for metal cluster cofactors in biological systems. To that end, we have targeted cyclophanes bearing β -diketiminate arms as our preferred ligand type because of the constraints imposed by the macrocycle defined the inter-metallic distance while simultaneously affording a predictable coordination environment. Results from our ongoing reactivity studies of these multimetallic complexes with dinitrogen, dioxygen, carbon dioxide, and related substrates will be presented.

FIRST ROW TRANSITION METAL MABIQ COMPLEXES AS (PHOTO)CATALYSTS FOR SMALL MOLECULE CHEMISTRY

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Inorganic photocatalysts are essential to the development of artificial photosystems and the concomitant generation of solar fuels. As part of our efforts to generate new earth-abundant photocatalysts, we have developed a series of mono- and bimetallic complexes, based on a macrocyclic biquinazoline ligand, Mabiq. The series includes complexes with formal oxidation states ranging from 0 to +3. The monometallic Co(II) complexes are able to evolve hydrogen upon reaction with proton sources under electrocatalytic conditions. The divalent metal-Mabiq complexes can be photoreduced to the formally monovalent forms, in the presence of appropriate sacrificial donors. Spectrosopic and DFT computational methods provide insight into the electronic structure, photochemical properties and reactivity of the compounds.

A DEEP CAVITAND RECEPTOR FUNCTIONALIZED WITH FE(II) AND MN(II) AMINOPYRIDINE COMPLEXES FOR BIOINSPIRED OXIDATION CATALYSIS.

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The mimicry of enzymatic catalysis with artificial systems has been a long standing goal of synthetic supramolecular chemistry.^{[1][2]} It is now widely accepted that, in order to rival the proficiency of enzymes, an artificial system must be built so that it defines a confined space where the substrate is isolated from bulk medium and exposed to direct contact with appropriate functional groups, a distinct feature of proteins and enzymes. Following this idea, we have developed a deep cavitand receptor functionalized with a bis(pyridyl)dipyrrolidine tetradentate ligand.^{[3][4]} Binding of divalent metal ions ($M^{2+} = Mn^{2+}$, Fe²⁺ and Zn²⁺) at the tetradentate ligand results in the formation of cavitand complexes $1 \cdot M(OTf)_2$. The complexes $1 \cdot M(OTf)_2$ (M = Fe(II) and Mn(II)) catalyze selective hydroxylation of aliphatic C-H bonds and epoxidation of olefins with hydrogen peroxide, exhibiting selectivity patterns consistent with the implication of high valent metal-oxo species. Furthermore, $1 \cdot Fe(OTf)_2$ reacts with IO₄⁻ to form an oxoiron(IV) complex $[1 \cdot Fe(O)]^{2+}$, without decomposition of the supramolecular container.



References

- 1) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Chem. Soc. Rev. 2014, 43, 1734-1787.
- 2) Meeuwissen, J.; Reek, J. N. H. Nat. Chem. 2010, 2, 615-621.
- 3) Olivo, G.; Cussó, O.; Borrell, M.; Costas, M. J. Biol. Inorg. Chem. 2017, 22, 425-452.
- 4) Oloo, W. N.; Que, L. Acc. Chem. Res. 2015, 48, 2612-2621.

PROTON-COUPLED ELECTRON TRANSFER IN CATALYSIS AND ENERGY CONVERSION

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Proton-coupled electron transfer (PCET) reactions play a vital role in a wide range of catalytic processes. This talk will focus on recent advances in the theory of PCET and applications to enzymes, molecular electrocatalysts, and nanoparticles. The quantum mechanical effects of the active electrons and transferring proton(s), as well as the motions of the proton donor-acceptor mode and solvent or protein environment, are included in a general theoretical formulation.^[1] This formulation enables the calculation of rate constants and kinetic isotope effects (KIEs) for comparison to experiment. Studies of the enzyme soybean lipoxygenase provide a physical explanation for the experimental observation of unusually large KIEs of up to 700 for C-H bond activation at room temperature. The calculations also elucidate the substantial impact of distal mutations on the magnitude and temperature dependence of the KIE in this enzyme.^[2] A combined experimental and theoretical study of a series of substituted benzimidazole-phenol model systems inspired by the Tyrz-His190 redox proton relay found in photosystem II provide insight into the physical principles underlying proton relays.^[3] Theory predicts a concerted two-proton transfer process associated with the electrochemical oxidation of the phenol, accompanied by a decrease in the redox potential of the phenol and a small KIE, when the benzimidazole substituents are strong proton acceptors such as primary or tertiary amines. Electrochemical, spectroelectrochemical, and KIE experiments are consistent with these predictions. Recent calculations on photoreduced zinc oxide nanocrystals have elucidated the effects of proton diffusion between sites within the nanocrystals as well as the nature of PCET to the nitroxyl radical TEMPO.^[4,5] This wide variety of applications illustrates the diversity and complexity of PCET in catalysis.

References

- 1) S. Hammes-Schiffer, J. Am. Chem. Soc. 2015, 137, 8860.
- 2) A. V. Soudackov, S. Hammes-Schiffer, Faraday Discuss. 2016, 195, 171.
- 3) M. T. Huynh, S. J. Mora, M. Villalba, M. E. Tejeda-Ferrari, P. A. Liddell, B. R. Cherry, A.-L. Teillout, C. W. Machan, C. P. Kubiak, D. Gust, T. A. Moore, S. Hammes-Schiffer, and A. L. Moore, ACS Cent. Sci. 2017, 3, 372.
- 4) S. Ghosh, J. Castillo-Lora, A. V. Soudackov, J. M. Mayer, and S. Hammes-Schiffer, Nano Lett. 2017, 17, 5762.
- 5) S. Ghosh, A. V. Soudackov, and S. Hammes-Schiffer, ACS Nano 2017, 11, 10295.

CATALYSIS BY GOLD(I) COMPLEXES: LIGAND AND ANION EFFECTS

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Gold(I) complexes have emerged in the last few years as excellent carbophilic Lewis acids that are able to activate the unsaturated C-C bonds (alkynes, allenes and alkenes) with outstanding efficiency towards the attack of a large variety of nucleophiles, thus enabling a broad range of transformations.^[1] The distinctive features of gold catalysis rely on the fact that reactions are promoted under milder conditions than other transition metal catalysts, lower temperatures, shorter reaction times and more tolerant to air and moisture and on attractive properties such as low toxicity and environmental benign nature. Several factors can potentially control the outcome of a gold-catalyzed reaction, such as the nature of the ligand, the use of additives, the choice of the counterion, the structure of the catalyst, etc. Abundant empirical information on these effects is now available, but a deep understanding is still lacking. The computational approach represents an important breakthrough towards a rational design of catalysts and reaction conditions, with ultimately predictive power. Based on DFT investigations, we provide here a clear picture of how ligands^[2] and anions^[3] influence the mechanisms of some key gold-catalyzed reactions.

a) A.S.K. Hashmi, Chem. Rev. 2007, 107, 3180; b) A. Arcadi, Chem. Rev. 2008, 108, 3266; c) D.J. Gorin, B.D. Sherry, F.D. Toste, Chem. Rev. 2008, 108, 3351; d) E. Jimenez-Nunez, A.M. Echavarren, Chem. Rev. 2008, 108, 3326.

a) C.A. Gaggioli, G. Ciancaleoni, L. Biasiolo, G. Bistoni, D. Zuccaccia, L. Belpassi, P. Belanzoni, F. Tarantelli, *Chem. Commun.* 2015, 51, 5990; b) C.A. Gaggioli, G. Ciancaleoni, D. Zuccaccia, G. Bistoni, L. Belpassi, F. Tarantelli, P. Belanzoni, *Organometallics* 2016, 35, 2275.

a) G. Ciancaleoni, L. Belpassi, D. Zuccaccia, F. Tarantelli, P. Belanzoni, ACS Catal 2015, 5, 803; b) M. Gatto, P. Belanzoni, L. Belpassi, L. Biasiolo, A. Del Zotto, F. Tarantelli, D. Zuccaccia, ACS Catal. 2016, 6, 7363; c) L. D'Amore, G. Ciancaleoni, L. Belpassi, F. Tarantelli, D. Zuccaccia, P. Belanzoni, Organometallics 2017, 36, 2364.

UNDERSTANDING THE ACTIVE ROLE OF THE OXIDANT IN THE OXIDATIVE COUPLING OF BENZOIC ACID AND ALKYNE

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Oxidative coupling reactions have emerged in the last years as an alternative to the classic cross-coupling reactivity. Although both share similarities, the oxidative version does not require prefunctionalization of the substrate. This fact, in conjunction with the presence of an oxidant to regenerate the catalytic cycle, expands the possibilities of couplings in new synthetic methodologies. However, the mechanistic knowledge of these reactions is still vastly unexplored and it is totally needed to develop new reactions in a rational way.

One of the main questions in oxidative coupling reactivity is the role of the oxidant. For example, in the oxidative coupling of benzoic acid and alkynes reported by Miura and Satoh, they found that the reaction is totally chemoselective when $Cu(OAc)_2$ is used as the oxidant and the reaction yields mixture when the oxidant is Ag(OAc).^[1,2]

Herein, we present a comprehensive theoretical study of this reaction, emphasizing the effect of the oxidant along the reaction pathway. We demonstrated that a collaborative model successfully explains the chemoselectivity of the reaction through the cooperative reductive elimination (CRE) pathway.^[3] In addition, we expanded this model to a ruthenium catalyzed oxidative coupling, where kinetic experiments confirms the cooperation in the rate determining step.



References:

- 1) K. Ueura, T. Satoh, M.Miura, Org. Lett. 2007, 9, 1407
- 2) K. Ueura, T. Satoh, M.Miura, J. Org. Chem. 2007, 72, 5362
- 3) I. Funes-Ardoiz, F. Maseras, Angew. Chem. Int. Ed. 2016, 55, 2764

Au(I)/Au(III) CATALYZED ARYLATION OF Csp²-H BONDS

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Oxidative addition is well established for late transition metals, but extremely rare in gold chemistry. Until now, catalytic cross-coupling reactions mediated by gold complexes required the use of stoichiometric amounts of strong external oxidants to promote Au(I) to Au(III) oxidations, or the use of strong electrophiles under photochemical conditions.¹

Our group has explored the reactivity of gold complexes toward elementary steps of transition metal catalysis,ⁱ and has shown that appropriate ligand design enables C-X oxidative addition reactions to be achieved with gold under mild conditions, opening the way to new reactivity patterns. We have recently demonstrated that hemi-labile (P,N) bidentate ligands can provide a suitable balance between reactivity and stability of the key Au(III) species.ⁱⁱ The derived cationic Au(I) complex readily promotes oxidative addition of a large scope of aryl iodides and bromides. The potential of (P,N) Au(I) complexes in Au(I)/Au(III) catalysis has also been demonstrated by the development of the first gold-catalyzed C-C cross-coupling from aryl halides.



We have recently obtained encouraging results in the C-H activation of indoles, giving rise to C3-arylated products, in contrast to other transition metal catalyzed systems.

- (a) L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *Science*, **2012**, 337, 1644; (b) G. Zhang, Y. Peng, L. Cui, L. Zhang, *Angew. Chem., Int. Ed.*, **2009**, 48, 3112; (c) M. N. Hopkinson, A. Tessier, A. Salisbury, G. T. Giuffredi, L. E. Combettes, A. D. Gee, V. Gouverneur, *Chem.-Eur. J.*, **2010**, *16*, 4739; (d) T. C. Boorman, I. Larrosa, *Chem. Soc. Rev.*, **2011**, *40*, 1910.
- 2) M. Joost, A. Amgoune, D. Bourissou, Angew. Chem. Int. Ed. 2015, 54, 15022.
- 3) A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, Nat. Commun. 2017, 8, 565.

PRODUCTION AND USAGE OF LIQUID SOLAR FUELS

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Sustainable and clean energy resources using solar energy are urgently required in order to solve global energy and environmental issues. This lecture focuses on the combination of production of liquid fuels such as formic acid and hydrogen peroxide using solar energy, so called liquid solar fuels rather than gaseous hydrogen, and their use in direct liquid fuel cells.^[1] In particular, photocatalytic production of hydrogen peroxide (H₂O₂) from seawater and dioxygen (O₂) in the air as a liquid solar fuel is combined with its usage in one-compartment H₂O₂ fuel cells.

We have developed a variety of photosynthetic reaction center models composed of organic electron donors and acceptors linked by covalent or non-covalent bonding, which undergo efficient charge separation and slow charge recombination.^[2] The efficient charge-separation step has been successfully combined with the catalytic water reduction step with earth-abundant metal catalysts to develop efficient photocatalytic hydrogen evolution systems.^[3] The photocatalytic oxidation of water with O₂ in the air to produce H₂O₂ has been achieved,^[4-6] together with the development of one-compartment H₂O₂ fuel cells.^[7-9] The photocatalytic oxidation of water with O₂ in the air with O₂ in the air was found to be enhanced significantly in seawater.^[10] Thus, the combination of the photocatalytic H₂O₂ production from seawater and O₂ using solar energy with one-compartment H₂O₂ fuel cells provides on-site production and usage of H₂O₂ as a more useful and promising liquid solar fuel than H₂.^[10,11] The solar-driven oxidation of H₂O by O₂ to produce H₂O₂ is also combined with catalytic oxidation of benzene by H₂O₂ to produce phenol, when the overall reaction is solar-driven hydroxylation of benzene by O₂, which is the greenest oxidant, with H₂O.^[12,13]

References

- 4) S. Fukuzumi, *Joule*, **2017**, *1*, 689.
- 5) S. Fukuzumi, K. Ohkubo, T. Suenobu, Acc. Chem. Res. 2014, 47, 1455.
- 6) S. Fukuzumi, D. Hong, Y. Yamada, J. Phys. Chem. Lett. 2013, 4, 3458.
- 7) S. Kato, J. Jung, T. Suenobu, S. Fukuzumi, Energy Environ. Sci. 2013, 6, 3756.
- 8) K. Mase, M. Yoneda, Y. Yamada, S. Fukuzumi, ACS Energy Lett. 2016, 1, 913.
- 9) S. Fukuzumi, Y.-M. Lee, W. Nam, Chem-Eur. J. 2018, 24, in press.
- 10) Y. Yamada, S. Yoshida, T. Honda, S. Fukuzumi, Energy Environ. Sci. 2011, 4, 2822.
- 11) Y. Yamada, M. Yoneda, S. Fukuzumi, Energy Environ. Sci. 2015, 8, 1698.
- 12) S. Fukuzumi, Y. Yamada, ChemElectroChem 2016, 3, 1978.
- 13) K. Mase, M. Yoneda, Y. Yamada, S. Fukuzumi, Nat. Commun. 2016, 7, 11470.
- 14) S. Fukuzumi, Y.-M. Lee, W. Nam, ChemSusChem, 2017, 10, 4264.
- 15) Y. Aratani, T. Suenobu, Y. Yamada, S. Fukuzumi, Inorg. Chem. 2016, 55, 5780.
- 16) J. W. Han, J. Jung, Y.-M. Lee, W. Nam, S. Fukuzumi, Chem. Sci. 2017, 8, 7119.



Predictive Catalysis: Transition-Metal Reactivity by Design

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Posters

[2+2+2] CYCLOADDITION OF ACETYLENE CATALYZED BY BIMETALLIC INDENYL FRAGMENTS: A MECHANISTIC DENSITY FUNCTIONAL STUDY

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The mechanistic aspects of the [2+2+2] cycloaddition of acetylene mediated by IndRh (Ind=(C₉H₇)⁻, indenyl anion) catalyst in the presence a second coordinated metal, i.e. Cr(CO)₃, have been investigated. A detailed exploration of the potential energy surfaces (PESs) was carried out by identifying intermediates and transition states using density functional theory (DFT) methodologies. For comparison, the monometallic parent systems CpRh and IndRh are included in the analysis. ^[1] The active center is rhodium nucleus, where the cycloaddition occurs. An analysis of inter-metal cooperative effects has been done to assess the role of the second metal center, that is chromium. The coordination of this latter metal to the benzene moiety may occur in syn or in anti-conformation. ^[2] This affects the energetics of the cyclo and also the mechanism. The reaction energies and barriers, the turn over frequency (TOF) ^[3] and the defined slippage parameter (a geometrical quantity related to the position of Rh with respect to the centroid of its coordinated cyclopentadienyl moiety) ^[4] of the complete catalytic cycles are discussed. In agreement with experiments ^[2], it emerges that the presence of the second metal favors the catalysis.

References

- (1) Orian, L.; Van Stralen, J.N.P.; Bickelhaupt, F.M. Organometallics 2007, 26, 3816–3830.
- (2) Ceccon, A.; Santi, S.; Orian, L.; Bisello, A. Coord. Chem. Rev. 2004, 248, 683-724.
- (3) Kozuch, S.; Shaik, S. Acc. Chem. Res. 2011, 44, 101-110.
- (4) Orian, L.; Swart, M.; Bikelhaupt, F.M.; ChemPhysChem 2014, 15,219-228.

IMINE METATHESIS CATALYZED BY A SILICA-SUPPORTED HAFNIUM IMIDO COMPLEX

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The well-defined silica-supported single-site metal $[(\equiv Si-O-)Hf(\eta^2-MeNCH_2)(\eta^1\sigma-NMe_2)(\eta^1\pi-HNMe_2)]$ was prepared by surface organometallic chemistry. Upon heating under dynamic vacuum the surface species evolved into an unprecedented hafnium complex, $[(\equiv Si-O-)Hf(=NMe)(\eta^1-HNMe_2)(\eta^1-NMe_2)]$. Both surface structures were characterized by microanalysis and the following spectroscopies: infrared, solid-state single and multiple quantum NMR, and extended X-ray absorption fine structure, all complemented by the advanced DNP-SENS characterization technique. The hafnium complex bearing methylimido fragments rapidly catalyzed imine metathesis under mild conditions.

References

1-Soldan, G., Aljuhani, M. A., Bootharaju, M. S., AbdulHalim, L. G., Parida, M. R., Emwas, A.-H., Mohammed, O. F. and Bakr, O. M. (2016), Gold Doping of Silver Nanoclusters: A 26-Fold Enhancement in the Luminescence Quantum Yield. Angew. Chem. Int. Ed. doi:10.1002/anie.201600267

2-Aljuhani M. A., Bootharaju M. S., Sinatra L., Basset J. M., Mohammed O. F., and Bakr O. M., Synthesis and Optical Properties of a Dithiolate/Phosphine-Protected Au 28 Nanocluster. J. Phys. Chem. C.DOI: 10.1021/acs.jpcc.6b10205.

COMBINING COMPUTATION AND SYNTHESIS IN CHIRAL LIGAND DESIGN: ESTABLISHING A STRUCTURE - SELECTIVITY RELATIONSHIP AND MECHANISTIC INSIGHTS.

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Prediction of ligand enantioselectivity prior to synthesis would be a cost and time effective way to develop new ligands. However, successful ligand development often relies on screening as many candidates as possible.^[1] Understanding the interactions that give rise to asymmetric induction is key to the rational design and improvement of chiral catalysts. This knowledge is derived from mechanistic studies, both experimental and theoretical, and most recently through the application of free energy relationships, which relate the effects of catalyst, ligand or substrate structural modifications to enantioselectivity in a quantitative way.^[2] The use of statistical and computational tools to aid our understanding of stereoselectivity of the system could also lead to meaningful prediction.^[3]

We present a experimental and computational investigation to aid ligand design in copper catalyzed conjugate addition to a challenging enone starting material; β -substituted cylclopentenones.^[4] A new asymmetric conjugate addition method was developed for β -substituted cylclopentenones to form quaternary centres using alkylzirconocene nucleophiles giving up to 97% yield and 92% ee.^[5] Key to the reaction's success was the design of chiral phosphoramidite ligands which was aided by a linear quantitative structure-selectivity relationship (QSSR). QSSR models were generated from the ligand screening data (a total of 36 ligands) which revealed electronic and steric parameters and led to the synthesis of more enantioselective ligands. DFT calculations of competing transition structures aids the interpretation of the electronic and steric terms present in the QSSR models.

References:

¹⁾ K. D. Collins, T. Gensch, F. Glorius. Nat. Chem. 2014, 6, 859–871.

a) M. S. Sigman, K. C. Harper, E. N. Bess and A. Milo, Acc. Chem. Res., 2016, 49, 1292–1301. b) R. Ardkhean, P. M. C. Roth, R. M. Maksymowicz, A. Curran, Q. Peng, R. S. Paton and S. P. Fletcher, ACS Catal., 2017, 7, 6729–6737

³⁾ a) Harper, K. C.; Bess, E. N.; Sigman, M. S. Nat. Chem. 2012, 4, 366–374.

⁴⁾ a) A. Alexakis, J. E. Bäckvall, N. Krause, O. Pàmies and M. Diéguez, Chem. Rev., 2008, 108, 2796–2823. b) K. W. Quasdorf and L. E. Overman, Nature, 2014, 516, 181–191.

⁵⁾ R. Ardkhean, M. Mortimore, R. S. Paton, S. P. Fletcher, Submitted.

DFT STUDY OF CO₂ ACTIVATION PROMOTED BY A CLASS OF THIOLATE-BRIDGED DI-IRON COMPLEXES WITH A [Cp*Fe(µ-SR)₂FeCp*] SCAFFOLD.

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Thiolate-bridged diiron clusters have been widely synthesized and structurally determined especially in the form of Fe₂S₂ clusters, due to their close similarity to hydrogenase active site.^[1] Only in recent years the idea of using such Fe₂S₂ systems as nitrogenases functional analogues has taken root. Indeed, diiron sulfide/thiolate compounds are also suitable candidates to replicate the minimal functional subunit of Mo(V)nitrogenase active site, the so called FeMo(V)-co.^[2] In this context, a class of systems with a common $[Cp^*Fe^{II}(\mu-SR)_2Fe^{II}Cp^*]$ (Cp^{*} = η^5 -C₅Me₅) scaffold has proved to possess excellent catalytic activity towards N-N bond reductive cleavage of nitrogenase-relevant substrates, such as hydrazine and derivatives.^{[3][4][5]} Additional interest in these bioinspired systems stems from the fact that nitrogenases are promiscuous enzymes, having the remarkable property of catalyzing the reduction of a series of substrates beside N₂, such as protons (to form H₂) and unsaturated hydrocarbons/CO (to form alkanes).^[6] The most fascinating "alternative" reducing reactivity is certainly that exerted towards CO₂, the more abundant greenhouse gas. In this scenario, it would be a fascinating and promising strategy to assess the proposed FeMo(V)-co analogues towards CO₂ activation and conversion, especially in light of the recent progresses in the field of noble-metalfree CO₂ homogeneous reduction.^{[7][8]} Thus, the present work aims to understand if, at least in principle, a CO₂ reduction reactivity could be retained or exhibited by biomimetic Fe₂S₂ systems, such as various [Cp*Fe^{II}(µ-SR)₂Fe^{II}Cp*] complexes. DFT has been used in order to study in detail CO₂ binding modes and affinity to these systems, with the aim of highlighting the role that this class of complexes plays in CO₂ activation. Additionally, theoretical studies regarding putative electrochemical/chemical reductive applications will be also proposed.

References:

- 1) Tard C., Pickett C.J., Chem. Rev. 2009, 109, 2245.
- 2) Hoffman B.M., Dean D.R., Seefeldt L.C., Acc. Chem. Res. 2009, 42, 609.
- 3) Li Y.Y., Wang B., Luo Y., Tong P., Zhao J., Luo L., Zhou Y., Chen S., Cheng. F, Qu J., Nat. Chem. 2013, 5, 320.
- 4) Chen Y., Zhou Y., Chen P., Tao Y., Li Y., Qu J. J. Am. Chem. Soc. 2008, 130, 15250.
- 5) Yuki M., Miyake Y., Nishibayashi Y. Organometallics, 2012, 31, 2953.
- 6) Rebelein J.B., Hu Y., Ribbe M.W., ChemBioChem, 2015, 16, 1993.
- 7) Federsel C., Boddien A., Jackstell R., Jennerjahn R., Dyson P.J., Scopelliti R., Laurenczy G., Beller M., Angew. Chem. 2010, 49, 9777.
- 8) Langer R., Diskin-Posner Y., Leitus G., Shimon L.J.W. Ben-David Y., Milstein D., Angew. Chem. 2011, 50, 9948.
SYNTHESIS OF OPEN-CAGE FULLERENE DERIVATIVES BY RHODIUM(I)-CATALYZED [2+2+2] CYCLOADDITION OF C₆₀ AND DIYNES

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Since the discovery of C_{60} in 1985 [1], fullerenes have attracted the attention of chemists due to their unique structure, properties and reactivity, along with their potential applications in a variety of fields ranging from materials science to biomedicine [2–5]. Many functionalized fullerene derivatives resulting from the structural modification of the fullerene cage have been reported over the last 30 years. Specifically, fullerene derivatives resulting from cycloaddition reactions involving [6,6] junctions of C_{60} have been reported [6]. The preparation of cyclohexadiene-fused C_{60} derivatives can be achieved by [2+2+2] cycloaddition reactions of C_{60} with alkynes [7–9]. These compounds have been found to be important intermediates in the synthesis of so-called open-cage fullerenes [10]. Here, we report the first example of [2+2+2] cycloaddition involving C_{60} and diynes under catalytic conditions promoted by a rhodium(I) catalyst, which leads to the formation of a series of open-cage bisfulleroids. The products obtained can be subjected to oxidative cleavage when exposed to light and O_2 . Additionally, further derivatisation by Suzuki-Miyaura cross-coupling reaction has also been achieved. The mechanism of the process has been studied by means of DFT calculations [11].



[1] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. Nature 1985, 318, 162.

[2] Langa, F.; Nierengarten, J. F. Fullerenes: principles and applications. 1st ed., Royal Society of Chemistry, Cambridge, 2011.

[3] Yan, W.; Seifermann, S. M.; Pierrat, P.; Bräse, S. Org. Biomol. Chem. 2015, 13, 25.

[4] Bagchi, D.; Bagchi, M.; Moriyama, H.; Shahidi, F. *Bio-nanotechnology: a revolution in food, biomedical, and health sciences.* 1st ed., Wiley-Blackwell, Chichester, **2013**.

[5] Cataldo, F.; Da Ros, T. *Medicinal chemistry and pharmacological potential of fullerenes and carbon nanotubes*; 1st ed., Springer, Dordrecht, **2008**.

[6] Hirsch, A.; Brettreich, M. Fullerenes: chemistry and reactions. 1st ed., Wiley-VCH, Weinheim, 2005.

[7] Hsiao, T.-Y.; Santhosh, K. C.; Liou, K.-F.; Cheng, C.-H J. Am. Chem Soc. 1998, 120, 12232.

[8] Liou, K.-F.; Cheng, C.-H. J. Chem. Soc. Chem. Commun. 1995, 1603.

[9] Inoue, H.; Yamaguchi, H.; Suzuki, T.; Akasaka, T.; Murata, S. Synlett 2000, 1178.

[10] Vougioukalakis, G. C.; Roubelakis, M. M.; Orfanopoulos, M. Chem. Soc. Rev. 2010, 39, 817.

[11] Artigas, A.; Lledó, A.; Pla-Quintana, A.; Roglans, A.; Solà, M. Chem. Eur. J. 2017, 21, 5067

RATIONAL DESIGN OF TETRADENTATE TRANSITION METAL LIGANDS FOR ATMOSPHERIC PRESSURE AMMONIA SYNTHESIS

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Ammonia (NH₃) is one of the most important compounds produced in industry. NH₃ production adds up to approximately 140 million tons per year. Still, the production in its present form is not efficient. Converting N₂ to NH₃ via the Haber-Bosch process accounts for about 3% of the world's greenhouse gas emission and more than 1% of the world's annual energy consumption due to the high pressure and temperature (150-300 atm, 400-500°C). In order to produce ammonia in a more environment-friendly and energy efficient way, one should find a method that could operate at room temperature and atmospheric pressure.

Interestingly, microorganisms in nature can fix dinitrogen and produce ammonia at ambient conditions. Thus, it would be reasonable to mimic the active site of nitrogenase enzymes and design artificial catalysts that could be competitive alternatives to the Haber-Bosch process.

In this work we investigate recently synthesized biomimetic catalysts¹⁻³ with DFT methods to understand their catalytic activity. These complexes contain a central metal atom surrounded by tetradentate trisphosphino scorpionate ligands (Figure 1). In recent years numerous similar complexes have been successfully synthesized that reduce dinitrogen into ammonia in the presence of proton and electron sources at atmospheric pressure. Since the experimental characterization of the intermediates is challenging, the exact steps of the catalytic cycle are not clear yet. By studying the Gibbs free enthalpy profile, we determine the exact reaction paths of these catalysts and identify the critical steps. Our results indicate that the reduction of N₂ most likely proceeds via the so-called hybrid pathway (-N₂ \rightarrow -NNH₂ \rightarrow -NH₂NH₂ \rightarrow 2 NH₃) and that the thermodynamical driving force disappears in the last steps of the cycle (-NH₂NH₂ \rightarrow 2 NH₃). These observations enable the rational re-design of the obtained profile.

The exploration of the catalytic mechanism requires careful examination of the spin states of all intermediates as the molecular spin quantum number of the experimentally characterized structures ranges from 0 to 2. Thus, we computed all (theoretically) possible spin states of a given intermediate in order to find the thermodynamically most stable species. This process was preceded by extensive test calculations based on experimental data (e.g. Mössbauer spectra) to confirm the reliability of the chosen density functional.



Figure 1. Reduction of dinitrogen to ammonia by EPPP scorpionate complexes at atmospheric pressure.

References:

¹⁾ J. Rittle., J.C. Peters, J. Am. Chem. Soc., 2016, 138, 4243-4248.

²⁾ T. Del Castillo, N. Thompson, J. C. Peters, J. Am. Chem. Soc. 2016, 138, 5341-5350.

³⁾ M. Chalkley, T. Del Castillo, B. Matson, J. Roddy, J. C. Peters, ACS Central Science, 2017, 3, 217-223.

THE PREFERENCE FOR DUAL-GOLD(I) CATALYSIS IN THE HYDRO(ALKOXYLATION VS PHENOXYLATION) OF ALKYNES

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Dinuclear gold complexes and their use in catalysis have received significant recent attention, but there are few critical comparisons of mono- versus dual gold-catalysed pathways.^[1,2] In this work, we studied the hydroalkoxylation and hydrophenoxylation of alkynes using density functional theory (DFT) calculations, and we compared two possible mechanisms that had been proposed previously on the basis of theoretical and experimental studies (see Figure 1), which unravel different preferences because of both the nature of the alkyne and alcohol and the non-innocent role of the counter-anion of a dual gold based catalyst.^[3] Entropy was found to have a significant effect, rendering the nucleophilic attack of the monoaurated intermediate [Au(L)(n²-alkyne)]⁺ difficult both kinetically and thermodynamically; this mechanism cannot easily form only the transalkene product that is observed experimentally. Instead, a reaction via a dual-gold catalysed mechanism presents much lower barriers. In addition, for the sake of direct comparison with recent results by Belanzoni and Zuccaccia,^[4] oversimplification of the N-heterocyclic carbene (NHC) ligand in the calculations might decrease the enthalpy barrier and lead to results that are not directly applicable to experiments. Moreover, the alkylic or arylic nature of the alkyne and/or alcohol is also tested.



Figure 1. Mono and dual gold catalyzed hydrophenoxylation of alkynes.

- 1) M. H. Larsen, K. N. Houk, A. S. K. Hashmi, J. Am. Chem. Soc. 2015, 137, 10668-10676.
- A. Gómez-Suárez, Y. Oonishi, A. R. Martin, S. V. C. Vummaleti, D. J. Nelson, D. B. Cordes, A. M. Z. Slawin, L. Cavallo, S. P. Nolan, A. Poater, Chem. – Eur. J. 2016, 22, 1125-1132.
- 3) È. Casals-Cruañas, O. F. González-Belman, P. Besalú-Sala, D. J. Nelson, A. Poater, Org. Biomol. Chem. 2017, 15, 6416-6425.
- M. Trinchillo, P. Belanzoni, L. Belpassi, L. Biasiolo, V. Busico, A. D'Amora, L. D'Amore, A. Del Zotto, F. Tarantelli, A. Tuzi, D. Zuccaccia, Organometallics 2016, 35, 641-654.

REACTIVITY OF THE BINUCLEAR NON-HEME IRON ENZYME Δ⁹ DESATURASE FROM THEORETICAL PERSPECTIVE

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Mono and binuclear non-heme iron sites in proteins serve as efficient catalysts of a broad set of oxidation reactions including activation of unreactive aliphatic C–H bonds for subsequent desaturation, hydroxylation, halogenation, peroxidation, electrophilic aromatic substitution, etc. Soluble stearoyl-acyl carrier protein Δ^9 desaturase (Δ^9 D) - one of the most important enzymes in the fatty-acid metabolism of plants - is a prominent example of such class of enzymes. This diferrous non-heme iron enzyme is capable of inserting a double bond into an alkyl chain of stearic acid via double H-atom abstraction. Based on a thorough investigation of the initial stages of reaction mechanism of Δ^9 D reported earlier by our group,^[1,2] more detailed reaction pathways have been formulated and examined using QM(DFT)/MM methodology. Crucial reaction steps were then carefully validated, carrying advanced density matrix renormalization group (DMRG)/CASPT2, and multiconfiguration pair-density functional theory (MC-PDFT) calculations that were used to obtain an additional insight into the electronic structure and reactivity of studied system.

¹⁾ M. Srnec, T. A. Rokob, J. K. Schwartz, Y. Kwak, L. Rulíšek, E. I. Solomon, Inorg. Chem. 2012, 51, 2806-2820.

²⁾ J. Chalupský, T. A. Rokob, Y. Kurashige, T. Yanai, E. I. Solomon, L. Rulíšek, M. Srnec J. Am. Chem. Soc. 2014, 136, 15977-15991.

MECHANISTICALLY DRIVEN DEVELOPMENT OF AN IRON CATALYST FOR SELECTIVE SYN-DIHYDROXYLATION OF ALKENES WITH AQUEOUS HYDROGEN PEROXIDE

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Product release is the rate determining step in the arene syn-dihydroxylation reaction taking place at Rieske oxygenase enzymes, and is envisioned as a difficult problem to be resolved in the design of iron catalysts for olefin cis-dihydroxylation with potential utility in organic synthesis^[1] 1b Herein a novel catalyst bearing a sterically encumbered tetradentate ligand based in the tpa (tpa = tris-(2-methylpyridyl)amine scaffold, [Fell(CF3SO3)2(5-tips3tpa)], **1** has been designed.

The steric demand of the ligand was as a key element to support a high activity by isolating the metal center, bimolecular decomposition paths, and product release. In syneraistic with а Lewis acid that helps the product, 1 provides good to



envisioned catalytic preventing facilitating combination sequestering excellent

yields of syn-diol products (up to 97% isolated yield), in short reaction times under mild experimental conditions using a slight excess of aqueous hydrogen peroxide, from the oxidation of a broad range of olefins. Predictable site selective cis-dihydroxylation of diolefins is shown. The encumbered nature of the ligand also provides a unique tool that has been used in combination with isotopic analysis to define the nature of the active species and the mechanism of O-O lysis. Furthermore 1 is shown to be a competent synthetic tool for preparing O-labelled diols using water as oxygen source.

[1] (a) Feng, Y.; Ke, C.-y.; Xue, G.; Que Jr., L., Chem. Commun. 2009, (1), 50; (b) Chen, K.; Que Jr., L., Angew. Chem. Int. Ed. 1999, 38 (15), 2227

DESIGN AND SYNTHESIS OF CHIRAL LIGANDS USING MULTIVARIATE MODELLING

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Asymmetric catalysis is at the core of modern synthetic chemistry but catalyst design has been driven by trial-and-error processes for decades. New techniques have recently emerged such as high-throughput experimental screening^[1,2] and physical-organic approaches.

The latter is expected to give a faster and systematic route to new catalysts. In particular, the statistical analysis of multivariate models coupled with synthetic and mechanistic expertise shows promise.^[3] Combining these separate areas will permit the development of more valuable and time effective approaches to design new ligands in asymmetric catalysis.

In this work, we present the elaboration of experimentally validated quantitative structure selectivity relationships in order to discover, design and synthesize new chiral ligands for asymmetric catalysis.

This general rational approach to improve asymmetric induction has been applied to a copper-catalysed asymmetric conjugate addition of alkylzirconium nucleophiles. The addition initially proceeded in 59% yield with 33% ee^[4] and it now gives up to 99% yield and 92% ee. Our work shows that a systematic approach to catalyst design can be straightforward and effective.



- 1) Collins, K. D.; Gensch, T.; Glorius, F. Nat. Chem. 2014, 6 (10), 859.
- 2) McNally, A.; Prier, C. K.; MacMillan, D. W. C. Science 2011, 334 (6059), 1114.
- 3) Harper, K. C.; Sigman, M. S. J. Org. Chem. 2013, 78 (7), 2813.
- 4) Roth, P. M. C.; Fletcher, S. P. Org. Lett. 2015, 17 (4), 912.

AEROBIC ELECTROCHEMICAL OXYGENATION OF HYDROCARBONS

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Activation of molecular oxygen is one of the holy grails in catalysis. Without a catalyst, the reaction between O₂ and an organic substrate has a high activation barrier and it proceeds via a free radical mechanism bringing to complete oxidation.^[1] Nature inspires us with fascinating copper and iron metalloenzymes that utilize air at room temperature, paradoxically under reducing conditions. The mechanism of these enzymes has been widely investigated both in vivo or using complexes that mimic their active sites.^[2-9] Surprisingly, reduction via electrolysis of these enzymes or similar biomimetic catalysts has been only sparingly reported and do not lead to alkane oxidation.^[10-13] In our work an iron-tungsten porous capsule was used as catalyst to hydroxylate light alkanes and cleave C=C bonds in alkenes at room temperature. The first step of the catalysis is the reduction of the metal center via electrolysis, followed by O₂ activation and hydrocarbon oxidation. The experimental results as well as relevant mechanistic studies will be reported.



Figure. A polyhedral (left) and stick (middle) presentation of the iron-tungsten capsule, {Fe^{III}₃₀ W^{VI}₇₂}. Irongreen, tungsten-black, oxygen-red. Not shown are the 25 disordered sulfate/bisulfate ligands coordinated to W and Fe within the capsule that supply a protic environment and NH_4^+ cations on the outside of the capsule. The pore into the capsule is pointed to by the arrowed line, which is shown in more detail on the right.

- 14) F. R. Mayo, Acc. Chem. Res. 1968, 1, 193-201.
- 15) D. A. Quist, D. E. Diaz, J. J. Liu, K.D. Karlin, J. Biol. Inorg. Chem. 2017, 22, 253
- 16) S. Hong, Y. M. Lee, K. Ray, W. Nam, Coord. Chem. Rev. 2017, 334, 25
- 17) X. Engelmann, I. Monte-Perez, K. Ray, Angew. Chem. Int. Ed. 2016, 55, 7632
- 18) L. Que, W. B. Tolman, Nature 2008 455, 333
- 19) F. Nastri, M. Chino, O. Maglio, A. Bhagi-Damodaran, Y. Lu, A. Lombardi, Chem. Soc. Rev.2016, 45, 5020
- 20) X. Huang, J. T. J. Groves, Biol. Inorg. Chem. 2017, 22, 185
- 21) A. Trehoux, J.-P. Mahy, F. Avenier, Coord. Chem. Rev.2016, 322, 142
- 22) K.-B.Cho, H. Hirao, S. Shaik, W. Nam, Chem. Soc. Rev. 2016, 45, 1197
- 23) A. K. Udit, M. G. Hill, H. B., Gray, J. Inorg. Biochem. 2006,100, 519
- 24) T. Michida, C. Saiki, C. Yamasaki, Y. Yamaoka, Chem. Pharm. Bull. 2005, 53, 151
- 25) S. E. Creager, S. A. Raybuck, R. W. Murray, J. Am. Chem. Soc. 1986,108, 4225
- 26) C. P. Horwitz, S. E. Creager, R. W. Murray, Inorg. Chem. 1990, 29, 1006

PHOTOACTIVE METAL-ORGANIC FRAMEWORKS AS CO₂ REDUCTION CATALYSTS

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Metal-organic frameworks (MOFs) are coordination compounds that are characterized by high surface areas and permanent porosity, formed from a combination of organic linkers with inorganic nodes.^[1,2,3] This "buildingblock" approach, whereby premade units are assembled into a continuous network, is known as reticular synthesis. Interestingly, the properties of MOFs can be easily modified by fine-tuning these units, for example, the use of photosensitive ligands yields photoactive MOFs which can be used in catalytic reactions.^[4] Herein we show a series of new MOFs developed using a [Ru(bpy)₃]²⁺-derived photosensitizer ligand combined with different metal ions (Co(II), Ni(II) and Zn(II)). With the use of 9-borabicyclo[3.3.1]nonane (9-BBN) as a hydrogen source and activated by light, the Co-based MOF effectively catalyzes the reduction of CO₂ into HCOOH and formic acids, resulting in yields of 8% and 30% respectively. Postcatalytic characterization of the recovered MOF shows outstanding stability and reusability with no reduction of yield upon subsequent catalytic cycles. Moreover, we were able to deposit these MOFs on a FTO surface *via* both liquid-phase epitaxy and electrodeposition techniques, finding the later to be a more efficient approach, with film growth carried out in ambient conditions in 30-60 minutes for a typical cycle.



References

- 1) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, Science. 2013, 341, 1230444
- 2) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.Y. Su, Chem. Soc. Rev. 2014, 43, 6011-6061
- 3) N. Zhu, G. Tobin, W. Schmitt, Chem. Commun., 2012, 48, 3638-3640
- 4) Z.-M. Zhang, T. Zhang, C. Wang, Z. Lin, L.-S. Long, and W. Lin, J. Am. Chem. Soc. 2015, 137, 3197–3200

THE MOLECULAR BASIS OF R513 ARGININE RECOGNITION AND METHYLATION IN CARDIAC CONDUCTION DISEASE

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The biochemical modifications of proteins after translation (protein post-translational modifications, PTMs) are essential players modulating protein function. From a biomedical point of view, exploring the post-translational modification pattern of proteins can provide insight into the complexity of pathogenic mechanisms.^[1] Protein PTMs include e.g. phosphorylation, methylation, and acetylation, which are catalyzed by dedicated enzymatic machineries. Protein methylation consists on the transfer of a methyl group from the cofactor S-adenosyl-L-methionine (SAM) to the protein.^[2] Protein methylation occurs mostly at lysine and arginine residues, and is catalyzed by specific lysine and arginine methyltransferases (PRMTs).^[3] Voltage-gated ion channels underlie excitability of neurons and cardiomyocytes, and malfunctioning of voltage-gated ion channels leads heart diseases. Arginine methylation to cardiac conduction disease. A Na_v1.5 peptide including the mutation G514C, which is associated to cardiac conduction disease, completely abrogated R513 methylation by PRMT3. By means of molecular dynamics simulations significant conformational differences were observed between the wild type Na_v1.5 peptide and the Na_v1.5 peptide including the G514C mutation.^[4] However, the molecular basis of the interaction between these two Na_v1.5 peptides and PRMT3 and the specific role of the G514C mutation in cardiac conduction disease is still unexplored.

In this project we aim to perform molecular dynamics (MD) and accelerated MD simulations to investigate the molecular basis of R513 recognition and methylation by PRMT3 and to reconstruct the process of biomolecular recognition that involve the Na_V1.5 peptide and PRMT3. In addition, we analyze the role of an allosteric drug on the conformational dynamics of the enzyme. Conformational dynamics of PRMT3 will be assessed using the shortest-path map recently introduced in our group.^[5]

References:

2) C. N. Pang, E. Gasteiger, M. R. Wilikins, BMC Genomics 2010, 11, 92

¹⁾ S. Li, L. M. lakoucheva, S. D. Mooney, P. Radivojac, Pac. Symp. Biocomput. 2010, 337

³⁾ A. J. Bannister, A. J. Schneider, T. Kouzarides, Cell 2002, 109, 801

⁴⁾ P. Beltrán-Álvarez, F. Feixas, S. Osuna, R. Díaz-Hernández, R. Brugada, S. Pagans, Amino Acids 2015, 47, 429

⁵⁾ A. Romero-Rivera, M. Garcia-Borràs, S. Osuna, ACS Catal 2017, 7, 8524

STUDY OF AG(I)/AG(III) TWO-ELECTRON REDOX CHEMISTRY IN CROSS-COUPLING REACTIONS

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Transition metal catalyzed cross-coupling reactions are a powerful tool for C-C and C-heteroatom bond formation. A myriad of metals has been studied to catalyze these transformations.^[1] Silver has a relevant role in homogenous catalysis for organic synthesis due to its Lewis acidity and as a one-electron oxidant.^{[2],[3]}. Nevertheless, the two-electron redox chemistry, typically involved in cross-coupling reactions, has never deeply studied. Recently, our group reported the ability of silver to undergo Ag(I)/Ag(III) two-electron redox catalysis for C-C and C-O cross-coupling reactions within a macrocyclic model ligand.^[4] This discovery makes silver an even more attracting metal to work with. Thus, owing to this unprecedented reactivity, in this contribution the two-electron redox Ag(I)/Ag(III) mechanism behavior is transferred from macrocyclic models to a non-cyclic substrate bearing an aminoquinoline directing group, aiming at functionalizing the *ortho* C-X bond from aryl amides with a variety of nucleophiles, leading to the formation of C-C, C-O. C-N and C-X bonds.



References

C.C. C. Johansoon Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.* 2012, *51*, 5062-5085.
 J. M. Weibel, A. Blanc, P. Pale, *Chem. Rev.* 2008, *108*, 3149-3173.
 A. S. K. Hashimi, Silver in Organic Chemistry, ed. M. Harmata, John Wiley & Sons, Inc, Hoboken, NJ, USA, 2010.

4) M. Font, F. Acuña-Parés, T. Parella, J. Serra, J. M. Luis, F. Lloret-Fillol, M. Costas, X. Ribas, Nat. Commun. 2014, 5, 4373.

COMPUTATIONAL MODELING OF VERSATILE PHOTOSENSITIZERS

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Nowadays, the most available renewable energy source on the planet is sunlight. Therefore, one of the most prolific chemical research lines in photovoltaics cells consists in the search for dyes, molecules to be used in the so-called Dye-Sensitized Solar Cells (DSSC). Solar cells are a promising alternative to the silicon photovoltaic cells because they are easier to build and very economical. The challenge today is to improve the yield of DSSC in the transformation of sunlight into electricity.^[1] Dyes used in DSSC can also be used in Organic Light Emitting Diodes (OLEDs) devices and in the water splitting process.^[2]

In this project, we have studied the electronic structure of sixteen copper photosensitizers (three have been synthetized and characterized in the lab) using different density functionals in the framework of Time-Dependent Density Functional Theory (TDDFT).^[3] We have analyzed LC- ω PBE functional by optimizing the attenuating parameter (ω).^[4] Our results show the importance of the improvement of several properties upon optimization of ω , such as the simulation of UV-Vis absorption spectra and REDOX potentials. Research is underway in our laboratories to improve the adjustment of the computationally simulated absorption spectra and find new molecules that present a wider range of absorption.

References

- [1] S. Zhang, et al. Sci. **2013**, *6*, 1443.
- [2] J. Fillol, et al. Nat. Chem. **2011**, *3*, 807.
- [3] C. Latouche, et al., J. Chem. Theory Comput. **2015**, *11*, 3281.
- [4] O. S. Bokareva, et al., J. Chem. Theory Comput. 2015, 11, 1700.

ISOLATION AND CHARACTERIZATION OF AN ELUSIVE $\eta 2$ -[RU^{IV}-OO]²⁺ INTERMEDIATE AFTER THE O-O BOND FORMATION IN RU CATALYSED WO: THE MISSING LINK

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The application of artificial photosynthesis to store solar energy into chemical bonds is one of the major challenges of our society.^[1] Since water is abundant and its oxidation produces O₂ as by-product, it is the most attractive source of electrons to be used in large scale. However, WO has been identified as the bottleneck, because it requires very high redox potentials only bearable by few species. Therefore, to design more efficient and robust WOC it is necessary to understand the intermediates involved in either the activation of water and the O-O bond formation.



Figure 1. Generation of the intermediates involved in the WO catalytic cycle and the peroxo species formed after the O-O.

We recently reported a catalytic and mechanistic study of a Ru-WOC based on an aminopyridyl ligand,^[2] which pointed towards a high valent [Ru^V=O]³⁺ as the active species responsible for the O-O bond formation. DFT studies showed that after the O-O bond formation a [Ru^{III}-OOH]²⁺ is formed, yielding a closed shell η^2 -[Ru^{IV}-OO]²⁺ intermediate after a PCET, which would finally release O₂. There has been a extended discussion about the electronic and coordination nature of such postulated peroxo species.^[3] Herein we report the isolation and characterization of this elusive η^2 -[Ru^{IV}-OO]²⁺ intermediate under catalytic conditions: the missing link after the O-O formation that has nor been reported so far. Characterization of the isolated η^2 -[Ru^{IV}-OO]²⁺ intermediate by means of X-ray, EXAFS, NMR, IR, HRMS and DFT shows a closed-shell heptacoordinated structure with a side-on coordination of the peroxo moiety.

a) N. Lewis, D. G. Nocera, PNAS. 2006, 103, 15729; T. Moore et. al., Acc. Chem. Res. 2009, 42, 1890; b) C. Casadevall, A. Call, Z. Codolà, F. Acuña-Parés, J. Lloret-Fillol, An. Quím., 2016, 112 (3), 133.

²⁾ C. Casadevall, Z. Codolà, M. Costas, J. Lloret-Fillol, *Chem. Eur. J.* **2016**, 22, 10111.

³⁾ J. J. Concepcion et. al., J. Am. Chem. Soc. 2010, 132, 1545; E. Garand et. al., Angew. Chem. Int. Ed. 2016, 55, 4079.

EPOXIDE HYDROLASE CONFORMATIONAL HETEROGENEITY FOR THE RESOLUTION OF BULKY EPOXIDE SUBSTRATES

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The conformational landscape of *Bacillus megaterium* Epoxide Hydrolase (BmEH) and how it is altered by mutations that confer the enzyme the ability to accept bulky epoxide substrates has been investigated. ^[1] Extensive Molecular Dynamics (MD) simulations coupled to active site volume calculations have unveiled relevant features of the enzyme conformational dynamics and function. Our long-timescale MD simulations identify a key conformational state not previously observed by means of X-ray crystallography and short MD simulations that presents the loop containing one of the catalytic residues Asp239 in a wide-open conformation, ^[2] which is likely involved in the binding of the epoxide substrate. Introduction of mutations M145S and F128A dramatically alters the conformational landscape of the enzyme. These singly mutated variants are able to accept bulkier epoxide substrates due to the disorder induced by mutation in the alphahelix containing the catalytic Tyr144 and some parts of the lid domain. These changes impact the enzyme active site, which is substantially wider and more complementary to the bulky pharmacologically-relevant epoxide substrates.^[3]

References:

- 1) X.-D. Kong, Q. Ma, J. Zhou, B.-B. Zeng and J.-H. Xu, Angew. Chem. Int. Ed. 2014, 153, 6641-6644.
- 2) E. Serrano-Hervas, M. Garcia-Borras and S. Osuna, Org. Biomol. Chem. 2017, 15, 8827-8835.
- 3) E. Serrano-Hervas, Guillem Casadevall, M. Garcia-Borras, Feixas F, S. Osuna, submitted for publication 2018.

DEVELOPMENT OF VISIBLE-LIGHT METALLAPHOTOREDOX STRATEGIES TOWARDS THE CLEAVAGE OF C_{SP}³-CI BONDS

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Recent photoredox catalytic methodologies based on the visible-light-induced generation of highly reactive radicals have allowed the construction of a large variety of selective C-C and C-heteroatom bonds.^[1] Most of these novel photocatalytic protocols are limited to highly active aryl and alkyl bromides and iodides as coupling partners.^[2] The cleavage of unactivated Csp³-Cl bonds is a difficult transformation, as a high energy barrier needs to be overcome. The inertness of chloroalkanes has precluded them as prevailing coupling partners in both conventional and photocatalytic cross-coupling reactions. Thus, the development of earth-abundant metal-based catalytic systems that enable the activation of Csp³-Cl bonds in combination of light might open a sustainable venue for employing readily available, inexpensive and bench-stable chloroalkanes in bond-forming reactions.

Herein we present our efforts to achieve the activation of chloroalkanes by means of a dual metal catalytic system: a photoredox copper complex, which has a moderate reduction potential, in combination with a cobalt or nickel coordination complex. The *in-situ* photogeneration of an open-shell low valent cobalt or nickel intermediate bearing penta- or tetracoordinate nitrogen-based ligands is a key design element to enable the activation of unactivated Csp³-Cl bonds. This approach has been employed to unveil a sustainable synthetic protocol towards the construction of carbocycles via intramolecular reductive cyclization of chloroalkanes that bear tethered alkene or alkyne moieties.^[3] The disclosed methodology shows broad functional group tolerance and operates under mild reaction conditions.^[4]



- a) K. L. Skubi, T. R. Blum, T. P. Yoon Chem. Rev. 2016, 116, 10035. b) J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan Nat. Rev. 2017, 1, 0052.
- 2) C. P. Johnston, R. T. Smith, S. Allmendinger, D. W. C. MacMillan Nature 2016, 536, 322.
- Examples of reductive cyclizations with alkyl bromides: a) H. Kim, C. Lee Angew. Chem. Int. Ed. 2012, 51, 12303. b) G. Revol, T. McCallum, M. Morin, F. Gagosz, L. Barriault Angew. Chem. Int. Ed. 2013, 52, 13342.
- 4) F. Ungeheuer, M. Claros, A. Casitas, J. Lloret-Fillol manuscript in preparation.

THE IMPACT OF DIAMINE BACKBONES ON C-H OXIDATION CATALYZED BY FE AND MN AMINOPYRIDINE COMPLEXES

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C-H oxidation represent a powerful method to transform large available hydrocarbons or complex natural products in valuable oxygenated building blocks. However, due to the inert nature of C-H bonds and their ubiquitous presence in organic molecules an efficient, selective and mild oxidation protocol is highly desired.^[11] Bioinspired aminopyridine based Mn and Fe complexes have been found to fulfill these requirements. The metal-oxo, generated in presence of H₂O₂ and carboxylic acid, is able to oxidize C-H bond for synthetic purposes.^[2] In most cases C-H site selectivity is dictated by the innate properties of C-H bonds^[1] but the electronic and steric properties of these catalyst can be tuned in order to shift the selectivity toward different sites. Recently, Font et al^[3] reported Fe catalysts in which the bulky tris-(isopropyl)silyl (TIPS) groups on the pyridine rings lead to remarkable regioselectivity in the oxidation of aliphatic substrates. Furthermore, these bulky groups enhanced the influence of the diamine backbone on the oxidation site selectivity. Following this work, herein we report the effect of systematic modification of N-alkyl group in ^{TIPS}MCP based complexes on the selectivity of the oxidation of model substrates.



Figure 1 a) Scheme of Iron and Manganese Complexes studied. b) Oxidation of trans-decalin as model substrate.

- 1) T. Newhouse, P. S. Baran, Angew Chem. Int. Ed. 2011, 50, 3362.
- 2) Z. Codolà, J. Lloret-Fillol, M. Costas in Prog. in Inorg. Chem. 2014, 447.
- 3) D. Font, M. Canta, M. Milan, O. Cussò, X. Ribas, R. J. M. Klein Gebbink, M. Costas, Angew. Chem. Int. Ed., 2016, 55, 5776-5779

CHIRAL IRON AND MANGANESE COMPLEXES WITH N4-TETRADENTATE LIGANDS AS CATALYSTS FOR ASYMMETRIC EPOXIDATION WITH AQUEOUS H₂O₂

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The selective oxofunctionalization of hydrocarbons is an important transformation in many biological and industrial processes.^[1] Considerable efforts have been invested in the discovery of simple and efficient catalyst systems that perform these reactions with non-toxic reagents. Biological systems have unique capabilities in this regard, so the biomimetic approach represents an attractive strategy.^[2] In effect, numerous synthetic iron and manganese catalyst with nonporphyrinic ligands modeling the catalytic performance of non-heme metal-containing monooxygenases have been reported and intensively investigated in the last two decades.^{[2][3]}

The nature of active sites was critical for the rational design of biomimetic catalysts and the complexes that use N4-donor ligands (**Figure 1**) are shown as one of the most successful catalysts for chemo-, regio- and enantioselective transformations with peroxide type oxidants. So far, asymmetric epoxidation is targeted as the reaction of interest because chiral epoxides are versatile building blocks in synthetic chemistry.^[4]

This work is focused on the elaboration of a new family of aminopyridine and aminobenzimidazol tetradentate ligands, and their corresponding iron and manganese complexes for their use in asymmetric epoxidation catalysis with H2O2 as terminal oxidant for substrates that remain difficult for current oxidation technologies.



Figure 1: Schematic representation of metal complexes with N4 ligands.

References

- 1) T. Newhouse, P. S. Baran. Angew. Chem. Int. Ed. 2011, 50, 3362.
- 2) L. Que, W. B. Tolman. Angew. Chem. Int. Ed. 2008, 455, 333.
- 3) a) K. Chen, L. Que, Jr. J. Am. Chem. Soc. 2001, 123, 6327. b) M. Costas, K. Chen, L. Que, Jr. Coord.Chem. Rev. 2000, 200, 517.
- 4) a) Y. Zhu, Q. Wang, R. G. Cornwall, Y. Shi. Chem. Rev. 2014, 114, 8199. b) O. Cussó, X. Ribas and M. Costas. Chem. Commun., 2015, 51, 14285.

DEVELOPMENT OF VISIBLE-LIGHT REDUCTIVE CYCLIZATION REACTIONS FROM UNACTIVATED CHLOROALKANES

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Free-radical generation from organohalides is among the most

useful means to access an open-shell reactive intermediate that has found numerous applications in chemical synthesis.^[1] The development of new strategies of free-radical generation avoids the use of highly toxic, environmentally hazardous or explosive reagents such as alkyl-stannanes or boranes.^[2,3] A good alternative to the use of these reagents is the visible-light photocatalysis utilizing photoactive transition-metal complexes. ^[4-6] In contrast to classical cross-coupling reactions, which rely on two-electron elementary steps, photoredox and metal dual catalysis takes advantage of the ability of first-row transition metals (TMs) to participate in single-electron transfer reactions. In this regard, nickel is at the forefront of photoredox metal dual catalysis, while the rest of the first row TMs pass unnoticed in this field. Thus, we used a family of photogenerated cobalt(I) complexes based on pentacoordinated polyaminopyridyl ligands that enable reductive cyclizations of unactivated chloroalkanes. The use of copper photoredox catalyst, instead of typical Ru and Ir polypyridyl complexes, makes the developed process appealing for green radical cyclizations. The discovery of highly robust and selective catalytic systems is speeded up by using a parallel photoredox screening platform for high-throughput experimentation.

Et₃N⁻⁺

Co

5mol

 Et_3N

Cu

2mol%

MeCN : EtOH (0,8 : 1,2) 30 °C, 24 h



- 2) Studer, A.; Amrein, S. Angew. Chem., Int. Ed. 2000, 39, 3080.
- 3) Parsons, A. Chem. Br. 2002, 38, 42.
- 4) Tellis, J. C.; Primer, D. N.; Molander, G. A. Science **2014**, 345, 433.
- 5) Zuo, Z.; Ahneman, D. T.; Chu, L.; Jack A. Terrett; Doyle, A. G.; MacMillan, D. W. C. Science 2014, 345, 437
- 6) Shaw, M. H.; Shurtleff, V. W.; Terrett, J. A.; Cuthbertson, J. D.; MacMillan, D. W. C. Science 2016, 352, 130





Science and

CHARACTERIZATION AND REACTIVITY STUDIES OF AN IRON(II)-SUPEROXO SPECIES

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Iron-containing mentalloenzymes are throughout the natural world and they participate in vital oxidative processes involving the activation of O₂. Thanks to the efforts carried out by many research groups the structure of many of these enzymes (e.g. cytochrome P450, Rieske dioxygenases) is now well established. Moreover, extensive mechanistic studies have been carried out on synthetic iron-oxygen adducts (e.g. iron(IV)-oxo, iron(III)-hydroperoxo and iron(III)-peroxo) mostly formed using artificial oxidants such as iodosylarenes (PhIO), peroxy acids (*m*CPBA) and hydroperoxides (H₂O₂) and only rarely by dioxygen^[1] activations.

Herein, we describe the preparation and characterization of an iron-dioxygen intermediate, whose electronic structure can be best defined as containing a superoxo unit attached to an iron(II)-center.^[2] Notably, examples of iron(II)-superoxide cores are extremely rare in the literature,^[3] although they have often been proposed as a reactive intermediate in biological oxidation reactions.

¹⁾ Y. Nishida, Y.-M. Lee, W. Nam, S. Fukuzumi, J. Am. Chem. Soc. 2014, 9136, 8042.

²⁾ I. Monte-Pérez, X. Engelmann, Y.-M- Lee, M. Yoo, E. Kumaran, E. R. Farquhar, E. Bill, J. England, W. Namm, M. Swart, K. Ray, Angew. Chem. Int. Ed. 2017, 56, 14384.

³⁾ K. Duerr, J. Olah, R. Davydov, M. Kleimann, J. Li, N. Lang, R. Puchta, E. Hübner, T. Drewello, J. N. Harey, N. Jux, I. Ivanovic-Burmazovic, Dalton Trans. 2010, 39, 2049.

COMPUTATIONAL STUDY OF THE CONFORMATIONAL DYNAMICS OF A MONOAMINE OXIDASE FROM *ASPERGILLUS NIGER* (MAO-N) THROUGH MOLECULAR DYNAMICS SIMULATIONS AND MARKOV STATE MODELS

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Approximately 40% of pharmaceutical and agrochemical compounds are synthesized from enantiomerically pure amine building blocks, which are obtained by resolving the corresponding racemate via chemical reduction of the corresponding imine or by means of biocatalytic processes. However, only primary and some secondary amines can be obtained with good conversions and enantioselectivities. Monoamine oxidases are flavoproteins that produce amine oxidations and are present in humans (MAO-A and MAO-B), but also in lower organisms. In 2008, Turner and co-workers reported the crystal structure of a monoamine oxidase from the fungus *Aspergillus Niger* that resulted to be a promising biocatalyst for the resolution of racemic amine mixtures in combination with chemical reductants, even though it showed poor activity towards (S)-α-methylbenzylamine.^[11] Directed Evolution (DE) was later on applied obtaining: MAO-N-D3, MAO-N-D5, MAO-N-D9, and MAO-N-D11. MAO-N-D3 showed higher activity towards cyclic secondary amines, whereas MAO-N-D5 presented better results for the oxidation of cyclic secondary and tertiary amines. MAO-N-D9 and MAO-N-D11 were found to be the most active variants towards a huge range of substrates.^{[2],[3],[4]} In this context, we aim to evaluate the conformational dynamics of MAO-N and the laboratory evolved variants through conventional microsecond time-scale Molecular Dynamics (MD) simulations in combination with Markov State Models (MSM) to better understand how the enzyme conformational dynamics affect the active site volume and shape, the substrate access, and its substrate scope.

References:

- 1) Atkin, K. E.; Reiss, R.; Koehler, V.; Bailey, K. R.; Hart, S.; Turkenburg, J. P.; Turner, N. J.; Brzozowski, A. M.; Grogan, G. *J. Mol. Biol.* **2008**, 384 (5), 1218–1231.
- 2) Dunsmore, C. J.; Carr, R.; Fleming, T.; Turner, N. J. J. Am. Chem. Soc. 2006, 128 (7), 2224–2225.
- 3) Carr, R.; Alexeeva, M.; Dawson, M. J.; Gotor-Fernández, V.; Humphrey, C. E.; Turner, N. J. ChemBioChem 2005, 6 (4), 637–639.
- 4) Ghislieri, D.; Green, A. P.; Pontini, M.; Willies, S. C.; Rowles, I.; Frank, A.; Grogan, G.; Turner, N. J., *Journal of the American Chemical Society* **2013**, *135* (29), 10863-10869.

A HIGHLY REACTIVE OXOIRON(IV) COMPLEX SUPPORTED BY BIOINSPIRED N₃O MACROCYCLIC LIGAND

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Oxo-iron(IV) species are implicated as a key reactive intermediate in nonheme enzymes for the C-H bond cleavage.^[1] Of crucial interest are the roles of the spin state and of the supporting ligand^[2] in determining the reactivity towards dioxygen activation and hydrogen atom transfer (HAT). Recently, the reactivity of an oxo-iron(IV) center has been significantly enhanced upon replacement of an NMe donor in the N4 macrocycle of TMC (TMC=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and TMCN-d₁₂ (TMCN-d₁₂=1,4,7,11-tetra(methyl-d₃)-1,4,7,11-tetraazacyclotetradecane) ligands by an O-atom (TMC^{mod}).^[3] Herein, we investigate in detail the connection between the ligand structure, spin state and reactivity and how ligand modification affects the HAT energy profile for the reaction of [Fe^{IV}(O)(TMC^{mod})]²⁺ with cyclohexane in all available spin states.



References:

- 1) M. Costas, M.P. Mehn, M.P. Jensen, L. Que Jr. Chem. Rev. 2004, 104, 939
- 2) S. Hong, H. So, H. Yoon, K.-B. Cho, Y.-M Lee, S. Fukuzumi, W. Nam, Dalton Trans. 2013, 42, 7842
- 3) I.M. Pérez, X. Engelmann, Y.-M Lee, M. Yoo, K. Elumamai, E. R. Farquahr, E. Bill, J. England, W. Naam,
- M. Swart, K. Ray, Angew. Chem. Int. Ed. 2017, 56, 14384

RATIONAL DESIGN OF HALF-SANDWICH GROUP 9 CATALYSTS FOR [2+2+2] ALKYNES CYCLOADDITIONS

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Nowadays, modern computational facilities allow us to predict reactivity in *silico* and tackle molecular systems that are otherwise difficult to rationalize. In this work, state-of-the-art relativistic density functional (DFT) methodologies are employed to design catalytic fragments for the [2+2+2] alkynes/alkynes-nitriles cycloaddition to benzene/pyridine. The very good selectivity and the possibility to maintain a solvent-free environment make this type of reactions very attractive and justify the continuing investigations.¹ The catalyst's structure is Cp'M, where Cp' is the cyclopentadienyl ligand (Cp) or a more extended aromatic/heteroaromatic moiety, and M is a group 9 metal (Co, Rh, Ir). The singlet potential energy surface of the process is explored by locating all intermediates/transition states and the catalysts' performance is calculated in terms of turnover frequency (TOF), by implementing the equations of the energy span model.^{2,3} The different bonding mode of the substrate to the catalyst, and, vicariously, the nature of Cp'-M coordination, is investigated using the activation strain model (ASA) and energy decomposition analysis (EDA) in order to follow the metal displacement (slippage) and connect structural information with the energy.⁴ Commonly, the highly symmetric coordination of the metal to the aromatic ligand is never achieved, but the distortions during the cycle can be larger or smaller under different conditions (different metal center, changes in the aromatic ligand, presence of an additional ancillary ligand, etc.) and this fluxionality is found to significantly influence the overall efficiency.



References:

(1) Tanaka, K. *Transition-metal-mediated aromatic ring construction*; Wiley: Hoboken, New Jersey, 2013.

- (2) Kozuch, S.; Shaik, S. Acc. Chem. Res. 2011, 44 (2), 101–110.
- (3) Orian, L.; Wolters, L. P.; Bickelhaupt, F. M. Chem. Eur. J. 2013, 19 (40), 13337–13347.
- (4) Bickelhaupt, F. M.; Houk, K. N. Angew. Chem. Int. Ed. 2017, 56 (34), 10070–10086.

CHEMOSELECTIVE ALIPHATIC C-H BOND OXIDATION ENABLED BY POLARITY REVERSAL

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The selective oxidation of C-H bonds can be a useful tool in organic chemistry because it can lead to develop new synthetic strategies.^[1,2] Indeed, it makes possible the introduction of a new functional group through the manipulation of the ubiquitous C-H bonds allowing an improvement in the step and atom economy of the paths. Nevertheless, the functionalization of unactivated C-H bonds shows several drawbacks. Firstly, these highly energetic bonds are typically inert so harsh reaction conditions and/or toxic reagents are required. Moreover, the different aliphatic C-H bonds within a molecule show similar BDE thus the achievement of site-selective oxidation is challenging in absence of directing group. Lastly, the first-formed oxygenated products are more reactive than the substrate so is difficult to prevent overoxidation processes and to obtain high degree of chemoselectivity.

In this work^[3] we show that fluorinated alcohols exert a polarity reversal on electron rich functional groups, directing iron and manganese catalyzed oxidation^[4] towards a priori stronger and unactivated C–H bonds. As a result, selective hydroxylation of methylenic sites in hydrocarbons and remote aliphatic C–H oxidation of otherwise sensitive alcohol, amide and amine substrates is achieved employing aqueous hydrogen peroxide as oxidant (**Figure 1**).





References:

- 1) J. F. Hartwig, M. A. Larsen, ACS Cent. Sci. 2016, 2, 281
- 2) M. S. Chen, M. C. White, Science 2010, 327, 566
- 3) V. Dantignana, M. Milan, O. Cussó, A. Company, M. Bietti, M. Costas, ACS Cent. Sci. 2017, 3, 1350
- 4) Z. Codola, J. Lloret-Fillol, M. Costas, Progress in Inorganic Chemistry 2014, 59, 447-532

EXPLORATIONS OF WATER OXIDATION WITHIN AN EXPLICITLY SOLVATED ENVIRONMENT

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Water oxidation catalysis is a crucial process in any device designed to convert solar energy into storable chemical energy. The search for efficient and stable homogenous water oxidation catalysts remains a scientific challenge, especially when considering those based on abundant transition metals. Computational methods based on quantum chemical calculations do allow for significant insights into the relevant catalytic mechanisms, however it is becoming increasingly clear that explicit solvent molecules are needed to obtain realistic descriptions of these catalytic mechanisms. Here we analyse and evaluate, based on ab-initio molecular dynamics, the effects of a changing solvent environment on the water oxidation mechanism of a mononuclear ruthenium based water oxidation catalyst. Moreover, proton and electron acceptors are included within the simulation box to more closely represent experimental conditions. This allows for a more detailed description of proton-coupled electron transfer processes.

References:

- 1) J.M. de Ruiter and F. Buda. Phys. Chem. Chem. Phys. 2017, 19, 4208-4215
- 2) J.M. de Ruiter et al. ACS Catal. 2016, 6, 7340-7349
- 3) A. Monti et al. J. Phys. Chem. C 2016, 120, 23074–23082.

ENANTIOSELECTIVE RHODIUM(I)-CARBENE MEDIATED CASCADES

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Metal carbenes are important reaction intermediates capable of mediating in numerous reactions.^[1] Rh(II) carbenoids, formed by the decomposition of diazo compounds with Rh(II) dimers, have shown great potential in stereoselective transformations. On the other hand, Rh(I) complexes that are known to mediate various asymmetric reactions have been little explored in carbenoid-mediated processes. A remarkable reactivity of metallacarbenes and alkynes is their metathesis reaction to give vinylcarbenes that can subsequently react opening the door to cascade processes.^[2]

We present in this poster cascade reactions of divneary/sulfony/hydrazones,^[3a] envneary/sulfony/hydrazones^[3b] and alleneynearylsulfonylhydrazones^[3c] under rhodium(I)/BINAP catalysis, that give access to sulfonated azacyclic frameworks in a highly enantioselective manner.



References

- Contemporary Carbene Chemistry (Eds.: Moss, R. A.; Doyle, M. P.), John Wiley & Sons, Hoboken, 2014. 1)
- For a review, see: a) Torres, O.; Pla-Quintana, A. Tetrahedron Lett. 2016, 57, 3881-3891. 2)
- a) Torres, O.; Parella, T.; Solà, M.; Roglans, A.; Pla-Quintana, A. Chem. Eur. J. 2015, 21, 16240-16245; b) Torres, O.; Roglans, A.; Pla-3) Quintana, A. Adv. Synth. Catal. 2016, 358, 3512-3516; c) Torres, O.; Solà, M.; Roglans, A.; Pla-Quintana, A. Chem. Commun. 2017, 53, 9922-9925.

Poster 29 P29

DIRECT SYNTHESIS OF POLYARYLS BY CONSECUTIVE OXIDATIVE CROSSCOUPLING OF PHENOLS WITH ARENES

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A novel strategy to prepare polyaryls (masked polyphenols) by an iron-catalyzed substrate-directed consecutive oxidative cross-coupling reaction between phenols and arenes was developed. ^[1] This sustainable transformation offers a selective synthetic strategy for the preparation of complex polyaryl compounds directly from readily available phenols. Our structure-selectivity relationship study revealed that the regioselectivity (*ortho, meta* or *para*) and chemoselectivity (C-coupling or O-coupling) of the multi-step process is directed by the *ortho*-groups (Scheme 1). Our mechanistic study that included EPR investigation disclosed that the electron spin-density distribution of the phenoxyl radicals govern the observed selectivity of the reaction. Finally, this consecutive oxidative cross-coupling methodology was implemented as a biomimetic strategy for the synthesis of protected fucols and other biphenolic oligomers.^[2]



- 1) A. Dyadyuk, K. Sudheendran, Y. Vainer, V. Vershinin, A. I. Shames, D. Pappo, Org. Lett., 2016, 18, 4324–4327.
- 2) V. Vershinin, A. Dyadyuk, D. Pappo, *Tetrahedron*, 2017, 73, 3660-3668.

INSIGHTS INTO THE RNA APTAMER-DFHBI HOST-GUEST COMPLEXATION-INDUCED PHOSPHORESCENCE

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The use of fluorophores to perform *in vivo* labelling and imaging has been an emerging strategy for studying cellular physiology. In this field, one simple approach for introducing a fluorescent tag into living cells and bacteria is their combination with RNA aptamer-fluorophore complexes. The fluorophore is a nonfluorescent chromophore, 3,5-difluoro-4-hydroxybenzylidene imidazolinone (DFHBI), that binds to a genetically encoded RNA and as a result the complex becomes fluorescent.^[1,2,3] The RNA host is commonly known as Spinach, because of the green light emitted by the host-guest complex, and is formed by two parallel guanine quadruplexes where the planar fluorophore is embedded.^[4] However, the specific host-guest interactions that take place between the DFHBI and its binding site, together with the photophysical changes that induce fluorescence are not well known. For this reason, we characterize the Spinach-DFHBI binding process taking into account the two possible isomers (*cis/trans*) of the DFHBI.^[5] Our results aim to explain the lack of fluorescence for the *trans* form of FHBDI, as well as that of the unfluorinated HBDI chromophore, which turns fluorescent in the green fluorescent protein but not in the Spinach aptamer.^[6]

- 1) J. S. Paige, K. Y. Wu, S. R. Jaffrey, Science 2011, 333, 642-646.
- 2) H. Huang, N. B. Suslov, N.-S. Li, S. A. Shelke, M. E. Evans, Y. Koldobskaya, P. A. Rice, J. A. Piccirilli, *Nat. Chem. Biol.* 2014, 10, 686-U128.
- 3) R. L. Strack, Nat. Protoc. 2014, 9, 146
- 4) W. Song, R. L. Strack, N. Svensen, S. R. Jaffrey, JACS 2014, 136, 1198-1201.
- 5) K. Y. Han, B. J. Leslie, J. Fei, J. Zhang, T. Ha, JACS 2013, 135, 19033-19038
- 6) I. Petkova, G. Dobrikov, N. Banerji, G. Duvanel, R. Perez, V. Dimitrov, P. Nikolov, E. Vauthey J. Phys. Chem. A, 2010, 114, 10–20

CONFORMATIONAL DYNAMICS OF HALOHYDRIN DEHALOGENASE VARIANTS USING MOLECULAR DYNAMICS SIMULATIONS AND MARKOV STATE MODELS

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Many enzymes present in Nature could be potentially used to synthesize chemically relevant chiral intermediates for drugs. One example is the enzyme halohydrin dehalogenase (HHDH)^[1], which catalyzes the enzymatic conversion of ethyl (S)-4-chloro-3-hydroxybutyrate (ECHB) into the corresponding epoxide. In the presence of a chloride ion, the enzyme can also catalyze an epoxide ring opening reaction yielding ethyl (R)-4-cyano-3-hydroxybutyrate (HN)^[2-3], which is a precursor of Lipitor, a drug used for lowering the levels of cholesterol in blood. The natural enzyme exhibits a poor activity towards the second non-natural reaction, however Fox et al.[3] reported a ~4000-fold activity increase using directed evolution (DE), with the addition of several distal mutations. With the final aim of designing new improved variants, we rationalize the effect of the included mutations into the enzyme structure. In particular, Molecular Dynamics (MD) simulations coupled to correlation-based programs were performed to evaluate the conformational dynamics of the different DE rounds of mutant enzymes. Additionally, we use Markov State Models (MSM) to better sample the enzyme conformational dynamics, in order to extract relevant thermodynamic and kinetic data. By analyzing the different ensemble of conformations, their populations and rates of conversion we elucidate the role of the distal mutations introduced to HHDH, and how they improve the activity of the enzyme towards the new non-natural reaction.

de Jong RM. EMBO J. 2003, 22 (19), 4933-4944. (1)

(2) (3) Nakamura T. Biochem Biophys Res Commun. 1991, 180 (1), 124–130.

Fox RJ. Nat Biotechnol. 2007, 25 (3), 338-344.

ACCELERATING (BIO)MOLECULAR RECOGNITON AND SELF-ASSEMBLY

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Some important processes such as (bio)molecular recognition, protein folding or self-assembly, usually take place on the micro- to millisecond or even longer time scales. Low-energy states relevant for these processes may be separated by high-energy barriers, which are rarely crossed over the course of conventional molecular dynamics simulations. Accelerated molecular dynamics (aMD) enhances sampling through modification of the system's Hamiltonian in a relatively simple way.^[1,2,3,4] In addition, it does not rely on the definition of a reaction coordinate or a set of collective variables (a priori knowledge of the underlying free energy landscape is not needed), and it conserves the essential details of the free-energy landscape.

Here we focus on the potential of aMD as a tool to efficiently explore the rough free energy landscape of proteins and other molecules and its applications to: 1) the study of fullerene recognition in nano-cages and host-guest interactions in cavitands; 2) the study of the role of conformational dynamics in the redox conformational protection of nitrogenase

- 1) D. Hamelberg, J. Mongan, J.A. McCammon, J. Chem. Phys. 2004, 120, 11919
- 2) P.R. Markwick, J.A. McCammon, Phys. Chem. Chem. Phys. 2011, 13, 20053
- 3) F. Feixas, S. Lindert, W. Sinko, J. A. McCammon, Biophys. Chem. 2014, 186, 31
- 4) Y. Miao, F. Feixas, C. Eun, J. A. McCammon, J. Comp. Chem. 2015, 36, 1536

[(L^{№4})Co^I-CO], THE SINK RESTING STATE. LIGHT PROMOTES THE COBALT-CO BOND CLEAVAGE ENHANCING ELECTROCATALYTIC CO2 REDUCTION.

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In the last years, pyridine-based cobalt complexes have emerged as active catalysts in both photo- and electrochemical CO₂-to-CO reduction process.^[1] However, very few investigations have been addressed to understand the reaction mechanism and identify the limiting factors in the cobalt-catalyzed CO₂ electrochemical reduction.^[2]

Herein we report the electrochemical CO₂ reduction catalysis by a model cobalt complex based on the Py^{Me2}tacn ligand (L^{N4}).^[3] The combination of electrochemical and spectroscopic techniques, together with the computational modelling of the catalytic cycle, allowed us the characterization of the resting state; a highly stable [L^{N4}Co^I-CO]⁺ intermediate (Figure 1). We found that light irradiation improve the catalytic activity of the system. We rationalize the enhancement in catalysis due to Co-CO cleavage induced by a MLCT center in the CO ligand according to the TD-DFT analysis and matching with the wavelength of the light source.



Figure 1. Mechanistic proposal for the light-assisted electrochemical reduction of CO₂ and orbitals involved in the MLCT UV-vis band at λ = 377 - 429 nm.

- 1) M. B. Chambers, X. Wang, M. Fontecave, Chem. Soc. Rev. 2017, 46, 761.
- 2) F. Wang, B. Cao, W.–P. To, C.-W. Tse, K. Li, X.-Y. Chang, C. Zang, S. L.-F. Chan, C.-M. Che, Catal. Sci. Technol. 2016, 6, 7408.
- 3) A. Call, F. Franco, N. Kandoth, S. Fernández, M. González-Béjar, J. Pérez-Prieto, J. M. Luis, J. Lloret-Fillol, 2017, Submitted.

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STUDY OF THE ROLE OF THE SUBSTRATES AND NUCLEOPHILES IN GOLD-CATALYZED CROSS-COUPLING REACTIONS

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In the recent years, gold has experienced a fast development as a transition metal capable to undergo homogeneous catalytic transformations. Our group has developed oxidant-free halide exchange, C(sp²)-O and C(sp²)-N bond-forming cross-coupling reactions using different aryl halide platforms bearing chelating groups.^[1,2] These transformations were envisioned to be feasible thanks to a Au(I)/Au(III) 2-electron redox catalytic pathway and, in some cases, reactive Au(III) intermediates were isolated and characterized. The nucleophiles that showed to be compatible for cross-coupling include aromatic and aliphatic alcohols, water, amines, amides and even imidazole. In this work, we aim at understanding the features that make an aryl halide substrate a suitable candidate for such reactions, as well as expanding the scope of substrates and extending also the scope of nucleophiles to carboxylic acids and amino acids, among others. The coupling products obtained are characterized by NMR and ESI-HRMS.

1) J. Serra, C. J. Whiteoak, F. Acuña-Parés, M. Font, J. M. Luis, J. Lloret-Fillol, X. Ribas, J. Am. Chem. Soc. 2015, 137, 13389.

2) J. Serra, T. Parella, X. Ribas, Chem. Sci. 2017, 8, 946.



X = Br, I **Nu**H = ROH, RCOOH, RR'NH, RCONH₂, amino acids

STEREOSELECTIVE SYNTHESIS OF OPTICALLY PURE NOBINS BY OXIDATIVE COUPLING BETWEEN AMINONAPHTHALENES AND 2-NAPHTHOLS

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2-amino-2-hydroxy-1,1'-binaphthyl (NOBIN) compounds are important class of structural motif with axial chirality that are used as ligands and catalysts in asymmetric transformations.^[1] The preparation of optically pure NOBINs mainly relies on resolution or multistep synthesis starting from optically pure BINOLs.^[2-3] As part of our group's on-going research, we have developed a novel method for efficient synthesis of chiral NOBIN frameworks by direct oxidative coupling between aminonaphthalenes incorporated with a chiral auxiliary and 2-naphthols.

The resulted NOBIN diastereoisomers are separated over column chromatography and the chiral auxiliary can be easily removed to furnish each of the NOBIN enantiomers in gram scale.

References:

- 1) K. Ding, L. Xin, J. Baoming, G. Hongchao, K. Masato, Current Organic Synthesis, 2005, 47,499-545.
- 2) M. Smrcina, M. Lorenc, V. Hanus, P. Sedmera, P. Kocovsky, J. Org. Chem. 1992, 57 (6), 1917-1920.
- 3) D. Salinger, R. Bruckner, SYNLETT, 2009, 1, 109-111.

HIGHLY ACTIVE N-HETEROCYCLIC CARBENE MN(I) ELECTROCATALYSTS FOR CO₂ REDUCTION

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In the last decade, fac-[Mn(CO)₃(N^N)X]ⁿ complexes (X = Br, n = 0 and X = CH₃CN, n = +1; N^N = polypyridyl ligands) have been shown to be competent molecular catalysts for selective electrochemical conversion of carbon dioxide to CO.^[1-2] Nevertheless, the development of novel ligand frameworks for Mn based CO₂ reduction electrocatalysts is nowadays mainly restrained to ancillary functionalization of the bipyridyl motif, whose electron storage capability plays an essential role in stabilizing the accumulation of electron density over the metal complex.

We report here the first purely organometallic *fac*-[Mn(CO)₃(bis-MeNHC)Br] (1) complex with unprecedented activity for selective electrocatalytic CO₂-to-CO reduction. It revealed to highly outperform the corresponding single NHC-containing Mn catalyst, namely [Mn(CO)₃(py-MeNHC)I] (2), in terms of selectivity (faradaic yield = 95%), catalytic turnovers (>100) and maximum TOF (TOF_{max}~10³ s⁻¹) under CO₂ in anhydrous CH₃CN (see Figure 1). Moreover, the addition of water (0.56 M) produces an impressive TOF_{max} increase of 2 orders of magnitude (~320000 s⁻¹). Spectroelectrochemistry (SEC) and DFT calculations reveal a strong electron-density accumulation over the metal center upon reduction due to the redox-innocent nature of the C^C ligand, which is ascribed as the origin of the enhanced reactivity towards CO₂ reduction in comparison with N^N and N^C systems.^[3]



Figure 1. CVs of 1 (black) and 2 (grey) under Ar (dashed lines) and CO₂ (full lines) in 0.1 M TBAPF₆/CH₃CN.

References

1) H.Takeda, C. Cometto, O. Ishitani, M. Robert, ACS Catalysis 2017, 7, 70.

2) Bourrez, M.; Molton, F.; Chardon-Noblat, S.; Deronzier, A. Angew. Chem. Int. Ed. 2011, 123, 10077

3) F. Franco, M. F. Pinto, B. Royo, J. Lloret-Fillol, J. Am. Chem. Soc., 2017, submitted.

SELECTIVE SEPARATION OF FULLERENES AND ENDOHEDRAL METALLOFULLERENES MEDIATED BY SUPRAMOLECULAR NANOCAPSULES

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From the early stages of fullerene research, it was shown that fulerenes were in general able to host atoms and even small molecules in their interior.^[1] Generally, fullerenes and Endohedral Metallofullerenes (EMFs), which are produced as a soot, need to be purified by a multistage high-performance liquid chromatography (HPLC).^[2] However, this conventional purification process may not be used for the effective purification of milligrams quantity of fullerenes or EMFs. To overcome these difficulties, large efforts have been geared toward the design of an efficient alternative strategy to obtain highly pure fullerenes ^[3] and EMFs ^[4]. In this context, a three-dimensional tetragonal prismatic molecular receptor ($4 \cdot (BArF)_8$) has been reported as a suitable tool for fullerenes soot purification.^[5] The nanocapsule was prepared by coordination-driven selfassembly reaction of two tetracarboxylate Zn^{II}-porphyrin and four Pd^{II}-based molecular clips. The exceptional behavior of ($4 \cdot (BArF)_8$) encouraged us to consider this system as an effective tool towards the design a strategy for EMFs soot purification. Moreover, the better features showed by Cu(II) instead of Pd(II) related with the metal-ligand bond lability, prompt us to design a novel Cu(II) based molecular receptor for fullerenes and EMFs soot purification, in analogy to $4 \cdot (BArF)_8$.



References

1) J. R. Heath et al., J. Am. Chem. Soc. 1985, 107, 7779 - 7780.

2) H.Shinohara et al., Rep. Prog. Phys. 2000, 63, 843.

3) C. García-Simón et al, Chem. Soc. Rev. 2016, 45, 40-62.

4) N. Chaur et al, Angew. Chem. Int. Ed. 2009, 48, 7514-7538.

5) C. García-Simón et al, Nat.Commun. 2004, 5, 5557.

INNOVATIVE METALLODRUGS DESIGN TO REACH DIFFERENT TARGETS AND TOOLS TO STUDY THEIR ACTION

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Metallodrugs can face human deceases, offering a much more diverse chemistry, and also having important therapeutic applications^[1]. The understanding of the mechanistic aspects involved in the action of metallodrugs is of great importance to overcome their validation in clinic. Platinum drugs are among the most important area of research because of cisplatin (most efficient anticancer metallodrug in clinic). The highlight in this field is the development of innovative anticancer Pt(II) compounds which design does not obey the classical cisplatin's rules. These innovative anticancer complexes can potentially achieve improvements over cisplatin^[2], as the variation in their structure lead to a different chemistry and distinctive interaction with biological models/ targets^[3, 4]. In our group of research we are interested in this kind of reactivity and in this contribution we will show some of the examples with most peculiar reactivity versus proteins and our modus operandi of studying these drugs mechanism, including binding the Pt core to a Tc unit which allows in vivo imaging^[5].

References

- [1] K. D. Mjos, C. Orvig, Chem Rev 2014, 114, 4540.
- [2] T. C. Johnstone, K. Suntharalingam, S. J. Lippard, Chem Rev 2016, 116, 3436.
- [3] L. Messori, T. Marzo, C. Gabbiani, A. A. Valdes, A. G. Quiroga, A. Merlino, Inorg Chem 2013, 52, 13827.
- [4] T. Marzo, F. Navas, A. Merlino, G. Ferraro, L. Messori, A.G. Quiroga, J. Inorg. Biochem. 2018, 181, 11.
- [5] L. Quental, P. Raposinho, F. Mendes, I. Santos, C. Navarro-Ranninger, A. Alvarez-Valdes, H. Huang, H. Chao, R. Rubbiani, G. Gasser, A. G. Quiroga, A. Paulo, *Dalton Trans.* 2017, 46, 14523.

COMPUTATIONAL MODELING AND DESIGN OF WATER OXIDATION ELECTROCATALYSTS

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Fueling our planet with clean and sustainable energy is one of the central challenges of the 21st century. In this regard, water electrolyzers have shown great promise, but its commercialization is still hampered by the existence of efficient and yet economic catalysts for the oxygen evolution half-reaction (OER). To overcome this issue, several approaches have been undertaken such as the synthesis of nature-inspired catalysts,^[1] the addition of dopants/promoters,^[2] or catalyst nanostructuring.^[3] While significant advances have been made with these strategies, further enhancement of OER electrocatalysts may require adopting strategies that are built upon a deeper understanding of this complex reaction.

In this talk, I will present a few recent works that demonstrate that density functional theory (DFT) methods are a very powerful and essential tool for the future design of OER catalysts.^[4] For example, DFT simulations can provide a unique atomic-scale description of the OER process that allow us to pinpoint the active sites responsible for the turnover of molecular oxygen,^[5] which otherwise is extremely difficult by means of experimental techniques. In addition, DFT calculations can be combined with linear scaling relations to shed light into the enhanced OER activity of doped oxide catalysts,^[6] and even guide the design of all earthabundant high-performance OER catalysts.^[7]

References

- A. D. Handoko, S. Deng, Y. Deng, A. W. F. Cheng, K. W. Chan, H. R. Tan, Y. Pan, E. S. Tok, C. H. Sowb, B. S. Yeo, Catal. Sci. Technol. 2016, 6, 269.
- 3) K. Fominykh, P. Chernev, I. Zaharieva, J. Sicklinger, G. Stefanic, M. Döblinger, A. Müller, A. Pokharel, S. Böcklein, C. Scheu, T. Bein, D. Fattakhova-Rohlfing, ACS Nano, **2015**, *9*, 5180.
- 4) J. Soriano-López, W. Schmitt, M. García-Melchor, Curr. Opin. Electrochem. 2018, 7, 22.
- 5) J. Fester, M. García-Melchor, A. S. Walton, M. Bajdich, Z. Li, L. Lammich, A. Vojvodic, J. V. Lauritsen, Nat. Commun. 2017, 8, 14169.
- 6) J. W. Desmond Ng, M. García-Melchor, M. Bajdich, C. Kirk, P. Chakthranont, A. Vojvodic, T. F. Jaramillo, *Nat. Energ.* 2016, *1*, 16053.
- B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, M. García-Melchor, J. Xu, M. Liu, F. Pelayo García de Arquer, C. Thang Dinh, F. Fan, M. Yuan, E. Yassitepe, A. Janmohamed, N. Chen, T. Regier, L. Han, H. L. Xin, L. Zheng, H. Yang, A. Vojvodic, E. H. Sargent, Science, **2016**, 352, 333.

¹⁾ C. S. Mullins, V. L. Pecoraro, Coord. Chem. Rev. 2008, 252, 416.

THE IMPORTANCE OF THE OXIDATION STATE OF THE METAL IN OLEFIN METATHESIS CATALYSIS

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Olefin metathesis is a powerful tool for the formation of carbon–carbon double bonds.^[1] For instance, several families of ruthenium (Ru) catalysts have been developed during the past 25 years for this reaction, and the corresponding reaction mechanism has been established. The latter is assumed to involve always the formation of a metallacycle.

In the past, some of us have highlighted the importance of steric and electronic properties of the so-called spectator N-heterocyclic (NHC) ligands ^[2] of Ru-benzylidene complexes for the design of effective catalysts for olefin metathesis. Presumably, the nature of the ligand would be responsible for the ability/inability of the metal center to achieve the necessary formal oxidation states for the catalytic process run on.

In the present study we make use of density functional theory (DFT) combined with the socalled Effective Oxidation State (EOS) analysis ^[3,4] to examine the relationship between the oxidation state of the metal in the initiation step of the mechanism and the efficiency of the catalysts. In particular, we tackle the Ru^{II} vs Ru^{IV} debate in Grubbs catalysts, as well as study in detail cheaper and cleaner iron catalysts ^[5,6] and molybdenum-based Schrock catalysts for this process.



Figure 1. The combination of oxidation state and type of metal in olefin metathesis catalysts.

- 1) G. C. Vougioukalakis, R. H. Grubbs, Chem. Rev. 2010, 110, 1746-1787.
- 2) C. A. Urbina-Blanco, A. Poater, T. Lebl, S. Manzini, A. M. Z. Slawin, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2013**, *135*, 7073–7079.
- 3) E. Ramos-Cordoba, V. Postils, P. Salvador, J. Chem. Theory Comput. 2015, 11, 1501-1508
- 4) G. Skara, M. Gimferrer, F. De Proft, P. Salvador, B. Pinter, Inorg. Chem. 2016, 55, 2185-2199.
- 5) A. Poater, E. Pump, S. V. C. Vummaleti, L. Cavallo, Chem. Phys. Lett. 2014, 610-611, 29-32.
- 6) A. Poater, S. V. C. Vummaleti, E. Pump, L. Cavallo, Dalton Trans. 2014, 43, 11216–11220.
DETECTION OF THERMOLABILE AND OTHER ELUSIVE SPECIES USING MASS SPECTROMETRY

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6) Understanding reaction mechanisms is a key step in the design of more efficient catalysts. However isolation and characterization of intermediates is often hampered by the short lifetime and thermolability of such species. Mass spectrometry is a potent tool that allows characterization of minor species in a reaction mixture. However, high temperatures (150°C) are typical ionization conditions, even in the soft ESI ionization, hampering its application in the characterization of intermediate species. To address this problem a Cryospray attachment is used allowing the characterization of very unstable intermediate species such as a novel low-spin hydroperoxoiron(III) species formed after the reaction of hydrogen peroxide and the ferrous precursor bearing the macrocyclic ligand PyNMe3 in acetonitrile at -40°C.^[1]

- ⁷⁾ Furthermore, when applying soft ionization conditions we were also able to characterize self-assembled architectures controlled by external stimuli, in this case light^[2] and follow the formation of dynamic host– guest supramolecular structures using competitive redox-guest, where binding and release processes are redox-controlled.^[3]
- 8)



- 11) 1) J. Serrano-Plana, F. Acuña-Parés, V. Dantignana, W. N. Oloo, E. Castillo, A. Draksharapu, C. J. Whiteoak, V. Martin-Diaconescu, M. G. Basallote, J. M. Luis, L. Que, M. Costas and A. Company. *Chem. Eur. J.* **2017** DOI: 10.1002/chem.201704851
- 12) 2) O. Han, Y. Luo, B. Damaschke, L. Gómez, X. Ribas, A. Jose, P. Peretzki, M. Seibt, G.H. Clever, Angew. Chem. Int. Ed. 2016, 55(1), 445.
- 13) 3) C. Colomban, G. Szalóki, M. Allain, L. Gómez, S. Goeb, M. Sallé, M. Costas, X. Ribas. Chem. Eur.J. 2017, 23,3016.
- 14) Company, A., Lloret-Fillol, J.; Gómez, L.; Costas, M. in Alkane C-H Activation by Single-Site Metal Catalysis, (2013) ed. P. J. Perez, Springer Netherlands, Dordrecht.
- 15) Prat, I., Gomez, L., Canta, M., Ribas X. and Costas, M. Chem. Eur. J. (2013), 19, 1908-1913.
- 16) Gomez, L., Canta, M., Font, Prat, I., Ribas, X. and Costas M., J. Org. Chem. 2013, 78, 1421-1433.

MECHANISTIC STUDY OF THE VANADIUM-CATALYZED AEROBIC C-C BOND OXIDATIVE CLEAVAGE OF VICINAL DIOLS

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A detailed mechanistic study of the oxidative carbon-carbon (C-C) cleavage of vicinal diols^[1] has been carried out using Density Functional Theory (DFT) based methods. The reaction is catalyzed by a V^V{amino-tri(phenolate)} complex, which is an efficient catalyst for CO₂ fixation that has been widely studied in our group. ^[2,3] The vanadium center evolves to V^{IV} and V^{III} species that are re-oxidized after the C-C bond cleavage by molecular oxygen producing the respective carbonylic derivative with high chemoselectivity and water as the only sub-product of the reaction.

Oxidative C-C bond cleavage of vicinal diols is a reaction of fundamental importance in organic synthesis as well as in lignin-cellulose valorization and the general context of renewable feedstock transformation. Therefore, elucidation of the reaction mechanism might prompt to adjust the catalytic system or the reaction conditions to increase the activity of the system.



1) Amadio, E.; Di Lorenzo, R.; Zonta, C.; Licini, G. Coord. Chem. Rev. 2015, 301-302, 147-162.

- 2) Peña Carrodeguas, L.; González-Fabra, J.; Castro-Gómez, F.; Bo, C.; Kleij, A. W. Chemistry A European Journal 2015, 21, 6115-6122.
- 3) González-Fabra, J.; Castro-Gómez, F.; Kleij, A. W.; Bo, C.; ChemSusChem, 2017, 10, 1233–1240.

SUSTAINABLE UGI-TYPE REACTIONS THROUGH IRON-CATALYZED C-H FUNTIONALIZATION

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 α -Amino amides are found in a wide range of natural products and pharmaceuticals and they have been used as intermediates for the synthesis of different heterocycles.^[1] Traditionally, these motifs could be synthesized straightforwardly by the Ugi multicomponent reaction,^[2] which involves the *in situ* formation of an imine from combining a primary amine and an aldehyde, and subsequent reaction with an isocyanide and a carboxylic acid. Recently, oxidative multicomponent reactions upon secondary or tertiary amines have emerged as a challenging alternative of the classical reaction, which occurred through the *in situ* oxidation of the corresponding amines. In this communication, we report an unprecedented and practical Ugi-type reaction upon *N*,*N*-dimethylanilines and isocyanides catalyzed by cost-efficient and eco-friendly iron salts, broadening the often limited scope of existing methodologies.^[3]



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- 1) (a) Schwieter, K. E.; Johnston, J. N. J. Am. Chem. Soc. 2016, 138, 14160. (b) Blaskovich, M. A. T. J. Med. Chem. 2016, 59, 10807.
- (a) Tron, G. C. Eur. J. Org. Chem. 2013, 10, 1849. (b) Wessjohann, L. A.; Rhoden, C. R. B.; Rivera, D. G.; Vercillo, O. E. Top. Heterocycl. Chem. 2010, 23, 199. (c) Dömling, A. Chem. Rev. 2006, 106, 17. (d) Dömling, A.; Ugi, I. Angew. Chem., Int. Ed. 2000, 39, 3168.
- (a) Singh, K.; Kaur, A.; Mithu, V. S.; Sharma, S. J. Org. Chem. 2017, 82, 5285. (b) Gandy, M. N.; Raston, C. L.; Stubbs, K. A. Chem. Commun. 2015, 51, 11041. (c) Dighe, S. U.; Kolle, S.; Batra, S. Eur. J. Org. Chem. 2015, 19, 4238. (d) Xie, C.; Han, L. Tetrahedron Lett. 2014, 55, 240. (e) Rueping, M.; Vila, C.; Bootwhicha, T. ACS Catal. 2013, 3, 1676. (f) Rueping, M.; Vila, C. Org. Lett. 2013, 15, 2092. (g) Vila, C.; Rueping, M. Green Chem. 2013, 15, 2056. (h) Ye, X.; Xie, C.; Huang, R.; Liu, J. Synlett 2012, 23, 409. (i) Ye, X.; Xie, C.; Pan, Y.; Han, L.; Xie, T. Org. Lett. 2010, 12, 4240. (j) Jiang, G.; Chen, J.; Huang, J.-S.; Che, C.-M. Org. Lett. 2009, 11, 4568. (k) Ngouansavanh, T.; Zhu, J. Angew. Chem., Int. Ed. 2007, 46, 5775.

Synthesis of β-benzyloxynitriles via Metal-Ligand Cooperative oxa-Michael Additions and Their Transformation to γ-amino Alcohol Derivatives

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Ruthenium PNN/PNP pincer complexes are attracting increasing attention for applications in homogeneous catalysis due to their "metal-ligand cooperative" mechanism for substrate activation, which involves aromatization/dearomatization of the pyridine moiety in the pincer scaffold.^[1] Our group recently reported on the use of Milstein's pyridine-based PNN ruthenium catalyst for oxa-Michael additions to unsaturated nitriles under mild conditions.^[2,3] Here we present our studies to expand the substrate scope, and demonstrate catalytic addition of benzyl alcohol to a variety of β -substituted unsaturated nitriles.^[4] The resulting β -benzyloxynitrile products can be hydrogenated to a variety of interesting building blocks, such as γ -amino alcohol derivatives and β -hydroxy nitriles, depending on the reaction conditions.^[5]



- (a)C. Gunanathan, D. Milstein, Acc. Chem. Res. 2011, 44, 588. (b) C. Gunanathan, D. Milstein, Chem. Rev. 2014, 114, 12024 –12087.
- 2) C. F. Nising, S. Brase, Chem. Soc. Rev. 2012, 41, 988-999.
- 3) S. Perdriau, D. S. Zijlstra, H. J. Heeres, J. G. de Vries, E, Otten, Angew. Chem. Int. Ed. 2015, 54, 4236-4240.
- 4) L. E. Eijsink, S. Perdriau, J. G. de Vries, E. Otten, Dalton Trans. 2016, 45, 16033-16039.
- (a) Y. Sawama, M. Masuda, S. Asai, R. Goto, S. Nagata, S. Nishimura, Y. Monguchi, H. Sajiki, *Org. Lett.* 2015, 17,434–437. (b) D.Y. Ma, D.X. Wang, J. Pan, Z.T. Huang, M.X. Wang, *J. Org. Chem.* 2008, 73, 4087–4091. (c) J. Neumann, C. Bornschein, H. Jiao, K. Junge, M. Beller, *Eur. J. Org. Chem* 2015, 27, 5944–5948. (d) P. Merino, I. Delso, T. Tejero, F. Cardona, M. Marradi, E. Faggi, C. Parmeggiani, A. Goti, *Eur. J. Org. Chem.* 2008, 17, 2929–2947. (e) D. H. Lenz, G. E. Norris, C. M. Taylorc, G. C. Slima, *Tetrahedron Letters* 2001, 42, 4589–4591.

CATALYTIC ALKANE FUNCTIONALIZATION VIA IRON-CARBENE INSERTION REACTION

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Saturated hydrocarbons are nature abundant reagents which upon functionalization constitute a potential vast and low cost feedstock for the synthesis of more valuable chemicals.^[1] However, conversion of Csp³-H into new C-C bonds is a difficult challenge due to their kinetically inert nature. To overcome this lack of reactivity, highly reactive reagents (superacids or radicals) or forcing reaction conditions are required, albeit these approaches usually compromise the selectivity of the process. An alternative to this energetically demanding processes has emerged within the field of Metal-carbene compounds LM=CR₂,^[2] although it is dominated by precious metals such as rhodium, silver and gold. In replacing these systems by earth-abundant metals iron rises as an optimal choice since it is of low cost, high natural abundance and low toxicity.^[3]

Herein we report our findings investigating the use of a low-valent iron organometallic species as catalysts for Csp³-H carbene insertion under mild conditions. Optimization of the reaction conditions highlights the role of Lewis acids additives as a source of selectivity. Attempts to identify operative intermediates in these intricate processes are also discussed.



Figure 1. Csp³-H bond functionalization iron-carbene catalysed.

- 1) R. G. Bergman, Nature 2007, 446, 391-394
- 2) M. M. Díaz-Requejo, A. Caballero, M. R. Fructos, P. J. Pérez, Alkane C- H Activation by Single-Site Metal Catalysis, Springer, Amsterdam, 2012, Chap.6.
- a) A. Conde, G. Sabenya, M. Rodríguez, V. Postils, J. M. Luis, M. M. Díaz-Requejo, M. Costas, P. J. Pérez, Angew. Chem. Int. Ed. 2016,55, 6530-6534; b) J. R. Griffin, C. I. Wendell, J. A. Garwin, M. C. White, J. Am. Chem. Soc., 2017, 139, 13624–13627

CAN MODERN DFT BE USED FOR PREDICTIVE MOLECULAR CATALYSIS? – COMPARING THEORY AND EXPERIMENT IN OLEFIN HYDROGENATIONS WITH RUTHENIUM XANTPHOS COMPLEXES

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DFT computations are the method of choice for the fast and reliable prediction of the structures and energies of organometallic compounds. Therefore, DFT computations should in principle be useful to predict the reaction rates and selectivities of catalytic reactions in molecular catalysis. However, popular density functionals often have failed to predict relative Gibbs free energies well enough, even though they give very accurate structures. In this context the past decade has witnessed an impressive improvement with regard to the quantitative accuracy of contemporary DFT computations, mainly by the introduction of dispersion corrections and the development of new density functionals.[1-4] Accordingly, the question arises if DFT computations can be used for predictive catalyst design prior to experimental art.

In this work we contribute to an answer by presenting accurate experimentally derived overall activation barriers (energy spans[5]) for the hydrogenation of cyclic olefins using molecularly defined ruthenium xantphos complexes (see Figure 1 below) together with DFT-computed complete reaction mechanisms. Furthermore, we present a thorough comparison of computed energy spans obtained by state-of-the-art DFT computations.

This work illustrates that by considering inherent experimental and computational boundaries DFT has reached a state which makes computational catalyst design prior to experimental work possible.[6]



[1] D. G. Gusev, Organometallics **2013**, *32*, 4239-4243

[2] M. Steinmetz, S. Grimme, ChemistryOpen 2013, 2, 115-124.

- [3] W. Lai, J. Yao, S. Shaik, H. Chen, J. Chem. Theory Comput. 2012, 8, 2991-2996.
- [4] R. Peverati, D. G. Truhlar, Phys. Chem. Chem. Phys. 2012, 14, 13171-13174.
- [5] S. Kozuch, S. Shaik, Acc. Chem. Res. 2011, 44, 101-110.
- [6] K. Rohmann, M. Hölscher, W. Leitner, J. Am. Chem. Soc. 2016, 138, 433-443.

F. M. Mück, J. A. Baus, M. Nutz, C. Burschka, J. Poater, F. M. Bickelhaupt, R. Tacke, Chem. Eur. J. 2015, 21, 16665

POSSIBILITY OF PHOTO-TRIGGERED ORGANOCATALYSTS BASED ON EXCITED STATE AROMATICITY

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Aromaticity and antiaromaticity in electronically excited states have emerged as useful concepts in organic photochemistry. They are governed by *Baird's rule* which says that cyclically conjugated molecules with $4n \pi$ -electrons are aromatic while those with $4n+2\pi$ -electrons are antiaromatic (Figure 1a).^[1] It is thus the opposite of Hückel's more well-known rule for the ground state. In recent years we have shown that excited state aromaticity can lead to sizable energetic stabilization on the order of 20 kcal/mol,^[2] and that Baird's rule can be used to develop new photochemical reactions, such as the photohydrogenation of benzene and polycyclic aromatic hydrocarbons.^[3]

In this conceptually oriented poster we discuss the possibility of using Baird's rule to design photo-triggered organocatalysts that are active only during irradiation and otherwise switched off (Figure 1b). This novel type of photocatalysts would open a new approach to precise external control of catalytic systems.



Figure 1. (a) Application of Baird's rule to simple hydrocarbons. (b) Schematic principle of phototriggered catalysis.

- (a) Baird, N. C. J. Am. Chem. Soc. 1972, 94, 4941. (b) Rosenberg, M.; Dahlstrand, C.; Kilså, K.; Ottosson, H. Chem. Rev. 2014. 114. 5379.
- Ueda, M.; Jorner, K.; Sung, Y. M.; Mori, T.; Xiao, Q.; Kim, D.; Ottosson, H.; Aida, T.; Itoh, Y. Nat. Commun. 2017, 8, 346.
- (a) Mohamed, R. K.; Mondal, S.; Jorner, K.; Faria Delgado, T.; Lobodin, V. V; Ottosson, H.; Alabugin, I. V. J. Am. Chem. Soc. 2015, 137, 15441. (b) Papadakis, R.; Li, H.; Bergman, J.; Lundstedt, A.; Jorner, K.; Ayub, R.; Haldar, S.; Jahn, B. O.; Denisova, A.; Zietz, B.; Lindh, R.; Sanyal, B.; Grennberg, H.; Leifer, K.; Ottosson, H. Nat. Commun. 2016, 7, 12962.

QUO VADIS ELECTRON? ELECTRON FLOW IN OPEN SHELL SYSTEMS

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In a recent article we demonstrated the ability to monitor electron flow in chemical transformations^[1] using intrinsic bond orbitals (IBOs).^[2] We showed that the changes of IBOs along a reaction path can be directly connected to the *curly arrow* formalism, which remains the most common way to rationalize chemical transformations. Our initial studies focused on closed shell systems^[3] and as such only dealt with transformations of electron pairs. We have now extended our approach to open shell systems. We here present the power of this formalism with examples ranging from simple organic transformations, such as a radical Smiles rearrangement,^[4] to C-H bond oxidation reactions with bioinspired transition metal oxo and hydroxo species.^[5] As a highlight, we show that our approach is even capable of differentiating between proton coupled electron transfer (PCET) and hydrogen atom transfer (HAT) pathways in oxidation reactions for the activation of X-H bonds.^[6]

References

- 1) G. Knizia, J. E. M. N. Klein, Angew. Chem. Int. Ed. 2015, 54, 5518-5522.
- 2) G. Knizia, J. Chem. Theory Comput. 2013, 9, 4834-4843.
- (a) L. Nunes Dos Santos Comprido, J. E. M. N. Klein, G. Knizia, J. Kastner, A. S. K. Hashmi, *Chem. Eur. J.* 2017, 23, 10901-10905; (b) J. E. M. N. Klein, G. Knizia, L. Nunes Dos Santos Comprido, J. Kastner, A. S. K. Hashmi, *Chem. Eur. J.* 2017, 23, asap, DOI: 10.1002/chem.201703815.
- 4) For a review see see: I. Allart-Simon, S. Gérard, J. Sapi, Molecules 2016, 21, 878.
- 5) For a representative review see: X. Engelmann, I. Monte-Pérez, K. Ray, Angew. Chem. Int. Ed. 2016, 55, 7632-7649.
- For reviews see: (a) S. Hammes-Schiffer, J. Am. Chem. Soc. 2015, 137, 8860-8871; (b) D. R. Weinberg, C. J. Gagliardi, J. F. Hull, C. F. Murphy, C. A. Kent, B. C. Westlake, A. Paul, D. H. Ess, D. G. McCafferty, T. J. Meyer, Chem. Rev. 2012, 112, 4016-4093; (c) J. J. Warren, T. A. Tronic, J. M. Mayer, Chem. Rev. 2010, 110, 6961-7001.

AB INITIO INSIGHTS INTO DINITROGEN PHOTOCLEAVAGE

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The quest for molecular catalysts that efficiently activate or cleave the dinitrogen molecule is ongoing. While many complexes capable of thermal dinitrogen activation are known, the photochemical cleavage of N₂ has received considerably less attention.^[1,2] Dinitrogen photocleavage has the potential to be developed into a particularly attractive process: energy from the solar spectrum is used to cleave the strong dinitrogen bond and is at least partially stored in the metal-nitrogen bonds that are formed concomitantly. The resulting metal nitrido complexes are amenable to a variety of further reactions that could incorporate nitrogen atoms into value-added chemicals and thus represent strategically important chemical intermediates.

Although the principle of photochemical dinitrogen activation has been demonstrated with six synthetic examples, the precise mechanisms are not understood and therefore it is unclear how to systematically improve its efficiency. To unravel the photophysical and photochemical processes involved in dinitrogen photocleavage, we analyse the electronic structure of the ground and excited states of specific synthetic examples^[2–4] using single- and multireference quantum chemical methods. Through the investigation of electronic structure changes along specific dissociation coordinates a detailed picture of the dissociation process(es) is obtained.



Electronic structure changes upon elongation of the N-N distance in $[Os^{(II,III)}_2(\mu-N_2)(NH_3)_{10}]^{5+}$ obtained by CASSCF calculation of the twelve lowest CASSCF(13,10) states.

- 1) Curley, J. J.; Cook, T. R.; Reece, S. Y.; Müller, P.; Cummins, C. C., J. Am. Chem. Soc. 2008, 130, 9394-9405.
- 2) Kunkely, H.; Vogler, A., Angew. Chem. Int. Ed. 2010, 49, 1591-1593.
- 3) Richardson, D. E.; Sen, J. P.; Buhr, J. D.; Taube, H., Inorg. Chem. 1982, 21, 3136-3140.
- 4) Laplaza, C. E.; Cummins, C. C., Science 1995, 268, 861-863.

P50 Poster 50

ON THE MECHANISM STABILIZING INTERMEDIATE SPIN STATE IN FE(II) POPRHYRINS

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Spin fluctuations in Fe(II)-porphyrins are at the heart of the functionality of heme-proteins. Although significant progress has been made in porphyrin chemistry, the mechanisms that rule spin states stabilization remain elusive. Here, the elements that stabilize the triplet ground state over the quintet spin state of the bare ferrous porphyrin have been discovered by the Stochastic-CASSCF quantum chemistry approach. Spin gaps among the six low-lying states, ${}^{3}B_{1g}$, ${}^{3}A_{2g}$, ${}^{3}E_{g}$, ${}^{5}A_{1g}$, ${}^{5}B_{2g}$ and, ${}^{5}E_{g}$ of the ferrous porphyrin have been investigated in great details. It is found that electron delocalization between the metal center and the π system of the macrocycle differentially stabilizes the intermediate spin. Out-of-plane iron d_{xz} and d_{yz} orbitals represent the communication channels between metal center and macrocycle. Electron delocalization greatly reduces onsite electron repulsion stabilizing the intermediate spin-state over the high spin state. Metal-to-ligand and ligand-to-metal charge transfer configurations are responsible for the electron delocalization. Our results find a qualitative analogue in aromatic resonance structures involving the metal center (see Figure below).



PITFALLS IN THE ABTS PEROXIDASE ACTIVITY TEST

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Hydrogen peroxide is a strong two-electron oxidant involved in multiple processes. From the biological point of view, it is a dangerous reactive oxygen species (ROS), generated as a by-product of aerobic respiration¹. Salen-manganese complexes are ROS scavengers whose catalytic and pharmacological properties have been studied for over 20 years². It is well established that this type of complexes protect cells from oxidative damage in several animal models. In this work, we have studied three artificial mimics (1-3, Scheme 1), already reported as peroxidase-like catalysts. However, during the course of further studies aimed at getting a better understanding of the kinetics of the processes involved, we observed a striking effect of the instrument used to monitor the kinetics that clearly reveals the occurrence of a photochemical process. Those kinetic studies on the reaction of salen-type manganese(III) complexes with hydrogen peroxide show that the ABTS test frequently used to determine the peroxidase activity can be seriously affected by the experimental conditions, so that in some cases there is a need to reevaluate the activity and also the conclusions about the mechanism of action of this kind of compound.



Scheme 1. Structure of complexes 1-3 and EUK-134.

- B. Day, Biochem. Pharmacol., 2009, 77, 285; b) M. Oszajca, M. Brindell, L. Orzel, J. M. Dabrowski, K. Spiewak, P. Labuz, M. Pacia, A. Stochel-Gaudyn, W. Macyk, R. van Eldik and G. Stochel, *Coord. Chem. Rev.*, **2016**, 327-328, 143.
- 2) M. Wagner, D. Brumelis and R. Gehr, Water Environ. Res., 2002, 74, 33

IMAM LIGANDS FOR LOW-COORDINATE LATE TRANSITION METAL COMPLEXES

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The design of new catalysts for the functionalization of inert C-H bonds is a compelling goal to be able to take advantage of hydrocarbon-based feedstock in a more selective, cost-effective and environmentally friendly way.^[1] The synthesis of biomimetic complexes inspired by active oxidant species involved in enzymatic catalytic cycles, notably metal-oxo intermediates, is one important route of investigation to overcome this limit.^[2] Late transition metal-oxo complexes (groups 9, 10, 11) are postulated to be potentially stronger oxidants than early-transition ones, but they have so far been elusive due to electronic structural requirements.^[3] One possible strategy to override this "Oxo Wall"^[3] is to synthesize low-coordinate precursors in square planar, tetrahedral or trigonal planar geometries. Bulky β -diketiminate ligands are widely investigated in order to access metal complexes with low coordination numbers and have been used to synthesize trigonal planar mononuclear Ni(II)^[4] and Cu(II) superoxo and bis(μ -oxo) complexes.^[5] Herein we propose a novel IMAM (IMinoAMido) ligands family (1) to access low-coordinate precursors and bearing an anionic donor to stabilize the high-valent late transition metal-oxo species. The new compounds were fully characterized through IR, NMR, HRMS, and their coordination properties with Fe, Ni, Co and Cu (2) were explored.



H,HIMAM1: R=iPr H,HIMAM 2: R=Me Me,MeIMAM1: R=iPr Me,MeIMAM 2: R=Me

(1)



(2)

References:

1) Labinger, J.A., Bercaw, J.E., Nature 2002, 417, 507

2) Que, L. Jr., Tolman, W.B., Nature 2008, 455, 333

3) Winkler, J.R, Gray, H.B., Struct. Bond. 2012, 142, 17

4) Holland, P.L., Cundari, T.R., Perez, L.L., Eckert, N.A., Lachicotte, R.J., J. Am. Chem. Soc. 2002, 124, 14416

5) Spencer, D. J. E, Aboelella N.W., Reynolds, A. M., Holland, P. L., Tolman, W. B., J. Am. Chem. Soc. 2002, 124, 10, 2108

CU-PEPTIDE CATALYSTS FOR WATER OXIDATION IN BORATE BUFFER -APPROACHES TO ADVANCED ELECTROCHEMICAL MEASUREMENTS IN THE EYE OF A STUDENT

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The transformation of the temporal renewable electric energy to chemical energy is a timely task. Electrolyzing water with the excess power and recover it by oxidizing the evolved hydrogen is an attractive renewable energy carrier cycle. Therefore the electrocatalytic capabilities of bio-inspired molecular catalysts that utilize peptide ligands and the abundant transition metal copper have been investigated. The presented research is focused on the behaviour of certain Cu-peptides as water oxidation electrocatalysts in borate buffer. This buffer allows conducting the electrocatalysis experiments in mild basic media.

The mechanisms of even the simplest systems are complicated and very hard to unfold. In the poster a student's perspective on the electrochemical processes will be shown. Some remarks on the role of the double layers and their changes upon polarization, the effect of adsorption-desorption processes on the measured currents and questions about the corrosion induced activity on glassy carbon electrodes will be presented.

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MECHANISM STUDY OF 2,2'-BIPIRIDINE-6,6-DICARBOXYLATE RU CATALYSTAS A WATER OXIDATION CATALYST

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In situ production of H₂ has been a hot topic^[iii] for some time now and catalysts that are able to perform this task are currently being researched,^[iv] such as our Ru catalyst. The full mechanism of 2,2'-bipyridine-6,6'-dicarboxylate Ru catalyst for water oxidation catalysis (WOC)^[v] using DFT calculations. The rate determining step is found at the dimer formation while the bond cleavage for the O₂ liberation process is barrier-less. Water appears not to be involved in the cleavage process. Taking into account the recent results by Concepcion's group^[vi] related to the same catalyst, where the Ru-O-Ru metallic core was proposed to be involved instead of the typical Ru-O-O-Ru one, coming from the direct interaction between the oxygens of two Ru=O moieties we report the mechanism including the possible open carboxylate and closed carboxylate structures (see Figure 1). The computational results confirm that the most common path (closed carboxylate) is strongly preferred, and consequently, the formation of such Ru-O-Ru moiety is impeded.



Figure 1. Closed and open carboxylate structures of our mechanism. Axial ligands omitted for clarity.

1)Morris, J.; Radu, M. Int. J. Hydrog. Energy 2010, 35, 7021-7023.

2) Kang, R.; Chen, K.; Yao, J.; Shaik, S.; Chen, H. Inorg. Chem. 2014, 53, 7130-7136.

3) Duan, L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L. Nat. Chem. 2012, 4, 418-423.

4) Concepcion, J. J.; Zhong, D. K.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. Chem. Commun. 2015, 51, 4105-4108.

SYNTHESIS AND CHARACTERIZATION OF ORGANOIRON COMPLEXES

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The use of Iron as catalyst for cross-coupling reactions has been an exploded field in the recent years. In fact, lots of researchers such as Nakamura, Ackerman and Cook have proven the applicability of these processes with successful results.^[1] In most cases, the involvement of an organometallic iron-carbon species as key reaction intermediate in the catalytic cycle has been postulated. However, the detection of such compounds has remained elusive.^[2]

Herein, a rare example of the synthesis and characterization of an organometallic aryl-iron(II) with CO insertion in the ligand is described. The complex is prepared through a C(sp²)-Br activation using a slightly modified model macrocyclic arene substrate previously used in our group^{[3],[4]} and an Iron(0) carbonyl precursor. Moreover, indirect evidence of the organoiron complex has been gathered by means of labelling studies. Finally, substitution of the methyl substituents in the amines of the macrocyclic ligand by *tert*-butyl groups affords the formation of the expected aryl-iron(II) complex without CO insertion.



REFERENCES

- [1] E. Nakamura Top Organomet. Chem. 2016, 56, 1.
- [2] E. Nakamura Chem. Rev., 2017, 117 (13), 9086.
- [3] O. Planas J. Am. Chem. Soc., 2016, 138 (43), 14388.
- [4] O. Planas J. Am. Chem. Soc., 2017, 139 (41), 14649.

EXPLORING THE ORIGIN FOR STAND-ALONE FUNCTION OF TRYPTOPHAN SYNTHASE THROUGH METADYNAMIC SIMULATIONS

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Tryptophan synthase (TrpS) catalyzes the formation of L-Tryptophan from L-Serine and indole glycerol phosphate (IGP). Experimental studies based on X-ray structures characterized TrpS as a dimer, with several key conformational states exhibiting open and closed active site conformations in both subunits.^[11] For this enzyme, an allosteric network between the α-subunit (TrpA) and the β-subunit (TrpB) keeps the proper conformations along the catalytic itinerary, and allows indole diffusion from TrpA to TrpB though an internal tunnel.^[11] Isolated subunits are usually less efficient in the absence of their protein partners, witch is not desirable for biosynthetic applications. To that end, Directed Evolution (DE) was applied to turn TrpB into a catalytically efficient stand-alone unit.^[21] In this work, conventional Molecular Dynamics and non-equilibrium metadynamics.^[3] simulations were used to investigate how distal mutations affect catalysis and prepare TrpB for stand-alone activity. In particular, we have computationally explored the differences in stability of several conformational states along the reaction coordinate for the wild-type and laboratory-evolved enzyme variants with different intermediates of the reaction mechanism. This work contributes to our current understanding of how allosteric networks can be recapitulated through distal mutations,^[4] which is of interest for engineering isolated enzyme subunits for biosynthetic applications.

1) Michael F. Dunn, Arch Biochem Biophys. 2012, 519. 154

2) Andrew R. Buller, Sabine Brinkmann-Chen, David K. Rommey, Michael Herger, Javier Murciano-Calle, and Frances H. Arnold, Proc Natl Acad Sci USA. **2015** *112*. 14599

- 3) Laio, A & Parrinello, M. Proc. Natl. Acad. of Sci. USA 2002. 99. 12562
- 4) Miguel A. Maria-Solano, Javier Iglesias-Fernández, and Sílvia Osuna, submitted for publication 2017.

CHARACTERIZATION OF INTERMEDIATES IN [Co^{II}(PY2^{TS}TACN)L] MEDIATED WATER REDUCTION — UNEXPECTED NON-INNOCENT CHARACTER OF PYRIDINE.

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Hydrogen is a most promising fuel for transport and energy storage in terms of sustainability, carbon neutrality and energy conversion, however its efficient production proves challenging. Active research, carried out to find new economically sustainable hydrogen production methodologies, is focusing on water reduction catalyzed by first row transition metals. In this context, we recently reported the synthesis and electro- and photocatalytic water reduction to H₂ by a new family of penta-coordinated monocationic complexes with the general formula [Co(L)(Py₂Tstacn)]⁺ⁿ, (L = MeCN, Cl; Py₂Tstacn = 1,4-di(picolyl)-7-(p-toluenesulfonyl)-1,4,7triazacyclononane).^{1,2} A Co(I)L reduced intermediate is proposed to form upon one electron reduction of the starting compound followed by generation of a putative Co(III)-H intermediate in the presence of O₂ and a proton source. To further understand the reaction mechanism spectroscopic and reactivity studies were undertaken with a focus on X-ray absorption spectroscopy as a direct probe of electronic and geometric structure of the intermediates. Interestingly the formally Co(I)-L species exhibits similar rising edge features to the Co(II) starting material suggesting a similar oxidation state at the metal center. Complementary experimental techniques in particular SQUID measurements and correlation to theoretical calculations suggest significant electron delocalization to the pyridine ligands upon reduction consistent with an active role for the ligand in the reduction process. Similar non-innocent behavior has previously been reported by Holland and coworkers in the L'Fe(pyridine)₂ (L' = 2,4-bis(2,6-diisopropylimino)pentyl).^{3,4} To further understand this effect Co complexes rings were

with electron withdrawing and electron donating substituted pyridine further investigated both experimentally and theoretically.

References

- 1) A. Call, Z. Codolà, F. Acuña-Parés, J. Lloret-Fillol, Chem. Eur J. 2014, 20, 6171
- 2) A. Call, C. Casadevall, F. Acuña-Parés, A. Casitas, J. Lloret-Fillol, *Chem. Sci.* 3) T. R. Dugan, E. Bill, K. C. MacLeod, G. J. Christian, R. E. Cowley, W. W.

Ye, F. Neese, P. L. Holland, J. Am. Chem. Soc. 2012, 134, 20352

4) R. A. Lewis, K. C. MacLeod, B. Q. Mercado, P. L. Holland, *Chem.* 2014, 50, 1111



2017, 8, 4739

Brennessel, S.

Commun.

DIRECT AROMATIC HYDROXYLATION REACTIONS WITH H₂O₂ CATALYZED BY HOMOGENEOUS NICKEL COMPLEXES SUPPORTED BY AMINO-PYRIDINE LIGANDS

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Phenol and its derivatives are ubiquitous motifs as precursors of dyes, pharmaceuticals and functional polymers. However, the selective oxidation of organic substrates, such as benzene or toluene, to obtain phenols belongs to one of the most challenging reactions in contemporary chemical research, both in industrial and academic areas. In recent years, the development of a direct aromatic hydroxylation reaction with environmentally and economically benign oxidants under mild reaction conditions has been of particular interest.^[1,2] Nevertheless, the direct introduction of a hydroxyl functionality on an aromatic C-H bond through chemical oxidation is challenging because of the notoriously low reactivity of aromatic C-H bonds (112 kcal·mol⁻¹) and the low product selectivity caused by over-oxidation of phenol products. Therefore, this work is focused on the investigation of new homogeneous catalysts for the direct C-H hydroxylation of aromatic substrates into the corresponding C-OH functionality under mild conditions. Basically, we focus on homogeneous nickel complexes as catalysts for aromatic oxygenation reactions with the main objective to exclusively oxidize the aromatic ring, avoiding side reactivity such as over-oxidation of phenols or aliphatic oxidations of lateral substituents. We focus into nickel as the metal catalyst because it is an earth-abundant element, as well as nickel being cheaper and more benign than noble metals. In addition, we exclusively use H₂O₂ as oxidant because it is considered as an environmentally friendly compound, generating only water as a by-product. Herein, we describe our investigations on the use of nickel(II) complexes derived from aminopyridine ligands in aromatic hydroxylation reactions.^[1] As part of our studies, we have investigated the use of different solvents, including perfluorinated solvent.



- 1) Morimoto, Y.; Bunno, S.; Fujieda, N.; Sugimoto, H.; Itoh, S., J. Am. Chem. Soc. 2015, 137(18), 5867-5870.
- Tsuji, T.; Zaoputra, A.A.; Hitomi, Y.; Mieda, K.; Ogura, T.; Shiota, Y.; Yoshizawa, K.; Sato, H.; Kodera, M., Angew. Chem. 2017, 129, 7887-7890.

COMPUTATIONAL STUDY OF THE SELECTIVE HYDROGENATION OF ALKYNES TO ALKENES ON 2D MATERIALS

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Ethylene is, by far, the most used hydrocarbon in chemical industry. It is the building block of most commercially available polymers, fibres and plastics. The worldwide production of this commodity chemical increases every year, and exceeded 150 million tonnes in 2016.^[1] The mechanism used in today's industry, steam cracking, requires for hydrocarbons to be heated to very high temperatures; at a smaller scale, acetylene semihydrogenation to ethylene has been reached through Pd-based catalysts in combination with promoters such as lead or organic ligands^{[2][3][4]}. A non-precious metal-based, energetically favourable alternative has been sought for decades; however, most of these materials are either less active or suffer from selectivity losses, namely overhydrogenation and oligomerization.^[4]

In our research, a better solution is assessed by means of state-of-the-art Density Functional Theory (DFT) methods. We find that exergonic semi-hydrogenation of acetylene to ethylene can be achieved electrochemically with a concerted reaction on a 2D-catalyst based on Earth-abundant elements with an applied overpotential of only -0.25V at room temperature. Interestingly, we find that the undesired over-hydrogenation of ethylene to ethane is unfavourable, rendering this 2D-material as an extremely selective hydrogenation catalyst.

The thermodynamics and kinetics of this process, as well as the effect of the surface coverage will be presented.

The potential scalability and efficiency of this method opens the way of synthesizing ethylene without the energy cost or environmental damage bound to the available synthetic route. Furthermore, the nature of the catalyst opens the possibility to an optimization of the yield and improvements on the reaction selectivity. Our DFT study also highlights the importance of ab-initio calculations in the rational design of selective hydrogenation catalysts



¹⁾ Research and Markets. "The Ethylene Technology Report 2016 - Research and

- Markets". www.researchandmarkets.com. Retrieved 19 June 2016.
- 2) García-Mota, M.; Bridier, B.; Pérez-Ramírez, J.; López, N. J. Catal. **2010**, *273*, 92-102.
- 3) Vile, Albani, D.; Nachtegaal, M.; Chen, Z.; Dontsova, D.; Antonietti, M.; López, N. Pérez-Ramírez, J. Angew. Chem.
- *Int. Ed.* **2015**, *54*, 11265-11269. 4) Furukawa, S.; Komatsu, T. *ACS Catal.* **2017**, *7*, 735-765.

⁵⁾ Torres, Ò.; Parella, T.; Solà, M.; Roglans, A.; Pla-Quintana, A. Chem. Eur. J. 2015, 21, 16240.

EDGING A LITTLE CLOSER TO NATURE'S DESIGN

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We have prepared iron complexes of penta- and hexa-dentate ethylenediamine-backboned aminopyridyl ligands containing single carboxylato donors in (unimaginative) efforts to mimic the non-heme iron O₂ activating enzymes since the active sites of these enzymes most often contain a single Asp or Gly donor. Despite this, reports of biomimetic activity with carboxylato-iron complexes are still relatively few by comparison to work on iron complexes based on analogous neutral N-donor only ligands. By doing this the redox properties of the iron complexes are, as anticipated, tuned towards the Fe³⁺ rather than Fe²⁺ resting oxidation state under ambient conditions. As a consequence reactivity patterns towards chemical oxidants (O₂, Ce(IV),^[1] CIO⁻, H₂O₂,^[2] ROOH, PhIO^[3]) are tuned. In this presentation the catalytically competent iron-based oxidants we have spectroscopically characterized, and their roles in intramolecular ligand^[2,4] or substrate^[2,3] oxidations reactions will be described. Recently it has been possible to apply one of the complexes to electrocatalytic substrate oxidation in water.^[6] There are however pitfalls (aside from difficult organic synthetic chemistry): Ambient light can play havoc since it can promote LMCT charge transfer in the Fe^{III}-carboxylato moiety with the consequence of decarboxylaton.^[6]



Electroactivation of [Fe^{III}(tpena)]²⁺ hits a sweet spot in oxidation power over a wide pH range (3-8). The resultant iron(IV)oxo complex shows radical character and aggressively and promisciously oxidises a range of organic substrates through HAT reactions. Total mineralisation can occur. Background water oxidation is minimal so oxidizing power is not wasted. There might be applications in water remediation.^[5]

- M. S. Vad, A. Lennartson, A. Nielsen, J. Harmer, J. E. McGrady, C. Frandsen, S. Mørup and C. J. McKenzie, *Chem. Commun.*, 2012, 48, 10880-10882.
- C. Wegeberg, F. R. Lauritsen, C. Frandsen, S. Mørup, W. R. Browne, C. J. McKenzie, Chem., Eur. J. 2017, accepted. DOI: 10.1002/chem.201704615
- A. Lennartson and C. J. McKenzie, Angew. Chem., Int. Ed., 2012, 51, 6767-6770; D. P. de Sousa, C. Wegeberg, M. V. Sørensen, S. Mørup, C. Frandsen, W. A. Donald and C. J. McKenzie, Chem., Eur. J. 2015, 22, 3521–3890.
- 4) A. Nielsen, F. B. Larsen, A. D. Bond, C. J. McKenzie, *Angew. Chem. Int. Ed.* **2006**, 45, 1602-1606.
- 5) D. P. de Sousa, C. J. Miller, Y. Chang, T. D. Waite, C. J. McKenzie, Inorg. Chem., 2017, DOI: acs.inorgchem.7b02208.
- 6) C. Wegeberg, V. Fernández, W. R. Browne, F. Maseras, C. J. McKenzie, manuscript in prepara

DESIGN of MULTIPART CATALYST with Co(II) for PHOTOCATALYTIC ORGANIC TRANSFORMATIONS

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The aim of the project is to find a new approach to control the reactivity and induce enantioselectivity in lightdriven catalytic H*-E umpolung reactions that could be achieved by creating a second coordination sphere around catalyst. The proposed ligand design for the catalyst consists of 2 main parts: polyaromatic moiety and a chiral NN-ligand for binding Co(II) ion, which are joined through a linker. The polyaromatic moiety can be used to attach the catalyst to graphene surface, nanotubes or C₆₀ through π - π stacking. This allows straightforward access to perform enantioselective flow-like transformations by introducing pro-chiral substrate and isolating chiral product.^{vii} Pyrene being the smallest perfused polycyclic hydrocarbon was selected for the 1st part, simple phenyl - as a spacer, dimethylcyclohexane-1,2-diamine and 2,2'-bipyrrolidine for the 2^d part. Two new ligands were synthesized in five linear steps with 49% and 76% isolated yields. The catalytic activity of correspondently obtained Co(II) complexes showed promising results in hydrogen evolution. More results are ongoing.



Call, A.; Casadevall, C.; Acuña-Parés, F.; Casitas, A.; Lloret-Fillol, J. Chem. Sci. 2017, 8, 4739-4749.

A PHOTOCHEMICAL PERSPECTIVE ON HETEROGENEOUS PHOTOCATALYSIS: METHANOL PHOTOOXIDATION ON TiO₂(110)

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Methanol and water on a single-crystal rutile TiO₂(110) surface are widely studied model systems for heterogeneous photocatalysis.^[1] We apply our solid-state approach - spin-polarized HSE06 density functional theory and Bethe Salpeter Equation calculations of periodic models - to compute the excited-state coordinate



for the photooxidation of methanol to formaldehyde on TiO₂(110).^[2-4] For our heterogeneous photocatalysis studies, we embrace a view similar to that adopted in molecular photochemistry (**a**, bottom). This is in contrast to the predominant view in heterogeneous photocatalysis that considers light-induced electron-hole pair formation followed by electron-hole separation resulting into independent electrons and holes that give the interfacial reduction and oxidation processes, respectively (**a**, top). Within this framework, the

simulations are generally done by simulating either the electron's or the hole's catalytic reaction. Instead, our results highlight the importance of treating the excited state as a bound exciton rather than independent electrons and holes (**b**). In this approach the electron-hole separation takes place in the course of the catalytic reaction. Moreover, the efficiency of the red-ox process can be explained in terms of the competition between: i) the population of different excited states, and ii) electron-hole pair separation and recombination at ground and excites states' crossings (**c**). In this poster, we will explain our approach and show how it has successfully explained relevant surface-science experiments like the excitation wavelength dependence of methanol photocatalytic oxidation on TiO₂(110).^[5]

- 2) A. Migani, L. Blancafort, J. Am. Chem. Soc. 2016, 138, 16165
- 3) A. Migani, L. Blancafort, J. Am. Chem. Soc. 2017, 139, 11845

¹⁾ A. Migani, L. Blancafort, In Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, 2017

⁴⁾ A. Migani, L. Blancafort, in preparation

⁵⁾ C. Xu, W. Yang, Z. Ren, D. Dai, Q. Guo, T. K. Minton, and X. Yang, J. Am. Chem. Soc. 2013, 135, 19039

HIGHLY ENANTIOSELECTIVE OXIDATION OF NON-ACTIVATED ALIPHATIC C-H BONDS WITH HYDROGEN PEROXIDE CATALYZED BY MANGANESE COMPLEXES

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The oxidation of non-activated aliphatic C-H bonds is a very powerful reaction because it can transform the inert C-H bond into a suitable site for further chemical elaboration.^[1-2] It also represents one of the most challenging reactions in modern synthetic organic chemistry because the multitude of aliphatic C-H bonds in a molecule makes site selective oxidation particularly difficult. Additional challenges are encountered in enantioselective C-H oxidations.^[3] Not surprisingly, examples of enantioselective sp³ C-H oxidation with non-enzymatic systems are rare and limited to relatively weak C-H bonds (benzylic, allylic and adjacent to heteroatom) most commonly with low substrate conversion.^[4] Examples of enantioselective oxidation of non-activated aliphatic C-H bonds remain exclusive to enzymes.^[5] Herein we describe the development of chiral manganese complexes with sterically demanding tetradentate aminopyridine ligands that catalyze the regio and enantioselective oxidation of methylenic groups in monosubstituted cyclohexanes using H_2O_2 as oxidant.^[6] Oxidation occurs at positions C3 and C4 of the cyclohexane ring, producing a chiral desymmetrization in the former product, with outstanding levels of regioselectivity (> 99:1 for C3 over C4) and enantioselectivity (up to 96% ee) in the reactions of Ncyclohexylalkanamides. To the best of our knowledge the current report constitutes the first example of enantioselective oxidation of a non-activated aliphatic C-H bond by a non-enzymatic system.



2) Cernak, T.; Dykstra, K. D.; Tyagarajan, S.; Vachal, P.; Krska, S. W., *Chem. Soc. Rev.* **2016**, *45*, 546–576 3) Zheng, C.; You, S.-L., *RSC Adv.* **2014**, *4*, 6173-6214

4) a) Frost, J. R.; Huber, S. M.; Breitenlechner, S.; Bannwarth, C.; Bach, T., *Angew. Chem. Int. Ed.* **2015**, *54*, 691-695 b) Groves, J. T.; Viski, P., *J. Am. Chem. Soc.* **1989**, *111*, 8537-8538 c) Srour, H.; Maux, P. L.; Simonneaux, G., *Inorg. Chem.* **2012**, *51*, 5850-5856 d) Murahashi, S.-I.; Noji, S.; Komiya, N., *Adv. Synth. Catal.* **2004**, *346*, 195-198

5) a) Narayan, A. R. H.; Jimenez-Oses, G.; Liu, P.; Negretti, S.; Zhao, W.; Gilbert, M. M.; Ramabhadran, R. O.; Yang, Y.-F.; Furan, L. R.; Li, Z.; Podust, L. M.; Montgomery, J.; Houk, K. N.; Sherman, D. H., *Nat. Chem.* **2015,** *7*, 653-660 b) Kille, S.; Zilly, F. E.; Acevedo, J. P.; Reetz, M. T., *Nat. Chem.* **2011,** *3*, 738–743 6) Milan, M.; Bietti, M.; Costas, M. *ACS Cent. Sci.* **2017**, *3*, 196-204

ELECTRONIC AND STRUCTURAL PROPERTIES OF IRON COMPLEXES WITH FORMAZANATE LIGANDS

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Complexes that show spin-crossover are well known for 6-coordinate, octahedral geometries. Due to a much weaker ligand field in 4-coordinate complexes, these (with very few exceptions)^[1] lead to high spin-states only. Here, we present 4-coordinate iron(II) complexes with formazanate ligands (L₂Fe), some of which show spin-crossover. The strong π -acceptor properties of these ligands leads to an unusual d-orbital splitting pattern that stabilizes the low-spin (S = 0) state in these compounds.^[2] We investigated the effect of steric and electronic changes in the ligand framework and a range of spectroscopic, magnetic and computational techniques is used to understand the origin of spin-crossover in these compounds. The redox behavior of the bis(formazanate) iron complexes has also been studied by cyclic voltammetry and isolation and characterization of the reduced compounds (Fe(I), S = 1/2) have been carried out.

Furthermore, the reactivity of isocyanide with L_2Fe leads to the formation of an octahedral diamagnetic complex. Moreover, attempted oxidative addition of alkyl halides to the Fe(I) complex [L_2Fe]⁻ allows the isolation of a high-spin mono(formazanate) iron complex, for which a rational synthesis was developed.



Figure1. Iron formazanate complexes.

- 1) a) J. J. Scepaniak, T. D. Harris, C. S. Vogel, J. Sutter, K. Meyer, J. M. Smith, J. Am. Chem. Soc. 2011, 133, 3824; (b) A. C. Bowman, C.
- Milsmann, E. Bill, Z. R. Turner, E. Lobkovsky, S. DeBeer, K. Wieghardt, P. J. Chirik, J. Am. Chem. Soc. 2011, 133, 17353.
- 2) R. Travieso-Puente, J. O. P. Broekman, M.-C. Chang, S. Demeshko, F. Meyer, E. Otten, J. Am. Chem. Soc. 2016, 138, 5503.

COPPER-CATALYZED S_N2' ALLYL-ALKYL AND ALLYL-BORYL COUPLINGS OF VINYL CYCLIC CARBONATES

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The use of *gem*-diborylalkanes as organoboron reagents has recently emerged as a new source of boron units with the particularity that also adds a carbon atom to the organic framework.^[1] In this sense, copper chloride was used as catalyst to activate the *gem*-diborylmethane reagent and to couple it with a series of vinyl cyclic carbonates. Previous synthetic methods which describe the borylation of allylic carbonates with B₂pin₂ through decarboxylation involve the loss of CO₂ but also the OR moiety from the $-OCO_2R$ leaving group.^[2] Therefore, the present reaction follows an S_N2' allylic substitution pathway, has an additional benefit being the hydroxyl group retained in the homoallylic boron scaffold (Scheme 1).



Scheme 1 Allyl-alkyl coupling between gem-diborylmethane and vinyl cyclic carbonates.

Interestingly, when the same reaction is carried out using the B₂pin₂ diboron reagent, two different allylborylated products can selectively be obtained depending on the ligand of choice (Scheme 2).



Scheme 2 Ligand controlled allyl-boryl coupling between B2pin2 and vinyl cyclic carbonates.

Finally, a direct application of those prepared homoallyl- and allylboronates is accomplished just by a simple oxidative work up, to obtain the corresponding 1,5-pent-2-ene diols and (E)-1,4-but-2-ene diols. Interestingly, those (E)-1,4-but-2-ene diols are highly valuable compounds which alternative routes to prepare them require the use of Grignard reagents.

References:

- 1) N. Miralles, R.J. Maza, E. Fernández, Adv. Synth. Catal. 2017, DOI: 10.1002/adsc.201701390.
- 2) (a) H. Ito, C. Kawakami, M. Sawamura, J. Am. Chem. Soc. 2005, 127, 16034; (b) C. Diner, K.J. Szabó, J. Am. Chem. Soc. 2017, 139, 2.

REACTIVITY OF 2-ELECTRON REDUCED FORMAZANATE BORON COMPOUNDS WITH ELECTROPHILES: FACILE N-H/N-C BOND HOMOLYSIS DUE TO FORMATION OF STABLE LIGAND RADICALS

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The majority of synthetic molecular catalysts change their oxidation state by changing the formal oxidation state of the central metal atom. In contrast, Nature often uses metalloenzymes in which there is a redox-active organic moieties which accumulate redox equivalents that can subsequently be used by the metalloenzyme to perform challenging multi-electron transformations.^[1] Inspired by these enzymatic systems, there is increasing interest in the chemistry of synthetic catalysts with redox-active ligands.^[2] Herein, we have explored the reactivity of a boron complex with redox-active formazanate ligand, LBPh₂ (L = PhNNC(*p*-*tol*)NNPh). Two-electron reduction of this main group complex generates the stable dianion [LBPh₂]²⁻, which is susceptible to electrophilic attack by BnBr and H₂O and yields products that derive from ligand benzylation and protonation, respectively (scheme 1). The resulting complexes are anionic boron analogues of leucoverdazyls. N-C and N-H bond homolysis of these compounds was studied by exchange NMR spectroscopy and kinetic experiments. The weak N-C and N-H bonds in these systems derive from the stability of the resulting borataverdazyl radical, in which the unpaired electron is delocalized over the four nitrogen atoms in the ligand backbone. We thus show the ability of this system to store [2e-/E⁺] on the organic ligand and convert it to E⁺ radicals, reactivity that has implications in energy storage applications such as hydrogen evolution.



Scheme 1. Synthesis of compounds ^{Bn}3⁻ and ^H3⁻.

References

- 1) J. W. Whittaker, Chem. Rev. 2003, 103, 2347.
- 2) W. I. Dzik, J. I. van der Vlugt, J. N. H. Reek, B. de Bruin Angew. Chem. Int. Ed. 2011, 50, 3356.

NON-HEME BIOMIMETIC COMPLEXES FEATURING NOVEL NNO-PHENOLATE LIGANDS AND SULFUR-RICH COFACTORS

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Sulfur is a multivalent, soft ligand that enables a high degree of covalent character in the bonds it forms to transition metal centres. Indeed, the coordination of thiolates to iron is of crucial biological importance, facilitating complex electron transport mechanisms, the stabilisation of high metal oxidation states, and the lowering of the energetic activation barrier for O₂ binding. These properties are of crucial importance for *isopenicillin N synthase* (IPNS), a remarkable mononuclear non-heme iron(II) enzyme that is capable of activating O₂ after binding to its native substrate (ACV) through a single Fe-S bond (Figure, left).^[1]

In this work, two novel tripodal NNO phenolate ligands, BenzImNNO and DiPhImNNO (Figure, middle), are presented as faithful structural models of the 2-His-1-carboxylate facial triad (2H1C),^[2] found at the active site of IPNS.^[1,3] Their coordination to iron and zinc is investigated, and different coordination modes are observed. Interestingly, the dinuclear iron(II) triflate complex of DiPhImNNO is found to serve as convenient synthon for ligand exchange involving monodentate thiolates, and the thiolates do not bridge (Figure, right). Here we present an analysis of the electronic properties of iron thiolate complexes involving both ligands and a range of monoanionic thiolates, and the role these properties may have on further reactivity.



[Fe²⁺-IPNS-ACV-NO-OH₂] Coordination of ACV to the active site of IPNS via a single Fe-S bond.



DiPhlmNNO



[Fe(ĸ²-DiPhImNNO)(SPh)]₂

- 1) P.L. Roach, J.E. Baldwin et al, *Nature.* **1997**, 387, 827
- 2) P.C.A. Bruijnincx, R.J.M. Klein Gebbink et al, Inorg. Chem., 2007, 46, 8391
- 3) L. Que, Nat. Struct. Biol., 2000, 7, 182

ONE- AND TWO-CENTER DECOMPOSITION OF NONLINEAR OPTICAL PROPERTIES

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Great attention has been paid to the materials characterized by a large nonlinear optical response, as they are commonly used in optical communication technology. Historically, there has been great interest in decomposing the global value of the NLOP, e.g. the molecular polarizability (α), into contributions of individual atoms or functional groups. Transferable group polarizabilities give insight about the value of the NLOP and also would allow for their prediction. The problem that arises with such decompositions is that the atomic contributions obtained from the straightforward decomposition of the NLOPs are origin-dependent. In 1990, Bader^[1] showed that α can be expressed as a sum of atomic (intrinsic) origin-independent contributions and a global charge-transfer term. However, a recent study of Mei et al.^[2] has shown that for general molecules the global charge-transfer term typically represents 60 to 90% of the overall value of α . Certainly, a better solution to the problem is yet to be found.

In this talk we will discuss how the NLOP can be decomposed into one- and two-center contributions (atoms or molecular fragments) in such a way that the origin-independence of the terms is ensured. Thus, the one-center terms are associated to intrinsic contributions, whereas the two-center ones will account for the interplay of the defined fragments to increase or decrease the overall NLOP. The transferability of the terms will be explored for a set of molecules, and the results obtained will be compared with previous decomposition schemes.

1) K. E. Laidig, R. F. W. Bader, J. Chem. Phys., 1990, 93, 7213.

²⁾ Ye Mei, Andrew C. Simmonett, Frank C. Pickard, IV, Robert A. DiStasio, Jr., Bernard R. Brooks, and Yihan Shao. J. Phys. Chem., 2015, 119, 5865-5882.

GETTING INSIGHT INTO THE Rh-Cu BIMETALLIC COOPERATION: A NEW CASE OF COOPERATIVE REDUCTIVE ELIMINATION

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The C-H activation in cross-coupling reactions have appeared as a green alternative that allows the formation of new C-C bond in a non-pre-functionalized position. In a non-neutral redox catalytic system, after reductive elimination, an oxidant is required. Different transition metals have been reported to be effective in these transformations but only with some selective oxidative partners. Recently, in our group, a perfect cooperation between Rh and Cu has been reported.^[1] Interestingly, the reductive elimination does not take place from a single metal but from a Rh-Cu intermediate. Herein, we study computationally another example of bimetallic Rh and Cu system.^[2] Many evidences point out the cooperation of both of them in the reductive elimination step.



(1) I. Funes-Ardoiz, F. Maseras, Angew. Chem. Int. Ed. 2016, 55, 2764

(2) Y. F. Wang, K. K. Toh, J. Y. Lee, S. Chiba, Angew. Chem. Int. Ed. 2011, 50, 5927

TERMINAL IRON(III)-OXO COMPLEXES

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Terminal iron(IV)-oxo compounds are one of the best explored systems in bioinorganic and biomimetic chemistry.^[1] Conversely, terminal iron(III)-oxo compounds, products of formal one-electron reduction of iron(IV)-oxo analogs, have been studied only scarcely. Herein, we report the generation of representative tetragonal and trigonal iron(III)-oxo complexes in the gas phase.^[2] Iron(III)-oxo complexes were prepared by two methods, either by oxidative cleavage of iron(II)-nitrate precursors or by one-electron reduction of iron(IV)-oxo compounds. All studied complexes were characterized by infrared and visible photodissociation spectroscopies, which provided Fe–O vibration frequencies and allowed assignment of spin states. The Fe–O vibration of the quartet state iron(III)-oxo complexes is located at the same frequency as that of their iron(IV)-oxo analogs. The position of the Fe–O vibration in the sextet state complexes is red-shifted by approximately 70 cm⁻¹. Therefore, the Fe–O vibration frequency reflects the spin state of iron center in terminal iron(III)-oxo compounds in contrast to iron(IV)-oxo compounds. Furthermore, we studied the effect of water coordination to the iron-oxo unit and found out that quartet state complexes undergo spin change upon water coordination. Our spectroscopic data provide a solid starting point for the identification and investigation of these reactive intermediates in the condensed phase.

References:

¹⁾ J. Hohenberger, K. Ray, K. Meyer, Nat. Commun. 2012, 3, 720

²⁾ E. Andris, R. Navrátil, J. Jašík, M. Puri, M. Costas, L. Que, Jr., J. Roithová, manuscript in preparati

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UNDERSTANDING OXIDATIVE ADDITION TO NICKEL: TOWARDS ROBUST AND PREDICTABLE SITE-SELECTIVE CROSS-COUPLING

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Nickel catalysis is a promising and rapidly-developing field, but our mechanistic understanding of important fundamental processes lags behind our synthetic chemistry capability. A seminal study of the oxidative addition of aryl halides to [Ni⁰(PEt₃)₄] proposed that electron transfer was the key step, with subsequent and competing processes leading to [NiX(PEt₃)₃] (plus ArH) or [Ni(Ar)X(PEt₃)₂];^[1] however, this is not necessarily relevant to modern catalyst systems. This presentation will report our work towards a fundamental understanding of oxidative addition to modern Ni⁰ systems, using experimental^{[2][3]} and theoretical methods^[4] (*Scheme 1*). These include: DFT studies show that oxidative addition to [Ni⁰(PR₃)₄] occurs *via* [Ni⁰(PR₃)₃] to yield mixtures of Ni¹ and Ni¹¹ directly;^[4] experimental studies of oxidative addition to [Ni⁰(COD)(dppf)] that rank the reactivity of 11 aryl (pseudo)halides quantitatively for the first time;^[2] and experimental and theoretical studies that show that aryl halides with certain functional groups reliably undergo selective cross-coupling in the presence of other aryl halide substrates.^[3]

Oxidative Addition to [Ni ⁰ (dppf)]	With S. Sproules, University of Glasgow, UK
Ph Ph	Reaction Rate:
P Ph ArX	$I > Br > CI > OTs > OTf > OCONEt_2 > OSO_2NMe_2 > OPiv > OMe \sim F$
$\begin{array}{c} Fe \\ \hline P \\ P \\ Ph \end{array}$	Mechanism:
Ph Ph + Ar-Ar	Oxidative addition to form Ni ^{II} ; comproportionation to form Ni ^I
Oxidative Addition to $[Ni(PMe_3)_4]$	With F. Maseras, ICIQ, Spain
Mo P PMe, Mo P X + ArH	Ph (i) DFT calculations to re-evaluate Kochi's
and	seminal study with [Ni(PEt ₃) ₄]
Me ₃ P PMe ₃ Me ₃ P PMe ₃ /or	(ii) Ni ¹ preferred for $X = I$; both formed
PMe ₃	$X + PMe_3$ for X = Br; Ni ^{II} preferred for X = CI
Site-Selectivity in Nickel-Catalysed Cross-Coupling	With Syngenta, Jealott's Hill, UK
	Selectivity is a function of σ_n but co-ordinating
	groups dominate. Oxidative Addition Rate is
X ArB(OH) ₂ , base	Ar increased substrates with some coordinating groups

- 1) T. T. Tsou and J. K. Kochi, J. Am. Chem. Soc., 1979, 101, 6319.
- 2) S. Bajo, G. Laidlaw, A. R. Kennedy, S. Sproules, and D. J. Nelson, Organometallics, 2017, 36, 1662.
- 3) A. K. Cooper, P. Burton, and D. J. Nelson, Manuscript Submitted

REVEALING THE IMPORTANCE OF ORBITAL INTERACTIONS AND PAULI REPULSION IN METALLOPHILICITY OF COINAGE METALS

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Closed-shell d¹⁰-d¹⁰ interactions are an interesting research target both from an experimental as well as from a theoretical perspective.^[1] From a practical point of view, these interactions can be used for the design of supramolecular (di-, oligo- or polymeric) structures. Furthermore, these structures show very interesting luminescent properties, including mechanochromic or vaporchromic behavior.^[2] Surprisingly, the bonding mechanism is still a subject of a long-standing debate; while the importance of relativity and dispersion in metallophilicity has been discussed in numerous studies.^[3] the existence of hybridization has also been speculated.^[4] In this talk, a quantitative molecular orbital analysis and energy decomposition of the

metallophilic interaction in atomic dimers (M⁺···M⁺) molecular perpendicular $[H_3P-M-X]_2$ (where M = Cu, X = F, Cl, Br, I) is discussed. Our studies prove, that the commonly accepted dispersive interactions, interactions and Pauli repulsion also play a crucial metallophilicity. While for M⁺····M⁺ the orbital is larger than the Pauli repulsion, leading to a net MO interaction. the bonding mechanism in



in

perpendicular [H₃P-M-X] dimers is different. Here Pauli repulsion is much larger and two-orbital-four-electron repulsion is dominant (see Figure).^[5] These results are of utmost importance for the fundamental knowledge and understanding of metallophilicity and for the future design of new materials.

^[1] a.) P. Pyykko, Chem. Soc. Rev. 2008, 37, 1967-1997; b.) H. Schmidbaur, A. Schier, Chem. Soc. Rev. 2008, 37, 1931-1951; c.) S. Sculfort, P. Braunstein, Chem. Soc. Rev. 2011, 40, 2741-2760; d.) H. Schmidbaur, A. Schier, Chem. Soc. Rev. 2012, 41, 370-412.

^[2] a.) C.-M. Che, S.-W. Lai, Coord. Chem. Rev. 2005, 249, 1296-1309; b.) D. L. Phillips, C.-M. Che, K. H. Leung, Z. Mao, M.-C. Tse, Coord. Chem.

Rev. 2005, 249, 1476-1490; c.) Z. N. Chen, N. Zhao, Y. Fan, J. Ni, Coord. Chem. Rev. 2009, 253, 1-20.

^[3] a.) P. Pyykko, Y. F. Zhao, Angew. Chem. Int. Ed. 1991, 30, 604-605; b.) J. Li, P. Pyykko, Chem. Phys. Lett. 1992, 197, 586-590; c.) P. Pyykko, J. Li, N. Runeberg, Chem. Phys. Lett. 1994, 218, 133-138

^[4] a.) P. K. Mehrotra, R. Hoffmann, Inorg. Chem. 1978, 17, 2187-2189; b.) Y. Jiang, S. Alvarez, R. Hoffmann, Inorg. Chem. 1985, 24, 749-757 [5] M. B. Brands, J. Nitsch, C. Fonseca Guerra, submitted

SELECTIVE, REMOTE C-H OXIDATION GUIDED BY SUPRAMOLECULAR INTERACTIONS

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The development of predictable, site-selective oxidation protocol of aliphatic C-H bonds stands a longstanding goal in organic synthesis. In the last decade, iron and manganese coordination complexes emerged as promising candidates to carry out such reactions. The hydroxylation selectivity, essentially dictated by the electronic and steric properties of the substrate, can be tuned to some extent by careful modification of the catalyst structure.^[1] However, when multiple C-H bonds display a comparable reactivity, such as in linear alkyl chains or elaborated structures, a selective oxidation could become rather challenging, affording (statistical) mixtures of products. Aiming at overcoming this limitation, we explored the feasibility of a different, supramolecular strategy to geometrically control the selectivity (Scheme 1).

The binding of a primary ammonium substrate to a receptor (18-crown-6 ether) anchored to the Mn catalyst exposes remote C8 and C9 C-H bonds to the oxidizing unit, thus allowing selective, remote oxidation of protonated amines. ^[2] Remarkably, this approach affords a selectivity that can be either not accessible with or orthogonal to more explored non-directed (or guided) approaches.



- 1) M. C. White, Science 2012, 335, 807-809; G. Olivo, O. Cussò, M. Costas, Chem. An Asian J. 2016, 11, 3148–3158
- 2) G. Olivo, G. Farinelli, A. Barbieri, O. Lanzalunga, S. Di Stefano, M. Costas, Angew. Chem. Int. Ed. 2017, DOI: 10.1002/anie.201709280.

IRON CATALYSTS WITH NON-INNOCENT LIGANDS FOR RING-OPENING POLYMERIZATION: A COMPUTATIONAL APPROACH

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Iron has emerged as a key player in homogeneous catalysis due to its earth abundance and chemical versatility. Aiming to develop sustainable protocols and materials, we target the synthesis of biodegradable polymers from renewable biomass-derived monomers such as ε-caprolactone and lactide.^[1]

In this study we present a series of iron–alkoxide species, stabilized by non-innocent (redox active) pyridine(diimine) scaffolds, that catalyze the ring-opening polymerization of various monomers.^{[2],[3]} We exploit computational models to characterize the intricate electronic structures of these complexes and elucidate the underlying reaction mechanisms at the atomic level of resolution. Detailed understanding of the role of the oxidation state of iron, initiating alkoxide groups, and stereoelectronic effects of non-innocent ligands would provide crucial information to computationally drive the design of new and improved catalysts.



- 1) D. K. Schneiderman, M. A. Hillmyer, *Macromolecules* 2017, 50, 3733.
- 2) A. B. Biernesser, K. R. Delle Chiaie, J. B. Curley, J. A. Byers, Angew. Chem. Int. Ed. 2016, 55, 5251.
- 3) K. R. Delle Chiaie, A. B. Biernesser, M. A. Ortuño, B. Dereli, D. A. Iovan, M. J. T. Wilding, B. Li, C. J. Cramer, J. A. Byers, submitted.

ADVANCED CU-PEPTIDE DESIGN FOR THE EFFICIENT ELECTROCATALYTIC PRODUCTION OF O₂

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Converting renewable electric power into H₂ by the electrolysis of water represents a reasonable alternative for the continuation of the flexible supply of our needs now tuned towards renewable energy sources. Catalysts for the electrolysis of water (e.g., H₂ production) that utilize first row transition metals, especially those which promote the more demanding oxygen evolving reaction (OER, also known as water oxidation catalysts, WOCs), are highly wanted. Despite the direct advantages of heterogeneous systems, molecular WOCs formed with organic ligands gain peculiar attention. Molecular systems can either change dynamically leading to *in-situ* formed compounds with characteristic activity, or exhibit remarkably long-lived molecular catalysis. Investigation and understanding of the pH-dependent behavior, stability and redox properties of the various metal-ligand combinations ought to be continual goals in accordance with their central role in both scenarios. We are studying versatile metallopeptides, paying special attention to copper. These systems are inspired by the natural polypeptides serving as the backbone of most metalloenzymes. My presentation focuses on new metal coordination options created by artificial peptide branching. We achieved substantial progress in the control of the stability and WOC performance of copper-branched peptide complexes.[1-3] Moreover, the molecular catalysts could be layered onto electrodes with polyelectrolytes that allowed operando surface studies.^[4] Most recently we have achieved an order of magnitude increase in the catalytic rate for WOC by introducing α -methyl substituents to a branched peptide backbone (to be submitted). The key to all targeted modifications was the modular design of this new ligand family.^[5]

References:

- 2) Ł. Szyrwiel, D. Lukács, D.F. Srankó, Z. Kerner, A. Kotynia, J. Brasun, B. Setner, Z. Szewczuk, K. Malec, J.S. Pap, RSC Adv. 2017, 7, 24657
- 3) J.S. Pap, Ł. Szyrwiel, Comm. Inorg. Chem. 2017, 37, 59
- 4) E. Farkas, D.F. Srankó, Z. Kerner, B. Setner, Z. Szewczuk, W. Malinka, R. Horvath, Ł. Szyrwiel, J.S. Pap, Chem. Sci. 2016, 7, 5249
- 5) Ł. Szyrwiel, Ł. Szczukowski, J.S. Pap, B. Setner, Z. Szewczuk, W. Malinka, Inorg. Chem. 2014, 53, 7951

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¹⁾ J.S. Pap, Ł. Szyrwiel, D.F. Srankó, Z. Kerner, B. Setner, Z. Szewczuk, W. Malinka, Chem. Commun. 2015, 51, 6322

HOMOGENEOUS COBALT CATALYSED AMIDES TO AMINES HYDROGENATION

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Amines constitute an important class of compounds with wide application in major industrial fields, such as in agrochemical and pharmaceutica^[1] For the synthesis of structurally complex compounds and natural products containing amine moieties, a route foresees the reduction of the amide to corresponding amine. Unfortunately, amides constitute one of the least reactive derivatives among all classes of carbonyl and traditionally, their reduction is performed using an excess of reducing agents producing stoichiometric amounts of waste-products.^[2]

Thus, catalytic hydrogenation using molecular hydrogen is of high interest as it offers an atom-economic and waste-free methodology.^[3]

Depending on the type of homogeneous catalyst, the hydrogenation of amides (Scheme 1, path A and B) can follow two distinct pathways: path A, which foresees the C-O bond cleavage to afford the more desired higher amine or, alternatively, the catalyst can promote the C-N bond breaking (path B), that leads to the formation of corresponding alcohol and amine; in the last decade, significant improvements in amide hydrogenation using homogeneous Ir and Ru-based catalysts have been achieved.^[4]

In this work, we have developed a three components catalytic system constituted by Co(N(Tf)₂)₂ as metallic precursor, 1,1,1-tris{bis(4-methoxyphenyl)phosphinomethyl}ethan as ligand and a Lewis acid as external additive, that is able to hydrogenate a wide range of amides; the presence of Lewis acid additive improves yields and selectivity of the higher desired amines.



1) Amines: Synthesis, Properties and Applications; S.A. Lawrence, Ed.; Cambridge University: Cambridge, 2006.

 a) H. C. Brown, S. Narasimhan and Y. M. Choi, Synthesis-Stuttgart, **1981**, 441-442; b) J. March, Advanced Organic Chenistry, 4th edn., Wiley, New york, **1992**; c) S. Werkmeister, K. Junge and M. Beller, Organic Process Research & Development, **2014**, 18, 289-302.

3) A. M. Smith, R. Whyman, Chem. Rev. 2014, 114, 5477.

a) A. A. Núñez Magro, G. R. Eastham and D. J. Cole-Hamilton, *Chem. Commun.* 2007, 3154-3156; b) D. L. Dodds, J. Klankermayer, S. Brosinski, W. Leitner and D. J. Cole-Hamilton, *Chem. Commun.*, 2012, 48, 12249-12262; c) J. Coetzee, D. L. Dodds, J. Klankermayer, S. Brosinski, W. Leitner, A. M. Z. Slawin and D. J. Cole-Hamilton, *Chem. Eur. J.*, 2013, 19, 11039-11050; d) J. R. Cabrero-Antonino, E. Alberico, K. Junge, H. Junge and M. Beller, *Chem. Sci.*, 2016, 7, 3432-3442; e) M. L. Yuan, J. H. Xie and Q. L. Zhou, *Chemcatchem*, 2016, 8, 3036-3040; f) M. L. Yuan, J. H. Xie, S. F. Zhu and Q. L. Zhou, *ACS Catal.*, 2016, 6, 3665-3669.
SOLVENT DYNAMICS CONTROLS THE SCHLENK EQUILIBRIUM OF GRIGNARD REAGENTS:

COMPUTATIONAL STUDY OF CH₃MGCL IN TETRAHYDROFURAN.

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The Schlenk equilibrium [1] is a complex reaction governing the presence of multiple chemical species in solution of Grignard reagents. [2] A full characterization at the molecular level of the transformation of CH₃MgCl into MgCl₂ and Mg(CH₃)₂ in tetrahydrofuran (THF) by means of ab initio molecular dynamics simulations with enhanced-sampling metadynamics was carried out. The reaction occurs via formation of dinuclear species bridged by chlorine atoms. At room temperature, the different chemical species involved in the reaction accept multiple solvation structures, with two to four THF molecules that can coordinate the Mg atoms. The energy difference between all dinuclear solvated structures is lower than 5 kcal mol⁻¹. The solvent is shown to be a direct key player driving the Schlenk mechanism. In particular, our study illustrates how the most stable symmetrically solvated dinuclear species, $(THF)CH_3Mg(\mu-Cl)_2MgCH_3(THF)$ and $(THF)CH_3Mg(\mu-Cl)(\mu-CH_3)MgCl(THF)$, need to evolve to less stable asymmetrically solvated species, $(THF)CH_3Mg(\mu-Cl)_2MgCH_3(THF)$ and $(THF)CH_3Mg(\mu-Cl)(\mu-CH_3)MgCl(THF)_2$, in order to yield ligand exchange or product dissociation. In addition, the transferred ligands are always departing from an axial position of a pentacoordinated Mg atom. Thus, solvent dynamics is key to successive Mg–Cl and Mg–CH3 bond cleavages because bond breaking occurs at the most solvated Mg atom and the formation of bonds takes place at the least solvated one. The dynamics of the solvent also contributes to keep relatively flat the free energy profile of the Schlenk equilibrium.

References (ACS Style): Left aligned, Arial Narrow 10.

¹⁾ W. Schlenk, W. Schlenk, Ber. Dtsch. Chem. Ges. A/B 2014, 62, 920-024.

²⁾ V. Grignard, C. r. d. l'Acad. Des Sciences 1900, 130, 1322-1324

SYNERGY OF EXPERIMENTS AND CALCULATIONS UNCOVERS THE MECHANISM OF UNSUSPECTED ARYL-EXCHANGES IN 16e [RhCp*Ar₂] COMPLEXES

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The reactivity of eighteen-electron octahedral organometallic complexes is assumed to start with a one-ligand dissociation to give sixteen-electron electrophilic species. $M^{III}Cp^*$ ($Cp^* = C_5Me_5$; M = Rh, Ir) systems continue arising attention for their reactivity and properties. For instance, very recently $Rh^{III}Cp^*$ complexes have been reported to catalyse the dehydrogenative coupling formation of bis-heteroarylated phenols via a 5-coordinate 16e complex.^[1]

In this communication, we report the synthesis of unusually stable 16e complexes [RhCp*Ar₂] (Ar = C_6F_5 = Pf, or $C_6F_3Cl_2$ -3,5 = Rf) as models of intermediates formed from octahedral complexes after L-dissociation. Experimental studies on these species uncover the existence of fast aryl transmetalations resulting in the formation of the aryl-mixed compound [RhCp*PfRf]. The initial mechanistic proposal was computationally discarded due to the high activation barrier (Figure 1, left). Experimental reexamination revealed that these exchanges were catalyzed by minute amounts of 18e (μ -OH)₂[RhCp*Ar]₂ as source of 16e [RhCp*Ar(OH)].^[2] This unexpected mechanism was confirmed by DFT calculations (Figure 1, right) and suggests that the OH group is an amazingly efficient bridging partner to reduce the activation barrier of transmetalation processes.



Figure 1. Calculated transition states and the corresponding ΔG^{\ddagger} for the direct mechanism (left) and for the OH-catalysed (right). Relevant bond distances (Å) are shown.

Only the cooperation of experimental studies and DFT calculations led to true understanding of the observed processes and prevented falling into misinterpretations, and the moral of this is that even *obvious* conclusions from clear observations should better be supported by additional data.

References

- 1) Wu, Q.; Chen, Y.; Yan, M.; Lu, Y.; Sun, W.-Y.; Zhao, J. Chem. Sci., 2017, 8, 169.
- 2) Peñas-Defrutos, M. N.; Bartolomé, C.; García-Melchor, M.; Espinet, P. Chem. Commun. 2018. DOI:10.1039/C7CC09352G

COBALT-CATALYZED C-H FUNCTIONALIZATION: REACTION INTERMEDIATES AND MECHANISM ELUCIDATION

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In the recent years, cobalt catalysis has emerged as a valuable approach for the construction of organic molecules.^[1] Although the reported methodologies, the synthesis of organometallic aryl-Co(III) species through C-H activation still remains in its infancy.^[2] This contribution describes the preparation and characterization of stable aryl-Co(III) compounds (NMR, HRMS, X-Ray) through C(sp²)-H activation within a 12-membered macrocyclic ligand.^[3] Subsequent insights obtained from the application of the isolable aryl-Co(III) intermediates in alkyne and diazo compound annulation reactions are disclosed (Figure 1).^[3,4]



Figure 1. Isolation of aryl-Coll and reactivity with alkynes and diazo compounds.

References

[1] M. Moselage, J. Li, L. Ackermann, ACS Catal. 2016, 6, 498.

[2] (a) K. Kanamori, W. E. Broderick, R. F. Jordan, R. D. Willett, J. I. Legg, J. Am. Chem. Soc. **1986**, 108, 7122. (b) T. Avilés. A. Dinis, M. J. Calhorda, P. C. Pinto, V. Felix, M. G. B, Drew, J. Organomet. Chem. **2001**, 625, 186. S. Maity, R. Kancherla, S. Pimparkar, D. Maiti. ACS Catal. **2016**, 6, 5493.

[3] O. Planas, C. J. Whiteoak, V. Martin-Diaconescu, I. Gamba, J. M. Luis, T. Parella, A. Company, X. Ribas, *J. Am. Chem. Soc.* **2016**, 138, 14388.

[4] O. Planas, S. Roldán-Gómez, V. Martin-Diaconescu, T. Parella, J. M. Luis, A. Company, X. Ribas, *J. Am. Chem. Soc.* 2017, 139, 14649.

THE ROLE OF THE METAL IN THE DUAL-METAL CATALYSED HYDROPHENOXYLATION OF DIPHENYLACETYLENE

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Recently, the hydrophenoxylation of alkynes mediated by a gold catalyst has been shown to occur through a bimetallic process where the active species are [Au(OPh)(IPr)] and [Au(n²-alkyne)(IPr)]⁺.^[1,2] On the other hand, Cazin and co-workers have reported an improvement of the hydrophenoxylation reaction by using a combination of [Cu(OPh)(IPr)] and [Au(n²-alkyne)(IPr)]⁺. Herein, we performed DFT calculations to rationalize the performance of the Cu/Au bimetallic system. We have studied the rate determining step (rds) proposed by Poater et al. for the potential initial reagents PhO-[M] and alkyne-[M] species. Silver was also included in this study in order to understand the effect of the metal. Moreover, the effect of the steric hindrance on the rds was investigated with less sterically demanding ligands such as IMes, SIMes and IMe. Overall, the [Cu]/[Au] system was computed to be superior to the [Au]/[Au] system, but the [Ag]/[Au] couple exhibited the lowest energy barrier for the rds providing an enhancement of the heterometallic catalysis. We show that the rds is quite sensitive to the ligand steric hindrance.^[3]

References:

- 1) A. Gómez-Suárez, Y. Oonishi, A. R. Martin, S. V. C. Vummaleti, D. J. Nelson, D. B. Cordes, A. M. Z. Slawin, L. Cavallo, S. P. Nolan and A. Poater, *Chem. Eur. J.* 2016, 22, 1125.
- 2) È. Casals-Cruañas, O. F. González-Belman, P. Besalú-Sala, D. J. Nelson and A. Poater, Org. Biomol. Chem. 2017, 15, 6416.
- 3) L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano and L. Cavallo, Organometallics 2016, 35, 2286.

STRUCTURE AND STABILITY OF B-DNA MODEL SYSTEMS IN NON-TERRAN BIO-SOLVENTS

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We have computationally analyzed a comprehensive series of Watson–Crick and mismatched B-DNA base pairs,^[1-3] in the gas phase and in several solvents, including toluene, chloroform, ammonia, methanol and water, using dispersion-corrected density functional theory and implicit solvation.^[4] Our analyses shed light on how the molecular-recognition machinery behind life's genetic code depends on the medium, in order to contribute to our understanding of the possibility or impossibility for life to exist on exoplanetary bodies. Calculations show how a common non-terran environment like ammonia, less polar than water, exhibits stronger hydrogen-bonding affinities, although showing reduced selectivities towards the correct incorporation of Watson–Crick base pairs into the backbone. Thus, we prove the viability of DNA replication in a non-terran environment.

- 1) J. Poater, M. Swart, C. Fonseca Guerra, F. M. Bickelhaupt, Org. Biomol. Chem. 2014, 12, 4691
- 2) T. A. Hamlin, J. Poater, C. Fonseca Guerra, F. M. Bickelhaupt, Phys. Chem. Chem. Phys. 2017, 19, 16969
- 3) J. Poater, M. Swart, C. Fonseca Guerra, F. M. Bickelhaupt, Chem. Comm. 2011, 47, 7326
- 4) J. Poater, M. Swart, C. Fonseca Guerra, F. M. Bickelhaupt, Comput. Theor. Chem. 2012, 998, 57

QUANTUM CHEMICAL STUDIES & MACHINE LEARNING OF 25K HETEROCYCLES FOR LIGAND DESIGN

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The advances in deep learning of the last years has led to a growing interest in applying machine learning (ML) to chemistry, with many fascinating results [1]. The quality of the results depends on training data, representation of the molecules, and the chosen model.

Advances in many technologies rely on the design of new transition metal (TM) complexes. We are interested in the design of TM complexes for small-molecule activation. We have computed the properties of 25K heterocycles [2] at DFT level and benchmarked different regression methods in property prediction. In addition to these results, tentative results of automatic design and optimization ligands will be presented.

1) Janet, J. and Kulik, H. Chemical Science, 2017, 8(7) 5137

²⁾ Pitt, W., et al. J. Med. Chem. 2009, 9, 2952.; Goh, Get al. J. of Comp. Chem. 2017

UNRAVELING MECHANISTIC ASPECTS OF THE ARYL-CO(III) MASKED-CARBENES INTERMEDIATES FROM A COBALT-CATALYZED C-H FUNCTIONALIZATION WITH DIAZO ESTERS: A COMPUTATIONAL STUDY.

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It has not been that long since cobalt catalysis emerged as a valuable asset to perform C-H bond activation.^[1] One example of current interes is the Co-carbene formation^[2] when coupling a diazocarbonyl compounds with the metal.^[3] Although these type of reactions are broadly studied, the C-H functionalization with high-valent aryl-Co-carbene intermediates is not fully developed,^[4] which implies a scarce in the experimental evidence and computational studies regarding its mechanism.^[5] Based on a previous report regarding the synthesis and characterization of aryl-cobalt(III) complexes through C-H activation,^[6] we decided to study the Co(III)-carbene species with those aryl-Co(III) complexes. In this work we report the computational studies carried out in parallel to the synthesis of a new family of aryl-Co(III)-carboxylate complexes (2a-X) and their reactivity with ethyl diazoacetate (EDA), and how these calculations predicted the presence of a **C-metalated cis-aryl-Co(III)-alkyl enolate** intermediate that can be seen as a tamed Co-carbene species to create C-C bonds via an uncommon intramolecular SN2-like pathway. We also try to explain the roll of some key factors in the catalytic process like the use of additives, the type of carboxylate and the effect of the acidity in the system.



References

1) a) Yoshino, T.; Matsunaga, S. Adv. Synth. Catal. 2017, 359, 1245; b) Ackermann, L. ACS Catal. 2016, 6, 498.

2) a) Bellow, J. A.; Stoian, Š. A.; van Tol, J.; Ozarowski, A.; Lord, R. L.; Groysman, S. J. Am. Chem. Soc. **2016**, 138, 5531; b) Mondal, K. C.; Samuel, P. P.; Roesky, H. W.; Carl, E.; Herbst-Irmer, R.; Stalke, D.; Schwederski, B.; Kaim, W.; Ungur, L.; Chibotaru, L. F.; Hermann, M.; Frenking, G. J. Am. Chem. Soc. **2014**, 136, 1770.

3) a) Jia, M.; Ma, S. Angew. Chem. Int. Ed. 2016, 55, 9134; b) Fructos, M. R.; Besora, M.; Braga, A. A. C.; Díaz-Requejo, M. M.; Maseras, F.; Pérez, P. J. Organometallics 2017, 36, 172.

4) a) Maity, S.; Kancherla, R.; Dhawa, U.; Hoque, E.; Pimparkar, S.; Maiti, D. ACS Catal. **2016**, 6, 5493; b) Avilés, T.; Dinis, A.; Calhorda, M. J.; Pinto, P. c.; Félix, V.; Drew, M. G. B. J. Organomet. Chem. **2001**, 625, 186.

5) b) Kim, J. H.; Greßies, S.; Glorius, F. Angew. Chem. Int. Ed. 2016, 55, 5577; b) Qu, S.; Cramer, C. J. J. Org. Chem. 2017, 82, 1195.

6) Planas, O.; Whiteoak, C. J.; Martin-Diaconescu, V.; Gamba, I.; Luis, J. M.; Parella, T.; Company, A.; Ribas, X. J. Am. Chem. Soc. 2016, 138, 14388.

ROLE OF CONFORMATIONAL DYNAMICS IN THE EVOLUTION OF RETRO-ALDOLASE ACTIVITY

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Enzymes exist as ensembles of conformations that are important for function. Tuning these populations of conformational states through mutation enables evolution toward additional activities. Here we computationally evaluate the population shifts induced by distal and active site mutations in a family of computationally designed and experimentally optimized retro-aldolases. The conformational landscape of these enzymes was significantly altered during evolution, as preexisting catalytically active conformational substates became major states in the most evolved variants.^[1] We further demonstrate that key residues responsible for these substate conversions can be predicted computationally. Significantly, the identified residues coincide with those positions mutated in the laboratory evolution experiments. This study establishes that distal mutations that affect enzyme catalytic activity can be predicted computationally and thus provides the enzyme (re)design field with a rational strategy to determine promising sites for enhancing activity through mutation.^[2]

¹⁾ Obexer, R.; Godina, A.; Garrabou, X.; Mittl, P. R. E.; Baker, D.; Griffiths, A. D.; Hilvert, D. Nat. Chem. 2017, 9 (1), 50–56

²⁾ Romero-Rivera, A.; Garcia-Borràs, M.; Osuna, S. ACS Catal., 2017, 7 (12), pp 8524–8532

ENGENDERING FUNCTIONALITY IN SPIRO- AND DISPIROHETEROCYCLES

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Borylative cyclizations of alkenes in the presence of appropriate leaving groups allow for the selective synthesis of target organoboron compounds with remarkable bioactivity.^[1,2]

Inspired by the efficient borylative exo-cyclization of alkenyl halides reported by Ito et al.,^[3] we have complemented the study focusing on the synthesis of boron-containing spiro compounds. Our work hypothesis is based on the regioselective addition of a borylcopper(I) specie to unactivated terminal alkenes, locating the C-Cu bond in the internal position. Interestingly, the new alkylcopper(I) specie efficiently reacts intramolecularly with the alkylhalide to generate a new C-C bond providing a cyclic system with a borylmethyl moiety that could be further functionalized.^[4]

In order to have deeper insights about the mechanism and the corresponding formation of these novel spiro compounds, DFT calculations were carried out to support the experimental results.^[5]



[2] Bunuel, E.; Cardenas, D. J. *Eur. J. Org. Chem.* **2016**, 5446

[3] Kubota, K.; Yamamoto, E.; Ito, H. *J. Am. Chem. Soc.* **2013**, 2635

[4] E. La Cascia, A. B. Cuenca, E. Fernandez, *Chem. Eur. J.* **2016**, 22, 18737.

[5] J. Jover, F. Maseras, Organometallics 2016, 35, 3221.

UNDERSTANDING THE HYDRO-METATHESIS REACTION OF 1-DECENE BY USING WELL-DEFINED SILICA SUPPORTED W, Mo, Ta CARBENE/CARBYNE COMPLEXES

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Metathesis reaction has become one of the standard methodologies for constructing C-C bonds in many organic transformation reactions, it is considered among the most important and future prosperity promising catalytic applications in the petrochemical field^[1-2]. This is owed to the numerous types of metathesis reactions that have been developed, for example; alkane, olefin, enyne metathesis^[3], etc. However, the one-step conversion of olefin to alkanes called as Hydro-metathesis reaction has not been well-explored.

To understand this reaction, we tested for the first time three different well-defined single site catalysts precursors; $[(\equiv Si-O-)W(CH_3)_5]$, $[(\equiv Si-O-)Mo(\equiv C^tBu)(CH_2^tBu)_2]$ and $[(\equiv Si-O)Ta(=CH^tBu)(CH_2^tBu)_2]$ (Figure 1) to convert directly 1-decene to petroleum range alkanes by hydro-metathesis reaction in batch reactor condition. These group V and VI catalysts precursors, are well-known for their high reactivity toward C–H and C–C bonds^[4], they were prepared using Surface Organometallic Chemistry (SOMC) approach^[5-7] which is based on attempting the bridge between homogeneous and heterogeneous catalysis.^[8]

In this work, we witnessed that silica supported W and Mo catalytic precursors are better catalysts for hydrometathesis reaction with TONs of 818 and 808 than Ta-based catalyst (TON of 334) after 3 days (Figure 2). Regarding the catalytic mechanism, we observed that different metals approach differently towards olefin; we found that Mo-based catalyst favors 2+2 cycloaddition of 1-decene forming metallocarbene, followed by reduction of the newly formed olefins to alkanes. However, in the case of W and Ta-based catalysts, a rapid isomerization of the double bond followed by olefin metathesis and reduction of the newly formed olefins were observed. This comparison provides us a better understanding that, if a catalyst is efficient in olefin metathesis reaction it would be a better catalyst for hydro-metathesis reaction. Comparing this with n-decane metathesis, we witnessed that we could get better conversion, as well as TON, starting from 1-decene to diesel range alkanes than n-decane. Therefore, we believe this study will open up many directions to efficiently use the olefins for various organic transformation reactions.



Figure 1. Well-defined silica supported [(≡Si-O-)W(CH₃)₅] 1, [(≡Si-O-)Mo(≡C^tBu)(CH₂^tBu)₂] 2 and [(≡Si-O)Ta(=CH^tBu)(CH₂^tBu)₂] 3



Figure 2. Time vs. TON plot for 1-decene hydro-metathesis reaction using catalysts $[(\equiv Si-O-)W(CH_3)_5], [(\equiv Si-O-)Mo(\equiv C^tBu)(CH_2^tBu)_2]$ and $[(\equiv Si-O)Ta(=CH^tBu)(CH_2^tBu)_2]$ in a batch reactor condition

- 1) R. H. Grubbs, Angew. Chem. Int. Ed. 2006, 45 (23), 3760-3765.
- 2) D. Astruc, New J. Chem. 2005, 29 (1), 42-56.
- 3) J. M. Basset, C. Coperet, D. Soulivong, M.Taoufik, J. T. Caza, Acc. Chem. Res. 2009, 43 (2), 323-334.
- 4) M. K. Samantaray, R. Dey, S. Kavitake, J. M. Basset, Springer: 2015; pp 155-187.
- 5) M. K. Samantaray, E. Callens, E. Abou-Hamad, A. J. Rossini, C. M. Widdifield, R. Dey, L. Emsley, J. M. Basset, *J. Am. Chem. Soc.* **2014**, *136* (3), 1054-1061.
- 6) D. Clark, R. Schrock, J. Am. Chem. Soc. 1978, 100 (21), 6774-6776.
- 7) E. Le Roux, M. Chabanas, A. Baudouin, A. de Mallmann, C. Copéret, E. A. Quadrelli, J. Thivolle-Cazat, J. M. Basset, W. Lukens,
- A. Lesage, J. Am. Chem. Soc. 2004, 126 (41), 13391-13399.
- 8) C. Copéret, M. Chabanas, R. P. Saint-Arroman, J. M. Basset, Angew. Chem. Int. Ed. 2003, 42 (2), 156-181.

CHARACTERIZATION OF REDOX-INDUCED ELECTRON TRANSFER PROCESSES

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Complexes that possess one or more non-innocent ligands that can be isolated in several oxidation states may exhibit so-called redox-induced electron transfer (RIET) reactions.^[1] For instance, dinuclear compounds exhibiting a bridging tetraoxolate ligand can experience redox reactions where the ligand is reduced and, at the same time, the transition metal centers are oxidized. The o-quinone – o-semiquinone – catecholate redox series (from more oxidized to more reduced) also allow RIET processes in mononuclear complexes exhibiting two or more of this type of ligands. For instance, the one-electron reduction of [Ni^{II}(3,6-dbsq)₂] (dbsq=3,6-di-tert-butyl-1,2-benzosemiquinonate) leads to an actual oxidation to the metal center to Ni^{III} and a simultaneous two-electron reduction of the ligands.^[2] In many cases, thought, the nature of the RIET process is not well established, as the proper characterization of the electronic structure of this type of compounds in terms of oxidation states is very challenging. Wieghardt et al.^[3] illustrated these difficulties with a series of square planar transition metal compounds with different metal centers and two bidentate O,O-, N,N- and O,N- *o*-semiquinonato(1-) radical ligands with different spin states (singlet, singlet diradical and triplet).

In this work, we apply the effective oxidation states (EOS) analysis^[4,5] to unravel the electronic structure of a family of compounds of this type. We show that the method is able to assign oxidation states of the metal center and ligands irrespective of the spin state. Finally, one-electron oxidation and reduction reactions are studied and analysed with EOS in order to identify and characterize possible RIET processes.

¹⁾ J. S. Miller, K. S. Min, Angew. Chem. Int. Ed. 2009, 48, 262

²⁾ C. W. Lange, C. G. Pierpont, Inorg. Chem. Acta, 1997, 263, 219

³⁾ P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, J. Amer. Chem. Soc. 2001, 123, 2213

³⁾ E. Ramos-Cordoba, V. Postils, P. Salvador, J. Chem. Theory Comput. 2015, 11, 1501-1508

⁴⁾ V. Postils, C. Delgado-Alonso, P. Salvador, Angew. Chem. Int. Ed. (submitted)

COPPER-CATALYZED CDC REACTIONS OF 1,3-DIOXOLANES TOWARD THE FORMATION OF QUATERNARY CENTERS

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Metal-catalyzed "*Cross Dehydrogenative Coupling*" (CDC) reactions have attracted tremendous interest owing to their capacity to activate inert C–H bonds.^[1] Despite the advances realized, the assembly of quaternary centers upon CDC reactions is rare^[2] and represents a challenging task of paramount importance in organic chemistry. Herein, we describe unprecedented copper(I)-catalyzed CDC reactions for the α -functionalization of amino esters with 2-substituted-1,3-dioxolanes. The key feature relies on the dual C(sp³)–H activation of 1,3-dioxolanes and glycine derivatives.^[3] Notably, our α -alkylation reactions proceed with total regioselectivity and chemoselectivity toward the formation of the quaternary center, even in presence of other functional groups within the 1,3-dioxolane core. Furthermore, this procedure could be extended to the manipulation of peptide derivatives.^[4] which could be of utmost interest in the field of proteomics.



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- 1) For selected reviews, see: a) Lv, L.; Li, Z. *Top. Curr. Chem.* **2016**, 374, 38. b) Girard, S. A.; Knauber, T.; Li, C.-J. *Angew. Chem. Int. Ed.* **2014**, 53, 74.
- Some examples of quaternary C-C bond formation with ethers: a) Du, P.; Li, H.; Wang, Y.; Cheng, J.; Wan, X. Org. Lett. 2014, 16, 6350. b) Sølvhø, A.; Ahlburg, A.; Madsen, R. Chem. Eur. J. 2015, 21, 16272. c) Ravelli, D.; Albini, A.; Fagnoni, M. Chem. Eur. J. 2011, 17, 572. d) Lan, Y.; Fan, P.; Li, X.-W.; Meng, F.-F.; Ahmad, T.; Xu, Y-H. Chem. Commun. 2017, 53, 12353.
- 3) a) Huo, C.; Chen, F.; Yuan, Y.; Xie, H.; Wang, Y. Org, Lett. 2015, 17, 5028. b) Zhao, Li.; Baslé, O.; Li, C.-J. Proc. Natl. Acad. Sci. USA 2009, 106, 4107. c) Li, Y., Wang, M.; Fan, W.; Qian, F.; Li, G.; Lu, H. J. Org. Chem. 2016, 81, 11743. d) Dian, L.; Zhao, H.; Zhang-Negrerie, D.; Du, Y. Adv. Synth Catal. 2016, 358, 2422. e) Wei, W.-T.; Song, R.-J.; Li, J.-H. Adv. Synth. Catal. 2004, 356, 1703.
- 4) San Segundo, M.; Guerrero, I.; Correa, A. Org. Lett. 2017, 19, 5288.

BIOMIMETIC APPROACH TO ALPHA-KETOGLUTARATE DEPENDANT OXYGENASES WITH NON-HEME IRON COMPLEXES

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 α -Ketoglutarate-dependant iron oxygenases belong to a large family of enzymes that are characterized by possessing a facial triad ligation containing 2 histidine and 1 carboxylate ligands. To perform the specific transformation in the substrate these enzymes need an α -ketoacid as a co-substrate; once the dioxygen (O₂) is activated the decarboxylation of the ketoacid occurs affording the active the ferryl species Fe(IV)=O which performs the desired oxygenation reaction.^[1] Several biomimetic approaches have been made to mimic the chemistry observed in these enzymes. For example, Paine *et al.* reported the use of tris-pirazolylborate and benzoylformate (BF) ligands; the activation of O₂, decarboxylation of the BF and oxidation of sulfides and alkenes were observed.^[2]

In this work iron complexes bearing a functionalized triazacyclononane (TACN) ring and BF ligands are reported, and the reactivity towards O_2 and sulfides are studied (Figure 1). Experimental observations indicate that the O_2 is selectively activated promoting the release of CO_2 and the formation of the oxidized sulfides, resembling the chemistry observed in the enzymes.



Figure 1. Reactivity of R-TACNFeBF towards O₂ and sulfides

- 1) S. Kal, L. Que J. Biol. Inorg. Chem. 2017, 22, 339
- 2) D. Sheet, T., K. Paine Chem. Sci. 2016, 7, 5322

MINDING THE GAP: EXPLORING THE MECHANISMS OF COBALT(III) CATALYSIS FOR BETTER RATIONAL DESIGN

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The growing challenges imposed by society's ever-increasing demand for tailor-made molecules such as pharmaceuticals, agrochemicals and materials call for the rational development of more sustainable synthetic methods based on abundant and affordable raw materials. Directed C–H functionalization methodologies^[1] are attractive tools for the generation of molecular complexity as they carry the promise of overcoming the limitations associated with traditional cross coupling reactions,^[2] namely, the need for prefunctionalization of starting materials and the production of stoichiometric amounts of waste. The recent surge in [Cp*Co^{III}] catalyzed C–H functionalizations, started by the pioneering report by Kanai and Matsunaga,^[3] highlights the potential of systems based on this earth-abundant metal. Despite the many applications developed, the scarce understanding of the underlying mechanisms constitutes a big gap preventing the rational design of novel transformations. Trapping reactive intermediates with stabilizing ligands along the reaction pathway has allowed us to unveil the mechanistic details of the [Cp*Co^{III}] catalyzed alkyne annulation reaction,^[4] offering for the first time an accurate description of the inner workings of [Cp*Co^{III}] catalysis, which in turn could be used to rationally optimize existing transformations. Herein, we report the use of this methodology for the study of additional stages in cobalt catalysis and their involvement in C–N bond forming processes.



- 1) Labinger, J. A.; Bercaw, J. E. Nature 2002, 417, 507.
- 2) Halford, B. Chem. Eng. News 2010, 88, 7.
- 3) Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. Angew. Chem. Int. Ed. 2013, 52, 2207.

Sanjosé-Orduna, J.; Gallego, D.; Garcia-Roca, A.; Martin, E.; Benet-Buchholz, J.; Perez-Temprano, M. H. Angew. Chem. Int. Ed. 2017, 56. 12137.

COMPUTATIONAL INSIGHTS INTO EPOXIDE HYDROLASE ASYMMETRIC HYDRATIONS OF EPOXIDES

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Epoxide hydrolase (EH) enzymes catalyze the hydration of racemic epoxides to yield their corresponding vicinal diols. These enzymes present different enantio- and regioselectivity depending upon either the substrate structure or the substitution pattern of the epoxide ring.^[1] Despite different mechanistic studies put forward to get insights into those fine details of the catalytic reaction,^[2-3] the factors that are governing the stereo- and regioselectivities of the process remain unknown. In this study, we computationally investigate the *Bacillus megaterium* epoxide hydrolase (BmEH)-mediated hydrolysis of racemic styrene oxide (*rac*-SO) and its *para*-nitro styrene oxide (*rac-p*-NSO) derivative using density functional theory (DFT) and an active site cluster model consisting of 195 and 197 atoms, respectively.^[4] Full reaction mechanisms for epoxide ring opening were evaluated considering the attack at both oxirane carbons and considering two possible orientations of the substrate at the BmEH active site.^[5] Our results indicate that for both SO and *p*-NSO substrates the BmEH enantio- and regioselectivity is opposite to the inherent (*R*)-BmEH selectivity, the attack at the benzylic position (C1) of the (*S*)-enantiomer being the most favoured chemical outcome.

- 3) M. E. S. Lind and F. Himo, ACS Catal., 2016, 8145-8155
- 4) E. Serrano-Hervás, M. Garcia-Borràs and S. Osuna, Org. Biomol. Chem., 2017,15, 8827-8835
- X.-D. Kong, S. Yuan, L. Li, S. Chen, J.-H. Xu and J. Zhou, Proc. Natl. Acad. Sci. U. S. A., 2014, 111, 15717– 157

¹⁾ J. Zhao, Y.-Y. Chu, A.-T. Li, X. Ju, X.-D. Kong, J. Pan, Y. Tang and J.-H. Xu, Adv. Synth. Catal., 2011, 353, 1510–1518.

B. A. Amrein, P. Bauer, F. Duarte, A. J. Carlsson, A. Naworyta, S. L. Mowbray, M. Widersten and S. C. L. Kamerlin, ACS Catal., 2015, 5, 5702-5713

ARTIFICIAL METALLOENZYMES FOR C-H OXIDATION

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Artificial metalloenzymes (ArMs) result from the anchoring of a catalytically competent abiotic cofactor within a protein scaffold.^[1,2] They have emerged as an attractive approach during the last decade: in a sense, these systems provide a bridge between homogeneous and enzymatic catalysis. In a biomimetic spirit, the well-defined secondary sphere coordination around the metal cofactor provided upon its incorporation within the protein cavity offers fascinating perspectives to optimize metal-catalyzed transformations with unprecedented selectivities.^[3]

Herein we explore the development of novel ArMs based on the streptavidin-biotin technology to serve as artificial alkane monooxygenases. Following a bioinspired approach, we anchor manganese- and iron-based alkane hydroxylation catalysts inside an engineered streptavidin host and use environmentally friendly oxidants.



References:

- [1] F. Schwizer, Y. Okamoto, T. Heinisch, Y. Gu, M. M. Pellizzoni, V. Lebrun, R. Reuter, V. Köhler, J. C. Lewis, T. R. Ward, Chem. Rev. 2018, 118, 142-231
- [2] Y. Lu, N. Yeung, N. Sieracki, N. M. Marshall Nature 2009, 460, 855
- [3] S. A. Cook, A. S. Borovik Acc. Chem. Res. 2015, 48, 2407

MECHANISTIC ORIENTED APPROACH TOWARDS OXIDATIVE CROSS-COUPLING REACTIONS OF PHENOLS BY IRON CATALYSIS

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Metal catalyzed oxidative coupling of phenols is a powerful method for preparing complex phenol-based materials by simple and sustainable means. As part of our group's interest to develop mechanistic-oriented oxidative coupling reactions, a set of catalytic systems that will ensure complete control over the chemoselectivity regardless the electronic nature of the phenolic coupling partners is under development.

Our study revealed that oxidative cross-coupling of phenols mediated by a multi-coordinated FeCl₃ catalyst proceeds via a chelated radical-anion coupling mechanism.^[1] Based on mechanistic studies, electrochemical methods and density functional theory (DFT) calculations, a general model was established to predict the feasibility of the cross-coupling for a given pair of phenols. The catalytic system was proved to be highly chemoselective for phenols that maintain complementary relationship (Scheme 1) but less efficient for noncomplementary phenolic coupling partners. Due to this mechanistic limitation, an alternative mechanistic route that involves coupling of readily oxidized phenols with poor nucleophilic phenolic partners has been developed. The novel catalytic system is based on Fe[TPP]Cl complex, which mediates outersphere coupling between a liberated phenoxyl radical and an iron-ligated phenolic coupling partner.^[2]



Scheme 1. Catalyst design for oxidative cross-coupling of phenols

[1] Libman, A.; Shalit, H.; Vainer, Y.; Narute, S.; Kozuch, S.; Pappo, D. *J. Am. Chem. Soc.* **2015**, *137*, 11453-11460. [2] Shalit, H.; Libman, A.; Pappo, D. *J. Am. Chem. Soc.* **2017**.

UNCONVENTIAONAL OXDIATION CHEMISTRY THROUGH CARBON BRIDGED DI-PHENANTHROLO EARTH-ABUNDANT METAL COMPLEXES

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Abstract: Phenanthroline-based macrocycles have rarely been studied. In this research, we synthesized and investigated a macrocycle where two 1,0-phenanthroline units are linked by one methylene group that included various substituents on the bridging carbon atom. In this way a new tetradentate, phenanthroline based ligand framework was obtained. The corresponding earth-abundant metal (Fe, Co, Ni, Cu) complexes exhibited the ability to activate weak C-H bonds subsequently followed by oxygenation with O₂ from air. For tertiary carbon-bridged di-phenanthrolo ligands, the benzylic position of the ligand methine arm was activated. The initial complexes as well as those after oxygenation were isolated and characterized by a variety of methods including X-ray crystallography. High resolution mass spectroscopy of activated cobalt (II) complexes prepared from ¹⁸O₂ was used to confirm that oxygen atom incorporated into the ligand framework is derived from molecular oxygen. For quaternary carbon atom bridged di-phenanthrolo earth-abundant metal complexes, interestingly weak allylic and benzylic C-H bonds of several substrates were activated and reacted to yield the corresponding oxygenates. The reactivity observed is different from prevalent oxidation mechanisms observed in catalysis by earth-abundant metal complexes that involve formation of metal-oxo species¹), or proceed by via radical or hydroperoxyl² intermediates.

References:

- 1) Ahmet Gunay and Klaus H. Theopold, Chem. Rev. 2010, 110, 1060; Genqiang Xue, Raymond De Hont, Eckard Münck and Lawrence Que Jr, Nature Chem. 2010, 2, 400
- 2) T. Punniyamurthy, Subbarayan Velusamy and Javed Iqbal, *Chem. Rev.* 2005, *105*,

EARLY SYMPTOMS OF 'MULTIPERSONAL' BEHAVIOR OF TRIPOD TRIPHOSPHINE LIGANDS WITH FIRST ROW TRANSITION METALS

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In the last decade polyphosphine ligands that feature C3 symmetry and are conformationally rigid have been successfully applied in various relevant topics of chemical research.^[1] In this work we highlight the unique and unprecedented reactivity observed with the tripodal triphosphine ligands based on the tris[3-methyl-1H-indol-2-yl]methane (HTIM) moiety with first row transition metals copper, nickel and cobalt. Remarkably, under biphasic reaction conditions, the reaction of Fe²⁺, Ni²⁺, Co²⁺, Cu²⁺ and Zn²⁺ chlorides in water with HTIM(P*i*Pr₂)₃ in organic solvent (CD₂Cl₂, EtOD; 10 % v/v) at room temperature and under air atmosphere exclusively leads to the formation of [(HTIM(PiPr₂)₃CuCl] in 67% yield, of which its purity was proven by CHN analysis. To the best of our knowledge, this marked selectivity is unprecedented for phosphine ligands and could potentially be exploited in the separation or processing of copper salts, since radioactive copper (⁶⁴Cu) is well-known for its application in immuno-positron emission tomography (PET).^[2] Moreover, we present the first study of the non-classical (X–H)⁻⁻M hydrogen bonding interaction in Cu^I complexes which was performed by use of X-ray diffraction data, AIM and NBO analysis. Quantitative formation of a metallated Ni(II) complex could be achieved under harsher conditions. which led to the the first example of a nickel catalyst able to perform hydrogenation of N-containing heterocycles. A series of substituted quinolones and quinoxalines was hydrogenated under mild conditions in good to excellent yields. Finally, reaction of Col₂ with HTIM(PPh₂)₃ leads to Co(II) disproportionation to Co(I) and Co(III) and is currently under investigation.



- Tsay, N. P. Mankad, J. C. Peters, *J. Am. Chem. Soc.* **2010**, *132*, 13975; M. Ciclosi, J. Lloret, F. Estevan, P. Lahuerta, M. Sanaú, J. Pérez-Prieto, *Angew. Chem. Int. Ed*, **2006**, *45*, 6741; M. Ciclosi, J. Lloret, F. Estevan, M. Sanau, J. Perez-Prieto, *Dalton Transactions* **2009**, 5077.
- 2) S. Juran, M. Walther, H. Stephan, R. Bergmann, J. Steinbach, W. Kraus, F. Emmerling, P. Comba, *Bioconjugate Chemistry* **2009**, *20*, 347.

THE BAIRD RULE IN ALL ITS GUISES

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From the discovery of benzene in 1825 to the present day, the concept of aromaticity has experienced several revolutions that have fueled the interest of both theoretical and experimental chemists. Very recently, several works^[1-3] have highlighted the importance of aromaticity in excited states. Aromaticity is essential to understand and predict many photochemical processes. This renaissance of excited state aromaticity represents an important revolution in the field of aromaticity. Although aromaticity is a property usually linked to the ground state of stable molecules, certain excited states are unquestionably aromatic. This is especially the case of annulenes in the lowest-lying triplet states whose aromaticity follows the 4N Baird rule.^[4] In this work, we apply this rule to discuss the aromaticity of all-metal clusters,^[5] we discuss the existence of Hückel-Baird hybrid aromatic species,^[6] and we show how Clar's rule can be extended to the lowest-lying triplet excited states of certain polycyclic aromatic molecules.^[7]

References:

- 1) H. Ottosson, Nat. Chem. 2012, 4, 969.
- 2) M. Rosenberg, C. Dahlstrand, K. Kilså, H. Ottosson, Chem. Rev. 2014, 114, 5379.
- 3) F. Feixas, J. Vandenbusche, P. Bultinck, E. Matito, M. Solà, Phys. Chem. Chem. Phys. 2011, 123, 20690.
- 4) N. C. Baird, J. Am. Chem. Soc. 1972, 94, 4941.
- 5) F. Feixas, E. Matito, J. Poater, M. Duran and M. Solà, Theor. Chem. Acc. 2011, 128, 419.
- 6) K. Jorner, F. Feixas, R. Ayub, R. Lindh, M. Solà, H. Ottosson Chem. Eur. J. 2016, 22, 2793.
- 7) R. Ayub, O. El Bakouri, K. Jorner, M. Solà and H. Ottosson, J. Org. Chem. 2017, 82, 6327.

PHOTOACTIVE METAL-ORGANIC FRAMEWORKS AS CO₂ REDUCTION CATALYSTS

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Metal-organic frameworks (MOFs) are coordination compounds that are characterized by high surface areas and permanent porosity, formed from a combination of organic linkers with inorganic nodes.^[1,2,3] This "buildingblock" approach, whereby premade units are assembled into a continuous network, is known as reticular synthesis. Interestingly, the properties of MOFs can be easily modified by fine-tuning these units, for example, the use of photosensitive ligands yields photoactive MOFs which can be used in catalytic reactions.^[4] Herein we show a series of new MOFs developed using a [Ru(bpy)₃]²⁺-derived photosensitizer ligand combined with different metal ions (Co(II), Ni(II) and Zn(II)). With the use of 9-borabicyclo[3.3.1]nonane (9-BBN) as a hydrogen source and activated by light, the Co-based MOF effectively catalyzes the reduction of CO₂ into HCOOH and formic acids, resulting in yields of 8% and 30% respectively. Postcatalytic characterization of the recovered MOF shows outstanding stability and reusability with no reduction of yield upon subsequent catalytic cycles. Moreover, we were able to deposit these MOFs on a FTO surface *via* both liquid-phase epitaxy and electrodeposition techniques, finding the later to be a more efficient approach, with film growth carried out in ambient conditions in 30-60 minutes for a typical cycle.



References

- 1) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, Science. 2013, 341, 1230444
- 2) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.Y. Su, Chem. Soc. Rev. 2014, 43, 6011-6061
- 3) N. Zhu, G. Tobin, W. Schmitt, Chem. Commun., 2012, 48, 3638-3640
- 4) Z.-M. Zhang, T. Zhang, C. Wang, Z. Lin, L.-S. Long, and W. Lin, J. Am. Chem. Soc. 2015, 137, 3197–3200

STRUCTURE AND REACTIVITY OF FE(IV)-OXO COMPLEX TRIPEPTIDE IN OXIDATION REACTIONS

WITH

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High-valent Fe(IV)-oxo complexes are active species which mediate oxidation of C-H bonds. Based on biological archetypes, synthetic combination of peptides and metal ions can be an important basis to create artificial catalysts for C-H bond activation process. We studied reactivity of Fe(IV)-oxo complex with Gly-Gly-His-N-methyl amide (GGHa) depending on a spin state for an oxidation reactions of propane and cyclohexane. As was recently shown, the best performance for the molecular structure of transition-metal complexes is observed with the BP86-D3/TDZP, including ZORA scalar relativistic corrections and COSMO solvation model.^[1] The ground state of the studied complex is triplet state as it was found for other biomimetic iron complexes.^[2] The energy gap between triplet and quintet states is large and varies depending on the functional used. Gibbs energy profiles show that the H atom transfer and rebound steps occur on triplet and quintet surfaces independently of each other. Taking into account the large quintet-triplet energy gap $\Delta E=24.5$ kcal/mol at the BP86-D3/TDZP level of theory, we can suggest that the quintet state of the Fe(IV)O-GGHa complex is thermally unreachable and the reaction proceeds only on the triplet surface. Such nonclassical single-state reactivity of iron(IV)-oxo complexes has been recently reported for Fe(IV)-oxo complex with macrocyclic tetracarbene ligand.[3]

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2) X. Shan, L. Jr. Que, J. Inorg. Biochem. 2006, 100, 421-433.

¹⁾ M. Swart, M. Gruden, Acc. Chem. Res. 2016, 49, 2690-2697.

³⁾ C. Kupper, B. Mondal, J. Serrano-Plana, I. Klawitter, F. Neese, M. Costas, S. Ye, F. Meyer, J. Am. Chem. Soc. 2017, 139, 8939–8949.

PHOTOCATALYTIC PROPERTIES OF ANTIFEROMAGNETICALLY COUPLED IRON DIMER

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The non-heme (L)Fe^{III} and (L)Fe^{III}-O-Fe^{III}(L) complexes (L = 1,1-di(pyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)ethan-1-amine) undergoes reduction under irradiation to the Fe^{III} state with concomitant oxidation of methanol to methanal, without the need for a secondary photosensitizer, Figure 2. Density Functional Theory (DFT) studies explain a mechanism in which irradiation results in charge transfer excitation of a Fe^{III}- μ -O-Fe^{III} complex to generate [(L)Fe^{IV}=O]²⁺ (observed transiently during irradiation in acetonitrile). DFT calculations indicate that photoexcitation of Fe^{III}- μ -O-Fe^{III} would result in population of anti-bonding orbitals and drive heterolytic cleavage to form a five coordinate Fe(II) species and an Fe(IV)=O species in an excited electronic state (HS) rather than in its intermediate spin (IS) ground state. Importantly, we show that the present system can use light to achieve a full catalytic cycle in methanol without the need for a secondary photosensitizer.



Figure 2 Single catalyst photocatalytic oxidation.

OXIDATION OF ALIPHATIC AND AROMATIC AMINO ACIDS WITH H_2O_2 CATALYZED BY A NONHEME IMINE BASED IRON COMPLEX

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Oxidative functionalization of amino acids catalyzed by nonheme iron complexes have received a great attention in recent years.^[1,2] In this context we have investigated the oxidation of a series of N-acetyl amino acid methyl esters with H₂O₂ using the iminopyridine iron (II) complex (Catalyst 1) ^[3] in order to obtain information on the reactivity and selectivity patterns in these oxidative processes.



Figure 1

Oxidation of aliphatic amino acids N-AcAlaOMe, N-AcValOMe, N-AcLeuOMe leads to exclusive α-C-H oxidation for the former a.a. and to both side-chain functionalization and α -C-H oxidation for the latter two a.a. with low efficiency. With N-AcProOMe the oxidation is more efficient and regioselective affording exclusively C-5 oxidation products in good yields. A marked preference for the aromatic ring hydroxylation^[4] over α -C-H and benzylic C-H oxidation was observed in the oxidation of the aromatic a.a. N-AcPheOMe, leading to the formation of tyrosine and its phenolic isomers with high yields.

¹⁾ T. J. Osberger, D. C. Rogness, J. T. Kohrt, A. F. Stepan, M. C. White, Nature, 2016, 537, 214

²⁾ A. I. Abouelatta, A. A.Campanali, A. R. Ekkati, M. Shamoun, S. Kalapugama, J. Kodanko, J. Inorg. Chem. 2009, 48, 7729

³⁾ G. Olivo, M. Nardi, D.Vidal, A.Barbieri, A.Lapi, L. Gomez, O. Lanzalunga, M. Costas, S. Di Stefano, J. Inorg. Chem. 2015, 54, 1014

⁴⁾ G. Capocasa, G. Olivo, A. Barbieri, O. Lanzalunga, S. Di Stefano, Catal. Sci. Technol., 2017, 7, 5677

EXPLORING CATALYTIC ACTIVITY BY B-DIKETIMINATE-LIKE METAL COMPLEXES ENTRAPPED IN SUPRAMOLECULAR NANOCAPSULES

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Catalytic reactions taking place in a confined space are found in nature, for example in the active center of enzymes. The special environment around the enzymatic active site leads to a highly selective transformations. In analogy to the spatial constraints imposed by enzymatic centers, the encapsulation of metal-based catalysts by a supramolecular nanocage could modulate their activity and selectivity via the second coordination sphere.^[1] The aim of this study is to encapsulate formazan and β -diketiminate-like metal complexes in a self-assembled nanocapsule, taking advantage of the well-known ability of Zn-metalloporphyrins to bind pyridine based ligands.^{[2][3]} Furthermore, comparing the catalytic activity of the supramolecular catalysts with regard to the catalyst operating in bulk solution, the role of the cage as a second coordination sphere of the catalyst can be investigated. Although, β -diketiminate complexes have been widely explored in stoichiometric studies, their use as catalysts is largely underdeveloped.



- 1) C. García-Simón et al., J. Am. Chem. Soc. 2015, 137, 2680
- 2) C. Colomban et al., Chem. Eur. J. 2017, 23, 3016
- 3) C. Colomban et al., Inorg. Chem. 2018

35 YEARS OF DISCRETE REACTION FIELD (DRF):

ITS LATEST IMPLEMENTATION IN GAMESS_UK, AND MORE

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Discrete Reaction Field (DRF)" stands for a QM/MM *embedding* approach and also for a *polarizable* force field, to be used in Molecular Dynamics or Monte Carlo simulations. It started more than 35 years ago, mainly for the treatment of active sites of proteins, embedded in a classical model of the rest of the system.

In the late seventies and early eighties, most force fields were restricted to *binary*, (effectively) *additive* interactions: point charges for (groups of) atoms and Lennard-Jones potentials for short-distance interactions: dispersion and Pauli-repulsion. The necessary parameters were usually considered as adjustable variables to be fitted to experimental or otherwise obtained data, *e.g.* structures, which made these parameters more or less interdependent and had meager physical meaning.

DRF was (and is) based on the separation of the *different nature* and *sources* of the additive (electrostatic) and the nonadditive interactions (polarization, dispersion and Pauli-repulsion). A charge distribution tells us where charges are, and for use in classical force fields, point charges should not only generate the electric *potential*, but also the *field* as good as possible. Therefore we developed code for obtaining them^[1,2]

The polarizability is a measure for the ease with which charges can be shifted by an external field: the more room the easier, and hence the polarizability of a conducting sphere with radius R is R³, *i.e.* a polarizability is in general *size* and *shape* dependent.

Even for two (classical) polarizable objects, the polarization is not additive, as becomes clear from Silberstein's equation^{[3]:}

$$\alpha_{\parallel} = \frac{\alpha_1 + \alpha_2 + 4\alpha_1\alpha_2 / r_{12}^3}{1 - 4\alpha_1\alpha_2 / r_{12}^6} \quad ; \quad \alpha_{\perp} = \frac{\alpha_1 + \alpha_2 - 2\alpha_1\alpha_2 / r_{12}^3}{1 - \alpha_1\alpha_2 / r_{12}^6} \quad ; \quad (r_{12}^6 > 4\alpha_1\alpha_2) \quad (1)$$

due to the induction by the field of the first order induced dipoles: the $\alpha_{_{//}}$ becomes larger, the $\alpha_{_{\perp}}$ smaller than the sum of the two individual α 's. For more than two objects in a field E⁰, the result can not be obtained in closed form. Instead, one has to extend Eq.1

to

$$\boldsymbol{\mu}_{p} = \boldsymbol{\alpha}_{p} \left[\mathbf{E}_{p}^{0} + \sum_{q \neq p} \mathbf{t}_{pq} \boldsymbol{\mu}_{q} \right] ; t_{st,ij} = \frac{r_{st,i} \bullet r_{st,j}}{r_{st}^{5}} - \frac{\delta_{ij}}{r_{st}^{3}} ; i, j \in \{x, y, z\}$$
(2)

and solve equations like $\mathbf{M} = \mathbf{E}^{0}[\mathbf{A}^{-1}-\mathbf{T}]^{-1}$ (or $[\mathbf{A}^{-1}-\mathbf{T}] \mathbf{M} = \mathbf{E}^{0}$) which gives a self-consistent solution of the many-body polarization problem in *any* external field, resulting in *effective* α 's: $\alpha_{p} = \mu_{p} / \mathbf{E}_{p}$.

Obviously, Eq. 1 goes wrong if $r_{12} \le (\alpha_1 \alpha_2)^{1/6}$. Then α_{\perp} goes through a singularity: the so-called polarization catastrophe. To avoid this, the interactions must be damped, for which we apply in general Thole's modified dipole interactions^[4] and its consequences for fields and potentials. This will be expanded on the poster.

The *input* α 's may be calculated by any quantum chemical method, or obtained from fitting to experimental values. This does not turning DRF into a semi-empirical approach: these parameters are independent of any result from solving Eq.2, and note that computing α 's to experimental accuracy is an arduous task.

Now that the polarization problem is solved, we can arrive at a fairly good expression for the classical dispersion energy:

$$U_{ab}^{disp} = -\frac{1}{4} \frac{Tr(\boldsymbol{\alpha}_{a} t_{ab}^{2} \boldsymbol{\alpha}_{b})}{\left(\sqrt{\boldsymbol{\alpha}_{a} / n_{a}} + \sqrt{\boldsymbol{\alpha}_{b} / n_{b}}\right)}$$
(3)

with the *effective* α 's obtained so far.

Since the polarizability is a measure for the *size* of a system, we take for the short-range repulsion something like the r^{12} term of a L.-J. potential:

$$U_{ab}^{rep} = -\frac{1}{4} U_{ab}^{disp} \frac{\left(R_{vdw,a} + R_{vdw,a}\right)^{6}}{r_{ab}^{6}} \qquad (4)$$

but there are other options. Although these expressions look like binary, by using the *effective* polarizabilities they comprise in fact many-particle effects.

For QM/MM applications one has to generate interaction integrals for potentials, inducing fields, reaction potentials, etc.. Originally we adapted expanded these^[5], with atomic positions as expanding centers, thus leading to simple combinations of overlap- and dipole-integrals for the interaction integrals. This was fine for small basis sets, but for more extended basis sets we developed 'exact' versions, without expansion.

DRF was originally was originally called the 'Direct' RF, where the reaction potential operator was made part of the actual hamiltonian, leading to one- and two-electron integrals, which can be added to the usual set, while e.g. the SCF program does not 'feel' the difference. Moreover, it does not only give the standard results but also a reasonable dispersion contribution to the QM/MM interaction energies^[6]. This worked so far only in the versions with expanded potentials etc.

This, as opposed to the now generally applied 'Average' RF, where the *molecular* field does the induction, which has to be generated *e.g.* in each SCF cycle.

A complete description of DRF can be found in a paper^[7] or the book^[8].

Up to 1985 DRF as QM/MM method was used in BIGMOL, from 1985-2000 in HONDO7(expanded), HONDO8(expanded;exact) and HONDO98(exact), GAMESS_UK(expanded), ZINDO(expanded), ADF(exact) and now in GAMESS_UK_2018(exact).

The poster will gives an overview of results: surprising interactions, details of reactions, physical properties, spectra,

References

- 1) B.T. Thole, P.Th. van Duijnen, *Theor. Chim. Acta.* **1983**, 63,209
- 2) M.Swart, P.Th. van Duijnen, J.G.Snijders, J.Comp.Chem. 2001, 22, 79
- 3) L.Silberstein, Philos. Mag. 1917, 33, 521
- 4) B.T. Thole, Chem. Phys. 1981, 59, 341
- 5) B.T. Thole, P.Th. van Duijnen, Theor. Chim. Acta 1980, 55,
- 6) B.T. Thole, P.Th. van Duijnen, Chem. Phys. 1982, 71, 211
- 7) P.Th. van Duijnen, F. Grozema, M.Swart, J.Mol.Sruct.(Theochem) 1999,464,191
- 8) P.Th.van Duijnen, M. Swart, L. Jensen, In: "Solvation Effects on Molecules and Biomolecules: Computational Methods and Applications ", (Ed.:
- S. Canuto, Springer) 2008 39

HIGHLY ENANTIOSELECTIVE ADDITION OF DIMETHYLZINC TO FLUORINATED ALKYL KETONES

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The addition of diorganozinc reagents to aldehydes and ketones, which, in its enantioselective version, makes possible to prepare enantiomerically enriched chiral alcohols, is, today, one of the most useful among the reactions of formation of C–C bonds. In this field, our group has shown that chiral 1,2-ethylenediamines derived from (R,R)- or (S,S)-1,2-diphenylethylenediamine and (S)- or (R)-2,2'-bis(bromomethyl)-1,1'-binaphthalene (Figure 1) are active catalysts in the challenging asymmetric nucleophilic addition of ZnR₂ (R = Me, Et) to trifluoroacetophenones.^[1] Additionally NMR spectroscopic studies carried out for the catalytic addition reaction of ZnEt₂ to PhCOCF₃ revealed unusual features for these diamines compared to TMEDA and bisoxazoline (BOX) catalysts.^[2]



Figure 1. Bulky diamine ligands used in the asymmetric nucleophilic addition of ZnR2 (R = Me, Et) to trifluoroacetophenones.

The great potential in biomedical and pharmaceutical fields of the products obtained in ours and related studies^[3] prompted us to improve the enantioselectivity of the nucleophilic addition reaction and to extend it to other fluorinated alkyl ketones PhCOCF₂X (X = H, Cl, CF₃). The results obtained are summarized in this communication. Very high yields and enantioselectivities were obtained in all the cases for the reaction with ZnMe₂ controlling the solvent and the temperature.

References

- 2) Calvillo-Barahona, M.; Casares, J. A.; Cordovilla, C.; Genov, M. N.; Martínez-Ilarduya, J. M.; Espinet, P. Chem. Eur. J. 2014, 20, 14800.
- 3) Sasaki, S.; Yamauchi, T.; Kanai, M.; Ishii, A.; Higashiyama, K. Bull. Chem. Soc. Jpn. 2015, 88, 200 and references therein.

¹⁾ Calvillo-Barahona, M.; Cordovilla, C.; Genov, M. N.; Martínez-Ilarduya, J. M.; Espinet, P. Dalton Trans. 2013, 42, 14576.

THE OXIDATIVE ADDITION OF ARYLIC C-X TO A PALLADIUM CATALYST

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We have carried out a series of calculations on the oxidative insertion of a palladium catalyst into the C–H bond of benzene, C–CI bond of chlorobenzene and the C–C bond of toluene, using relativistic density functional theory.^[1-4] The activation strain model of reactivity, together with Kohn-Sham molecular orbital analysis, reveal detailed insight into the operative bonding mechanisms of the oxidative additions. Our results demonstrate that the arylic C–CI bond activation is preferred over the arylic C–H and C–C bonds, due to the relatively weaker C–CI bond and good donor-acceptor orbital interactions. Furthermore, the activation of the toluene C–C bond is associated with the highest reaction barrier, because the C–C bond must first partially dissociate in order for optimal overlap between palladium's 4d orbitals and C–C σ^* acceptor orbital.



References:

1) Vermeeren, P.; Sun, X.; Bickelhaupt, F. M. *Manuscript in preparation*

- 2) Wolters, L. P.; Bickelhaupt, F.M. d¹⁰-ML₂ Complexes: Structure, Bonding, and Catalytic Activity. *Computational Studies in Organometallic Chemistry*. Springer International Publishing, **2014**. 139-161
- 3) Bickelhaupt, F. M. J. Comput. Chem. 1999, 20, 114-128
- 4) Bickelhaupt, F. M.; Houk, K. N. Angew. Chem. Int. Ed. 2017, 56, 10070-10086

REACTIVITY INDICES FOR DIELS-ALDER REGIOSELECTIVITY PREDICTION IN FULLERENES

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Endohedral metallofullerenes (EMFs) involve the encapsulation of metals or small molecules inside a fullerene cavity. The high applicability of such nanomaterials has caught the attention of medicine and material sciences. Due to that, the study of their structure, stability and reactivity has gained importance in the past recent years.

The Diels-Alder cycloaddition (amongst other reactions) is highly affected by the nature of the encapsulated cluster within a fullerene cage.^[1]

There are many features that are known to affect the regioselectivity of fullerenes and EMFs (charge transfer, pyramidalization, C-C bond length, \dots)^[2] by either enhancing it or decreasing it. The overall effect of such features, however, is difficult to predict, and nowadays there is still not a clear path to anticipate the regioselectivity of the Diels-Alder reaction on fullerenes and their metallic derivatives.

Because of that, in this work we propose a group of reactivity indices to predict the regioselectivity on fullerenes in the Diels-Alder reaction. These indices are based on some pertinent modifications of the the delocalization index (DI) within the context of atoms in molecules (AIM). One of them is actually related to the second-order atomic Fukui indices (AFI).^[3]

In the Diels-Alder reaction, fullerenes act as dienophiles. Empty C_{60} and C_{78} fullerenes, the derivatives of C_{78} with Sc_3N and Ti_2C have been used to test and calibrate the proposed indices.

References

¹⁾ C. M. Cardona, A. Kitaygorodoskiy, L. Echegoyen. J. Am. Chem. Soc. 2005, 127, 10448

M. Garcia-Borràs, S. Osuna, J. M. Luis, M. Swart, M. Solà. Advances in Physics and Chemistry (Ed. M. V. Putz & O. Ori), Springer Netherlands. 2015, Chapter 4, 67

³⁾ R. F. W. Bader, M. E. Stephens. J. Am. Chem. Soc. 1975, 97, 7391

COMBINATION OF IRON COORDINATION COMPOUNDS AND PEPTIDES IN BIOINSPIRED OXIDATION REACTIONS: DESIGNING ARTIFICIAL ENZYMES

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The asymmetric oxidation of hydrocarbons allows the conversion of cheap and widely available molecules in chiral building blocks useful in organic synthesis. However, the introduction of stereoselectivity in catalytic oxidation reactions of inert substrates remains a long standing goal.

The challenge of achieving high selectivity in the oxidation of hydrocarbons has been solved in nature by the use of metalloenzymes.^[1] The metal in their active site is surrounded by nitrogen, oxygen or sulphur donor molecules, which have an important influence in the reactivity of this systems. Moreover, the secondary coordination sphere also plays a crucial role in the activity of the enzyme. Indeed, the protein environment of the active site can be engaged in non-covalent interactions allowing the proper orientation of the substrate in the cavity of the enzyme favoring high selectivity.

A possible approach to mimic the selectivity obtained by metalloenzymes can be the use of bioinspired catalysts in combination with peptides. The latter can act as metal ligands and at the same time can shape the second coordination sphere of the metal, which is capable to establish non-covalent interactions with the substrates. These features play an important role in defining the reactivity of the metal center and the chemo- and regioselectivity of the reactions. Moreover, due to the inherent chirality of the peptides, stereoselective transformations can also be mediated. In this communication, we will show our progress in creating catalysts that combine coordination complexes and peptides to create selective oxidation catalysts.^[2-3]



- 1) L. Que Jr, W. B. Tolman. Nature 2008, 455, 333
- 2) O. Cussó, X. Ribas, J. Lloret-Fillol, M. Costas. Angew. Chem. Int. Ed. 2015, 54, 2729
- 3) O. Cussó, M. W. Giuliano, S. J. Miller, M. Costas. Chem. Sci. 2017, 8, 3660

A DEEP CAVITAND RECEPTOR FUNCTIONALIZED WITH Fe(II) AND Mn(II) AMINOPYRIDINE COMPLEXES FOR BIOINSPIRED OXIDATION REACTIONS.

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Enzymes in nature have the capability to accommodate substrates (smaller molecules) in a certain conformation. These interactions channel the reaction along a specific path.^[1] There is a wide range of simple synthetic metal complexes that mimics the activity of the metal center of the enzyme, ^[2] but there is a lack of more elaborated synthetic structures that resemble the enzyme. Cavitands are supramolecular receptors with aromatic walls that provides an isolated environment similar to the interiors of enzymes that can bind smaller molecules inside due to its bowl-shape.^[3]

In this context, our approach is to functionalize the upper rim of a cavitand to build a biomimetic metal complex with an appended structured environment. We synthesized an Fe(II), Mn(II) and Zn(II) metal complexes attached to a cavitand that can recognize smaller molecules by an array of weak interactions. The catalytic activity of this supramolecular Fe(II) and Mn(II) non-heme complexes in enzyme like oxidation reactions is studied. From this platform, also high-valent intermediate species, Fe(IV)=O, can be generated upon reaction with an external oxidant. The reactivity of this intermediate is invesigated for OAT. This is the first time that an Fe(IV)=O has been generated in a supramolecular platform.



Figure 1. XRD of the metallocavitand obtained upon the reaction with FeCl2

Referencias:

¹⁾ Ringe, D.; Petsko, G. A. Science. 2008, 320, 1428–1429.

²⁾ Olivo G, Cusso O, Costas M. Chem. As. J. 2016 11:3148-3158.

³⁾ Purse, B. W.; Rebek, J. Jr. PNAS. 2005, 102, 10777–10782.

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ROTATING SANDWICH COMPLEXES

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The origin for the rotational barrier of organometallic vs inorganic sandwich complexes has remained enigmatic for the past decades. The best known examples are ferrocene^[1] (**Fc**) complex and its inorganic analogue titanodecaphosphacene^[2] (**TdP**). In both cases the central metal is coordinated on both sides to a five-membered anionic ring, whose idealized structure can exist in either D_{5d} or D_{5h} symmetry. Here, we investigate in detail^[3] what causes the difference observed in the rotational barrier of **Fc** vs. **TdP**, with values of respectively ca. 1 kcal·mol⁻¹ (**Fc**) vs. ca. 8 kcal·mol⁻¹ (**TdP**). Through the use of spin-state consistent density functional approximations and Energy Decomposition Analysis^[4] (EDA) we decomposed the chemical bond into components that contribute to stability in a chemical way and in this way determined what causes this surprisingly large difference in rotational barrier. Orbital interactions are shown to be the determining factor. Furthermore, we performed a complete rotation for both complexes in steps of 5 degrees, during which we investigated the change of complex stability and previously mentioned factors corresponding to it.



References:

- 1) R. B. Woodward, M. Rosenblum, M. C. Whiting, J. Am. Chem. Soc., 1952, 74 (13), 3458–3459.
- 2) E. Urnežius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, P. v. R. Schleyer, Science, 2002, 295, 832-834.
- 3) F. Vlahovic, M. Gruden, M. Swart, Chem. Eur. J. 2018, online, DOI: 10.1002/chem.201704829
- 4) F. M. Bickelhaupt, E. J. Baerends, Rev. Comput. Chem., Wiley-VCH, New York, 2000, 15, 1-86.

LIGHT-INDUCED OXYGEN ACTIVATION BY A MONONUCLEAR IRON(III) COMPLEX

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The hexadentate carboxylato ligand of an iron(III) complex^[1-3] undergoes decarboxylation, oxidative C-N cleavage and subsequent imine formation, when dissolved in organic solvents under ambient conditions. The imine formation is a two-step process, where the first step is light-dependent, and the second is oxygen-dependent. DFT calculations suggest that the light-initiated process occurs through the *mer*-diastereoisomer of [Fe(tpena)]²⁺ to form an iron(II)-methylene complex upon carbon dioxide release, which in turn can activate oxygen to form a reactive intermediate and ultimately C-N cleavage with the release of formaldehyde to form [Fe(SBPy₃)(MeCN)]²⁺. The release of carbon dioxide and formaldehyde has experimentally been detected, and the conversion with its transient intermediates has been tracked with time-resolved UV-visible, Mössbauer, resonance Raman and EPR spectroscopy.



References

- [1] A. Lennartson, C. J. McKenzie, Angew. Chem. Int. Ed. 2012, 51, 6767-6770.
- [2] M. S. Vad, A. Lennartson, A. Nielsen, J. Harmer, J. E. McGrady, C. Frandsen, S. Morup, C. J. McKenzie, Chem. Commun. 2012, 48, 10880-10882.
- [3] D. P. de Sousa, C. Wegeberg, M. S. Vad, S. Mørup, C. Frandsen, W. A. Donald and C. J. McKenzie, Chem., Eur. J. 2016, 22, 3810-3820

CATALYSIS BY DESIGN": AL-SBA15 AS A WELL-DEFINED SURFACE LIGAND FOR A SINGLE ATOM W-BASED HETEROGENEOUS CATALYSTS: APPLICATION TO SELECTIVE METATHESIS OF PROPANE

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The design of a well-defined aluminum hydroxyl group on the inner surface of the mesopores of SBA-15, [(\equiv Si $-O-Si\equiv$) (\equiv Si $-O)_2$ Al-OH] is obtained by reacting DIBAL on SBA-15 treated at 700°C ¹⁻² followed by oxidation with N₂O. The IR spectra of adsorbed pyridine show that the materials incorporate strong Al Lewis acid sites (80 % of the total Aluminum sites)³.

This highly electrophilic support surface was used to create a single well-defined surface organo-tungsten fragment $[(\equiv Si-O-Si\equiv) (\equiv Si-O-)_2AI-O-W(\equiv CtBu)(CH_2tBu)_2]$ by the reaction of the surface $[(\equiv Si-O-Si\equiv)(\equiv Si-O)_2AI-OH]$ groups with $W(\equiv Ct-Bu)(CH_2-tBu)_3$. A further reaction with hydrogen under mild conditions (0.6 mbar, 3 h, room temperature) afforded the tungsten carbyne bishydride $[(\equiv Si-O-Si\equiv)(\equiv Si-O-)_2AI-O-W(H)_2(\equiv C-tBu)]$.

The performances of each of the W-supported catalysts were assessed for propane metathesis under dynamic conditions at 150 °C. The $[(\equiv Si-O-Si\equiv) (\equiv Si-O_2AI-O-W(H)_2(\equiv CtBu)]$ was found to be a multifunctional single-site catalyst with promising properties, giving the highest turnover number (TON = 800) and the highest reported selectivity for butane (45 %) *vs.* ethane (32 %) known for oxide supported W-complex catalysts (silica, silica-alumina or alumina).

The results demonstrate that electronic modifications of the surface oxide ligand via the creation of a strong AI Lewis acid center as an anchoring site for organometallic complexes through the OH groups markedly improved the catalytic properties of the supported organo-tungsten species.

[3] B. Werghi E. Pump, E. Abou-Hamad,, A. Bendjeriou-Sedjerari,, L. Cavallo and J.-M. Basset, Chemical science 2018, DOI: 10.1039/C7SC05200F

^[1] B. Werghi, A. Bendjeriou-Sedjerari, J. Sofack-Kreutzer, A. Jedidi, E. Abou-Hamad, L. Cavallo and J.-M. Basset, Chemical Science, 2015, 6, 5456-5 B.

^[2] B.Werghi, A. Bendjeriou-Sedjerari, A. Jedidi, E. Abou-Hamad, L. Cavallo and J.-M. Basset, Organometallics, 2016, 35, 3288-3294


Predictive Catalysis: Transition-Metal Reactivity by Design

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