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GEQO
TARRAGONA
SEPTEMBER 17-19 **2014**
EXPERT GROUP MEETING ON ORGANOMETALLIC CHEMISTRY

BOOK OF ABSTRACTS

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XXXII Conference Expert Group Meeting on Organometallic Chemistry (GEQO)

Program and abstracts
September 17-19, 2014
Tarragona, Spain

Universitat Rovira i Virgili

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Preface

Dear Colleagues,

On behalf of the Organizing Committee, I am pleased to welcome you to Tarragona, Spain, for the GEQO XXXII meeting. In the present edition we have approximately 230 attendees from 9 countries. Despite the economic problems in several countries, the number of attendees as well as their long distance travelling and the quality of the abstracts, is an indication of the interest on organometallic and catalysis research, as an attractive field of science.

The interdisciplinarity of the meeting, has approached inorganic chemists, organic chemists, physical chemists, experts on catalysis and senior researchers from the industry.

This year the focus is on generate an appropriate atmosphere to discuss chemistry and participate of new ideas. Therefore, we have assembled a full scientific schedule designed to foster new relationships and collaborative opportunities, particularly for those in the early stages of their scientific career.

We hope that you enjoy the meeting and the city of Tarragona, which is officially declared a World Heritage Site by the UNESCO due to the singular artistic and architectural patrimony, but also because of the clean and sweeping beaches with their fine and golden sand.

Best regards,
Elena Fernández (chair of GEQO XXXII)

Local Organizing Committee:
Elena Fernández, Carmen Claver, Anna Masdeu-Bultó, Cyril Godard

PROGRAM | SCHEDULE

	September 17	September 18	September 19
		Session 2 **Chair: L. Oro**	**Session 5** **Chair: F. Jalón**
9:00		PL2: B. H. Lipshutz	PL4: Ch. Moberg
10:00		S2: X. Ribas	S8: J. L. Mascareñas
10:30		O3: S. A. Westcott	O9: J. A. Molina de la Torre
10:45		O4: L. Rodriguez	O10: X. Verdaguer
11:00		Coffee	Coffee
		Session 3 **Chair: P. Crochet**	**Session 6** **Chair: A. C. Albéniz**
11:30	Registration	S3: S. Conejero	S9: R. Paciello
12:00	Registration	S4: M. A. Ruiz	S10: T. R. Belderrain
12:30	Registration	O5: I. Favier	O11: D. Grainger
12:45	Registration	O6: A. Johnson	O12: A. Prades
13:00	Registration	S5: U. Piarulli	S11: C. Tejel
13:30	Registration	Lunch	Lunch
	Session 1 **Chair: M. Pericàs**	**Session 4** **Chair: A. Lladós**	**Session 7** **Chair: P. J. Pérez**
15:00-15:30	Wellcome	PL3: S. Hashmi	PL5: M. Fujita
15:30	PL1: G.Lloyd-Jones	“	“
16:00	“	S6: J. A. Mata	S12: B. Menjón
16:30	S1: J. C. Carretero	S7: J. Carbó	S13: P. Sadler
17:00	O1: R. Arévalo	O7: I. Rivilla	Closing Remarks
17:15	O2: L. M. Broomfield	O8: X. Sala	
17:30	End of lectures	End of lectures	GEQO Members Meeting
18:00	Free time	Free time	Free time
19:00	Free time	Free time	Free time
19:30	Poster Session 1	Poster Session 2	Free time
21:00	Dinner	Dinner	Banquet Dinner

PLENARY LECTURES

Getting (un)dressed for a Reaction

Guy C. Lloyd-Jones,

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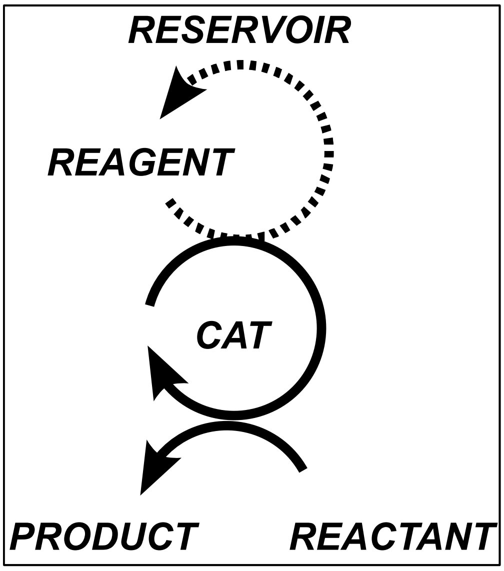
Work hypothesis and objective:

Transition metal coupling of suitably functionalized organic reactants has revolutionized organic synthesis. Understanding the mechanism of such processes is a key component in their successful design, application and development,[1] in academia through to industry.

Results:

The delivery of the reactant from a precursor reagent will be the major topic of the presentation. This will feature selected examples from mechanistic studies into the catalysis of C-X bond forming reactions using strategic combinations of isotopic labelling, NMR, kinetics, mass spectrometry calorimetry, computation, X-ray crystallography, and small-angle neutron scattering. What has emerged from these studies, and been of particular interest to us, is the way in which a variety of subtle chemical and physical changes and unanticipated consequences can conspire to facilitate a useful reaction or to inhibit undesired ones. A recurring theme is that the controlled delivery or release of reactants can be a key part of the success of the overall chemical process.[2,3]



[1] L. T. Ball, G. C. Lloyd-Jones and C. A. Russell *J. Am. Chem. Soc.* **2014**,*136*, 254–264 and *Science,* **2012**, *337*, 1644-1648.

[2] A. J. J. Lennox and G. C. Lloyd-Jones *J. Am. Chem. Soc.*, **2012**, *134*, 7431-7441

[3] C. Poree and G. C. Lloyd-Jones *J. Am. Chem. Soc.*, **2014**, *136*, submitted,

Transitioning Organic Synthesis from Organic Solvents to Water.

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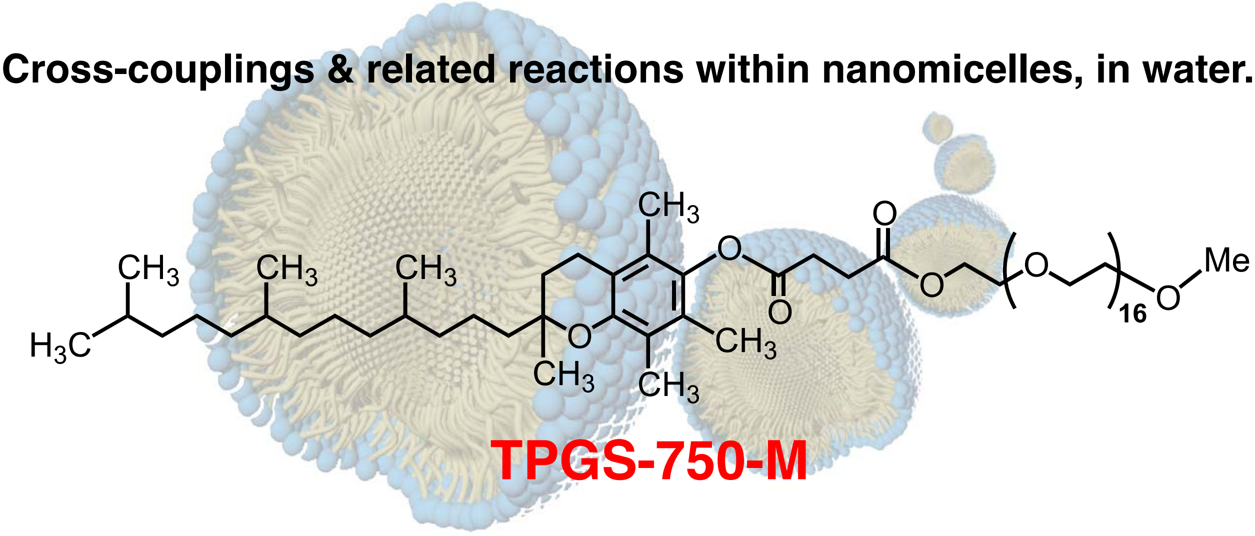
New technology for effecting a variety of transition metal-catalyzed cross-coupling and related reactions under green chemistry conditions; *i.e.,* in water at room temperature, will be described. These are enabled by virtue of the "designer" surfactant TPGS-750-M, which forms nanomicelles upon dissolution in water, in which the reactions take place.[1] No organic solvents are used as reaction media; hence, associated E Factors are very low, and the aqueous medium can be recycled.[2] Representative reactions to be discussed include *unpublished* results on: (1) Ni-catalyzed Suzuki couplings; (2) asymmetric biaryl couplings; (3) S_NAr reactions of aromatic and heteroaromatics; and (4) hydrogenation reactions.

Cross-couplings & related reactions within nanomicelles, in water.



1. Lipshutz, B. H.; Ghorai, S. *Aldrichimica Acta*, **2012**, *45*, 3.
2. Lipshutz, B. H.; Isley, N. A.; Fennewald, J. C.; Slack, E. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 10952;

Two Gold, One Gold, No Gold

A. Stephen K. Hashmi

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Email: hashmi@hashmi.de

Work hypothesis and objective:

Homogeneous catalysis by gold has become a powerful tool for synthesis[1] and an intriguing field for the studies of organometallic mechanisms.[2] New methodologies have been developed, but in a gold rush like this one has to act with care, some reactions might in fact not involve gold, others follow a kind of classical organometallic principle which involves one gold center. Finally, one could even envision reactions depending on an activation of the substrates by two gold centers.

Results:

In the last three years we developed a family of reactions basing on the principle of dual activation. The substrate is activated by **two** gold(I) complexes and then the reaction proceeds through a series of steps which are highly innovative for the whole field of organometallic catalysis (e.g. Figure 1).[3] Apart from the unique mechanistic insights, many of the methods are of significant for the synthesis of extended π-systems for material science or can be used for anellation reactions utilizing alkyl side-chains for the formation of the new rings.[4]

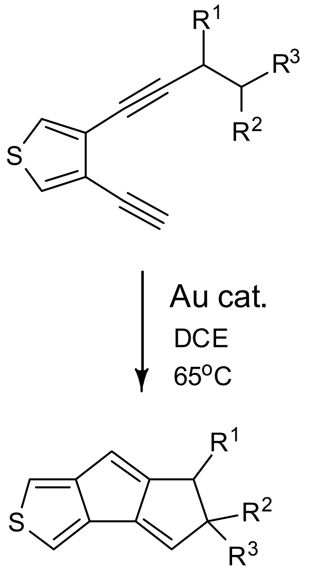


Figure 1

[1] M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.*, **2012**, *41*, 2448-2462.

[2] A. S. K. Hashmi, *Angew. Chem. Int. Ed.,* **2010**, *49*, 5232-5241.

[3] A. S. K. Hashmi, I. Braun, M. Rudolph, F. Rominger, *Organometallics*, **2012**, *31*, 644–661.

[4] A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wieteck, M. Rudolph, F. Rominger, *Angew. Chem. Int. Ed.*, **2012**, *51*, 4456-4460.

Recycling in Asymmetric Catalysis.

Christina Moberg, **Robin Hertzberg, Anna Laurell**

KTH Royal Institute of Technology, Department of Chemistry

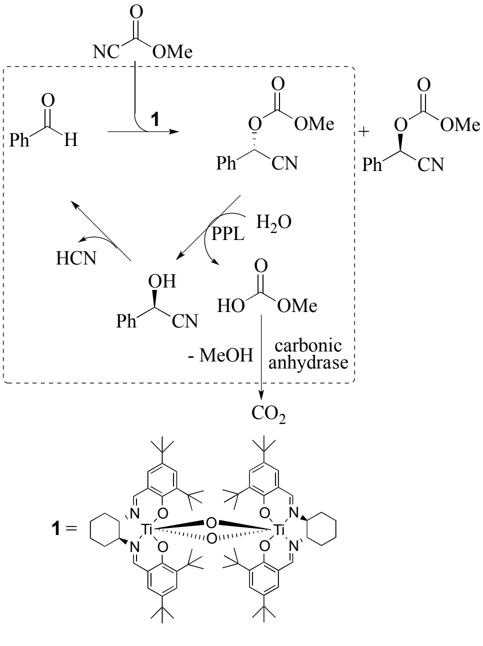
Email: kimo@kth.se

Work hypothesis and objective:

Recycling of the undesired product enantiomer from an enantioselective reaction to achiral starting material is an attractive option for improving the enantiomeric purity of the product. Although the principle of microscopic reversibility states that the reverse reaction cannot favor reaction of the *S*-enantiomer in case the forward, product-forming, reaction favors formation of *R*, chemical energy input via influx of a sacrificial reagent with high chemical energy and the removal of a compound with lower energy may serve as the driving force for a cyclic process.

Results:

We have developed minor enantiomer recycling procedures driven by thermodynamically favoured transformation of acetyl cyanide to acetate, [1] as well as of methyl cyanoformate to carbon dioxide (scheme).[2] The reactions are characterized by steadily increasing yields and enantiomeric ratios. The procedures have been applied to the synthesis of compounds which have been difficult to obtain with high enantiomeric purity by conventional methods.



Scheme

[1] E. Wingstrand, A. Laurell, L. Fransson, K. Hult, C. Moberg, *Chem. Eur. J.* **2009**, *15*, 12107–12113. L. Fransson, A. Laurell, K. Widyan, E. Wingstrand, K. Hult, C. Moberg, *ChemCatChem* **2010**, *2*, 683–693.

[2] A. Laurell, C. Moberg, To be submitted.

Crystalline Sponge Method Updated: From Crystal-Free X-ray Structure Determination to Mechanistic Study

Makoto Fujita

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Recently, we reported a new protocol for X-ray single crystal diffraction (SCD) analysis that does not require the crystallization of the sample.[1,2) In our method, tiny crystals of porous complexes are soaked in the solution of a target, where the complexes can absorb the target molecules. The crystallographic analysis clearly determines the absorbed guest structures along with the host frameworks. As the SCD analysis is carried out with only one tiny crystal, the required sample amount is of the nano-to-microgram order. With chiral guests, the space group of the crystal turned into chiral, enabling the determination of absolute configuration of the guests from the anomalous scattering from the host ZnI_2 component. We demonstrate that even ~50 ng of a sample is enough to be analyzed. In this talk, a focus will be on the updated crystalline sponge method emphasizing the scope and limitation as well as on the snapshot observation of chemical reactions in the crystals.3)

Application to the mechanistic study of an organometallic transformation. Pd-mediated aromatic bromination intrigues synthetic and organometallic chemists due the synthetic utility but, more importantly, due to a proposed mechanism involving an uncommon Pd(IV)/Pd(II) catalytic cycle. Here, we report the X-ray snapshot observation of a Pd reaction center during a Pd-mediated aromatic bromination in the crystalline sponge. Upon treating a single crystal with *N*-bromosuccinimde, sequential X-ray snapshots revealed that the aryl-Pd(II)-L species embedded in the network pores was converted to the brominated aryl product through a transient aryl-Pd(II)-Br species. This X-ray snapshot method relies on crystalline sponges to provide important mechanistic insight previously unobtainable.

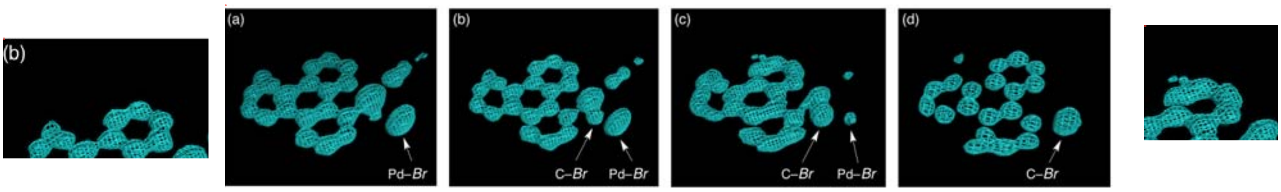

Figure 1. Time-dependent X-ray diffraction data in the conversion from Ar-Pd-Br into Ar-Br. (a)–(c) Electron density maps (F_o) obtained at 2 h, 6 h, and 15 h after the wash described in context and (d) that in the final state (the structure of Figure 3c). The bromine atoms of disappearing Pd–Br and forming C–Br bonds are indicated with arrows. All maps are depicted within 2.5 Å-thick slice of the azatriphenylene moiety and contoured at the absolute 0.95σ level.

1) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen, M. Fujita *Nature* **2013**, *495*, 461-466.; Corrigendum: *Nature* **2013**, *501*, 262
2) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, M. Fujita *Nat. Protoc.* **2014**, *9*, 246-252.
3) K. Ikemoto , Y. Inokuma , K. Rissanen , and M. Fujita *J. Am. Chem. Soc.* **2014**, *136*, in press.

SESSION LECTURES

S01

Catalytic Asymmetric [3+2] Cycloaddition of Azomethine Ylides: New Synthetic Applications

Juan Carlos Carretero

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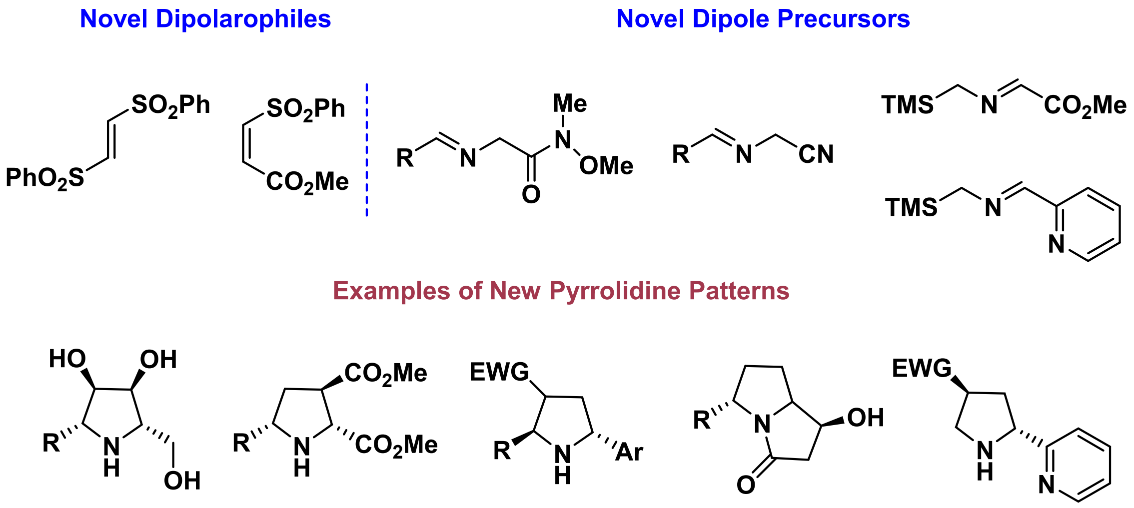
Pyrrolidines and derivatives are privileged scaffolds in synthetic and medicinal chemistry. The catalytic asymmetric 1,3-dipolar cycloaddition of azomethine ylides with activated olefins is one of the most straightforward approaches for the preparation of optically active substituted 2-carboxylate pyrrolidine derivatives[1].

In the last years our group has been engaged in the improvement of the structural scope of the substitution pattern at the pyrrolidine adduct by developing new procedures in metal-catalyzed asymmetric 1,3-dipolar cycloaddition of azomethine ylides. These protocols include the use of unreported types of activated dipolarophiles[2] (e.g. functionalized vinyl sulfones and 1,3-dienes) and dipole precursors, such as α-iminonitriles[3], α-iminoamides[4] and α-silylimines[5], which have allowed the enantioselective access to a wide variety of novel substituted pyrrolidines and derivatives, including biologically active compounds.



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5. a) Hernández-Toribio, J.; Padilla, S.; Adrio, J.; Carretero, J.C. *Angew. Chem. Int. Ed.*, **2012,** *51,* 8854. b) Pascual-Escudero, A.; García-Esguevillas, M.; Padilla, S.; Adrio, J.; Carretero, J.C. *Org. Lett.* **2014**, *16*, 2228.

Model systems for unraveling fundamental redox processes of coinage metals

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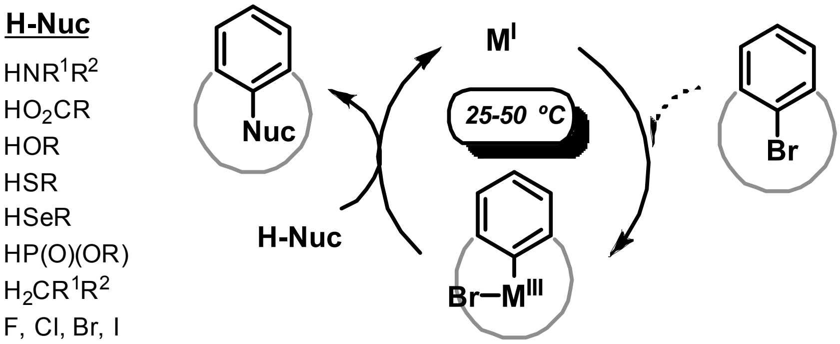
The mechanistic understanding of transition metal-catalyzed chemical transformations is of fundamental importance to design optimized methodologies for the synthesis of target products. We are interested in coinage metal catalysis, with special focus in unravelling the detailed molecular mechanisms and redox chemistry involved in C-C and C-heteroatom cross-coupling reactions. Here we present the unprecedented isolation of elusive aryl-copper(III)-halide species directly involved in C-heteroatom catalytic reactions using model aryl halide substrates. In situ spectroscopic studies of Cu-catalyzed C-X (X= F, Cl, Br, I), C-N, C-O, C-S, C-Se, C-P and C-C coupling reactions provides definitive evidence for the involvement of an aryl-copper(III)-halide intermediate in a redox Cu(I)/Cu(III) catalytic mechanism. On the other hand, analogous two-electron redox catalytic cycles, which are most common in noble metal organometallic reactivity, have never been considered for silver. Herein, we show that an unprecedented Ag(I)/Ag(III) catalytic cycle is operative in model C-O and C-C cross-coupling reactions. We anticipate our study as the starting point for expanding Ag(I)/Ag(III) redox chemistry into new methodologies for organic synthesis, resembling well-known copper or palladium cross-coupling catalysis. Furthermore, findings described herein dismiss the generally accepted conception that silver redox chemistry can only arise from one electron processes.



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[2] M. Font, F. Acuña-Parés, T. Parella, J. Serra, J. M. Luis, J. Lloret-Fillol, M. Costas, X. Ribas, *Nat. Commun.* **2014**, *under revision.*

Reactivity Studies on Electron-Defficient Pt(II) and Pt(IV) Complexes Stabilized by N-heterocyclic Carbene Ligands.

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Coordinatively unsaturated platinum complexes in +2 and +4 oxidation states are believed to play an important role in numerous stoichiometric and catalytic processes.[1] In particular, these species have been suggested as key intermediates in Shilov-type chemistry for the functionalization of carbon-hydrogen bonds. Nevertheless, the reactivity of these low-electron count Pt(II) and Pt(IV) complexes has been limitedly explored due to their intrinsic instability. Therefore, their isolation can provide with valuable information with regard to the factors that make possible the activation of C-H bonds as well as the formation of new carbon-heteroatom bonds.

During the last years, our group has geared its research activities toward the isolation of 14-electron Pt(II) complexes stabilized by N-heterocyclic carbene (NHC) ligands.[2] The nature of the NHC (sterics and electronics) controls the reactivity of the platinum complexes. This presentation will focus, in part, on the interaction of these species with molecules such as dihydrogen and boranes, and on their oxidation with halogens leading to the formation of C-X bonds through the intermediacy of transient or stable platinum complexes in +3 or +4 oxidation states.

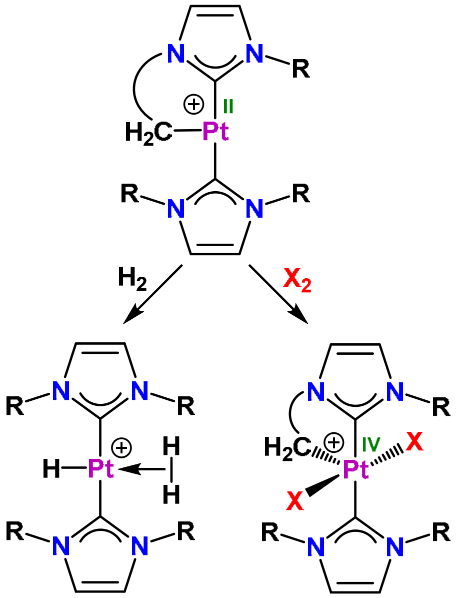

Figure 1

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S04

Chemistry of Unsaturated Cyclopentadienyl Dimolybdenum Radicals.

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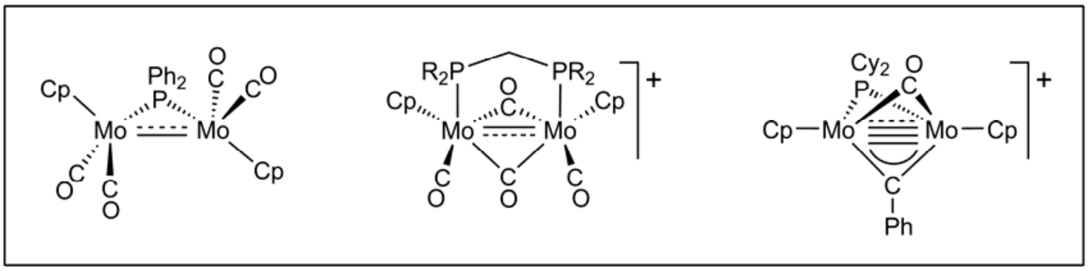
The chemistry of metal-based radicals is an area of interest in the current organometallic research, mainly because these species are involved as active intermediates or catalysts in many fundamental reactions such as ligand substitution, isomerization, atom transfer, electron transfer or metal-metal bond formation. Most of the work in this area, however, has focused on the reactivity of mononuclear radicals, whereas the chemistry of binuclear species, particularly those having metal-metal bonds, has remained comparatively little explored, perhaps due to their easy degradation to mononuclear products. In this session presentation we will overview work carried out in our laboratory over the last fifteen years concerning the generation, structural characterization and reactivity of different cyclopentadienyl dimolybdenum radicals stabilized by P-donor bridging ligands such as diphosphines or dialkyl- and diarylphosphides, and having metal-metal formal bond orders ranging from 1.5 to 3.5. As it will be shown, these binuclear species are very reactive towards a great variety of reagents under mild conditions, and are involved in processes analogous to those characteristic of mononuclear radicals. Moreover the presence of the unsaturated dimetal centre in these substrates often induces coordination modes or reorganizations eventually leading to products that cannot be prepared using more conventional (i.e. electron precise) precursors.



Supramolecular ligand-ligand and ligand-substrate interactions for highly selective transition metal catalysis.

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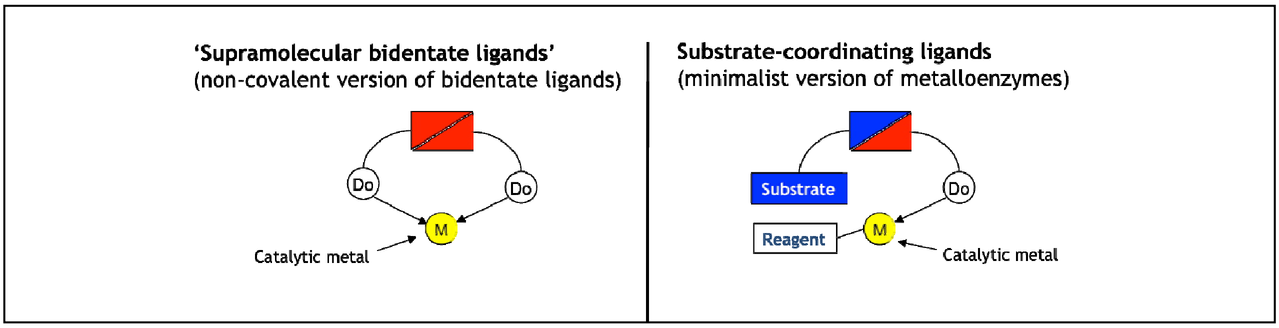
In the last decade, supramolecular approaches to the development of new ligands for asymmetric catalysis have gained momentum.[1] The term 'supramolecular ligand' encompasses all the ligands possessing, besides the atom(s) coordinating the catalytic metal, an additional functionality capable of non-covalent interactions (mainly hydrogen or coordinative bonds) which can play the following role: (i) self-assemble two monodentate ligands to form a so-called 'supramolecular bidentate ligand'; (ii) bind the substrate(s) in proximity to the catalytic metal center in analogy to metalloenzymes. Both these approaches cause reduced degrees of freedom in the catalytically active metal complexes, which is expected to result in more pre-organised systems with better capacity of controlling the metal-catalysed reaction.



Here we present our approaches to the application of supramolecular interactions to asymmetric catalytic reactions.[2]

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Applications of heterobimetallic complexes in tandem reactions and catalysts immobilization onto graphene

Jose A. Mata

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Complexes with N-heterocyclic carbene (NHC) ligands are an important class of transition metal-based catalysts. From the electronic properties, the σ-donor capacity of NHC ligands leads to strong metal-carbon bonds that provide stable complexes suitable to operate under harsh conditions. These important properties and applications make NHC ligands good candidates for the preparation of reusable based-catalysts.[1]

Chemically derived graphenes (CDGs) such us graphene oxide and reduced graphene oxide are ideal candidates for immobilization due to its inertness, stability, large scale availability and the presence of functional groups. Immobilization of molecular catalysts bearing functionalized NHC ligands allows the rationale modification of ligands to control the steric and electronic properties of the metal active center. A highly active and well defined catalyst combined with the possibility of separating from products and reuse is very attractive from the industrial point of view.[2]

In this work, we will show our approach to the immobilization of NHC-Metal complexes onto graphene and the applications of heterobimetallic complexes in tandem catalytic processes.

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Computational Tools for Understanding and Predicting the Performance of Organometallic Catalysts: QSAR and Dynamic approaches.

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Work hypothesis and objective:

The traditional approach to the modelling of organometallic reactivity consists of the location of minima and transition-states (TS) on static *Potential Energy Surfaces* (PES). As an alternative to TS-based approaches, other methodologies define descriptors for ground-sate properties to look for quantitative relationships with the activity or selectivity. They are usually referred as quantitative structure-activity relationship (QSAR) or –selectivity (QSPR) approaches. Despite acceptance in the pharmaceutical world and their potential utility, the use of QSAR approaches in the design of catalysts is still rare. Moreover, classical and Car-Parrinello molecular dynamics simulations represent a step forward with respect to static calculations of PES, providing a dynamic view and accounting for explicit solvent, pH and macroscopic counterion effects.

Results:

Here, we will present our attempts to apply QSAR and dynamic approaches to the study catalytic process such as hydroformylation by Rh-phosphane and asymmetric cyclopropanation by Cu-oxazoline. Using a modified version of energy decomposition analysis (EDA), we could separate and quantify the σ-donor/π-acceptor contributions to Rh-P bond and correlate them with the activity of Rh-catalyzed hydroformylation.[1] Quantitative QSAR models for a dataset of 20 ligands were achieved by defining 3D descriptors that account for electrostatic and shape features of the catalysts. For the asymmetric processes we propose a modelling based on *quantitative quadrant diagram* representation of the catalysts, measuring the quadrant occupation with the *distance-weighted volume* (V_W) descriptor.[2]

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Cycloaddition Strategies based on Transition Metals.

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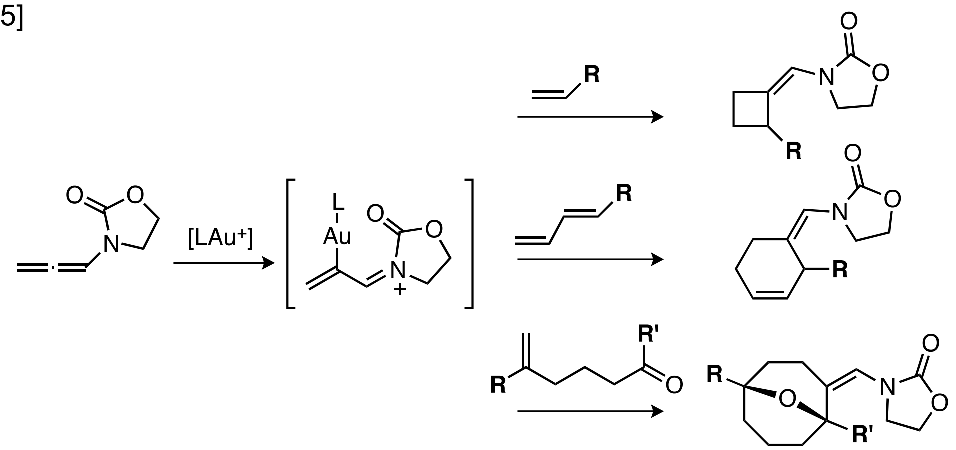
Work hypothesis and objective:

Cycloaddition reactions allow the direct assembly of cyclic skeletons from acyclic precursors, and therefore represent invaluable tools to streamline the synthesis of complex polycyclic products. While classical cycloadditions are somewhat restricted to specific, electronically complementary reactants, the potential of cycloaddition chemistry can be enormously expanded by taking advantage of the coordination and activation capabilities of metal complexes. [1]

Results:

In recent years we have unveiled several new cycloaddition modes of alkylidenecyclopropanes by using palladium or nickel catalysts.[2] We have also developed several platinum or gold-catalyzed reactions of allenes consisting of formal (4 + 3) and (4 + 2) cycloadditions.[3] The intermolecular version of these reactions could be better accomplished by using allenamides as cycloaddition partners. These substrates work as efficient two carbon components in a variety of gold-catalyzed cycloadditions with different types of alkenyl derivatives (see scheme).[4] Most recently, our work in cycloaddition chemistry is moving towards the discovery of "anomalous" annulations involving C-H activation processes.[5]



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S09

Catalytic and direct carboxylation of olefins with CO_2: One-pot synthesis of α,β-unsaturated carboxylic acid salts.

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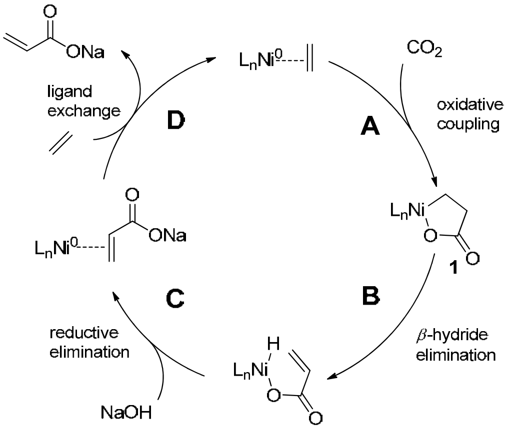
Work hypothesis and objective:

The catalytic synthesis of acrylates from the cheap and abundantly available C_1 building block CO_2 and alkenes has been an unsolved problem in catalysis research, both in academia and industry, for more than three decades. Acrylates and their downstream products are ubiquitous as hygiene products, coatings, adhesives or plastics *etc*. in daily life and are manufactured globally on a multi million ton level. A CO_2-based route to such world-scale chemicals is, therefore, economically most attractive, but, due to thermodynamic and kinetic hurdles, also challenging. Metallalactones (**1**) have been discussed as possible intermediates in a catalytic cycle since the revolutionary work of Hoberg,[1] but the reaction has existed until recently.[2,3]

Results:

Herein, we present catalysts from the Nickel group for the direct carboxylation of alkenes with CO_2 in the presence of a base. The one-pot reaction allows for the direct and selective synthesis of a wide range of α,β-unsaturated carboxylates. Thus, it is e.g. possible to synthesize in one-step potassium sorbate from piperylene, CO_2 and a potassium salt and sodium acrylate from ethylene, CO_2 and a sodium salt. Both are industrially important products, whose syntheses hitherto required multiple steps.



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Copper and Palladium Catalyzed Carbene Transfer from Diazocompounds: Reactions Insights

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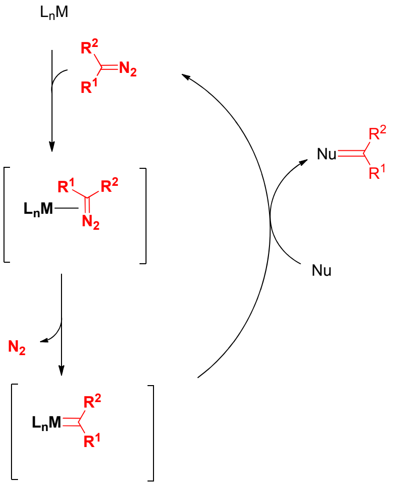
Work hypothesis and objective:

A suitable way for carbene transfer to an organic substrate consists in the nitrogen extrusion from a diazo compound in presence of a transition metal complex (Scheme).[1] This method has been employed, for instance, for direct C=C and C–H functionalization. Among the metals used for this transformations, copper[1] and palladium[2] catalysts have been studied deeply. However, in some of these systems there are some points that still remained not very clear: i. e. factors which influence the metal-carbenoid stability, nature of the interaction of the diazo compound and the metal center, etc.

Our group has described the use of Tp^xCuL (Tp^x = trispyrazolylborate; L = solvent)[3] and $(NHC)Pd(sty)_2$ (NHC = N-heterocyclic carbene; sty = styrene)[4] as catalyst precursors for the addition of carbene, from diazoesters, to different substrates. The understanding of the steps of our catalytic systems could allow us to design new catalysts with better activities and selectivities.

Results:

Herein, we report the detection and isolation of some intermediates involved the carbene tranfer processes using several Tp^xCuL and palladium(0) bearing phosphane-functionalized NHC ligands complexes. On the basis of these findings and the kinetic experiments carried out we have made different mechanistic proposals for both catalytic systems.



Scheme

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Pyramidalyzation of Metallic Fragments: Novel Pseudo-Tetrahedral Rh(I) and Rh(III) Complexes

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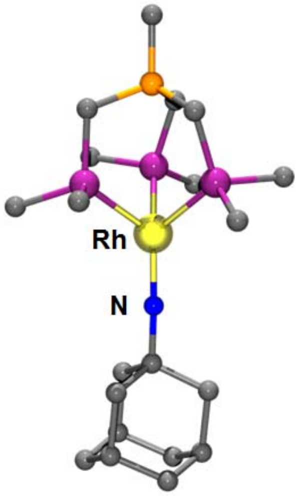
The topology of polydentate ligands (described by the disposition of the donor atoms) determines to some extent the geometry around a transition-metal center in a metal complex, while the character of the donor atoms allows the control over electronic properties. A conjunction of both characteristics will eventually impact on the reactivity of metal complexes and can open synthetic pathways to new types of compounds. In this context, complexes of the late transition metals with M=X multiple bonds (X=CR_2, NR, O) represent a synthetic challenge, partly overcome by preparative chemists, but with noticeable gaps in the second- and third-row elements.

In this communication we will illustrate that housing a transition metal such as rhodium(I) -whose chemistry is dominated by square-planar geometries- in pyramidal environments allows the access to interesting reactions such as oxygen fixation or catalytic coupling reactions.[1] Moreover, we will showcase that rhodium(I) and rhodium(III) complexes in pseudo-tetrahedral environments are not only accessible but they can be isolated as stable compounds. The decisive stabilization of this unknown geometry for rhodium in the oxidation states +1 and +3 is a consequence of the synergy between a high-field and strongly donating tripodal ligand, $[PhB(CH_2PPh_2)_3]^-$, and highly π-loaded donors such as alkynes or imido ligands (see figure).[2] The multiplicity of the Rh=X bonds will be highlighted and some selected reactions of these type of complexes will be interpreted in terms of bonding and geometrical changes.



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Trifluoromethyl compounds of heavy transition metals

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Work hypothesis and objective:

Trifluoromethyl compounds of the late transition metals, [M]–CF_3, show an interesting dual behavior. They usually exhibit an enhanced thermal stability when compared to their non-fluorinated counterparts, but at the same time display an appealing reactivity that includes CF_3-group transfer (trifluoromethylation) and C–F bond activation processes.[1]

Results:

Taking advantage of the aforementioned stability, it has been possible to prepare and isolate carbonyl derivatives of Au(I) [2] and Pt(IV),[3] for which no similar methyl compounds are known. In these [M]–CO compounds, the CO molecule is acting as a mainly σ-donor ligand (sometimes referred to as *"nonclassical"*).

Concerning the referred C–F bond activation, it is possible to accomplish fluoride abstraction from a CF_3 group, which leads to the formation of an electrophilic difluorocarbene moiety (see graphic below). Our approach to these thermally unstable and highly reactive [M]=CF_2 species has been carried out at three levels, as they have been: 1) detected at low temperature by ^{19}F NMR spectroscopy; 2) stabilized by coordination of a donor molecule L lacking α-H atoms, [M]=$CF_2 \cdot L$; and 3) reacted with a number of nucleophiles bearing α-H atoms, giving rise to various functionalized carbenes derived thereof.

A general overview of all these chemical features will be presented.

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Catalytic Organometallic Anticancer Complexes

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Work hypothesis and objective:

Organometallic half-sandwich complexes of low-spin d^6 metal ions can act as both catalysts and anticancer agents [1]. Transfer hydrogenation catalysis includes the biologically important reduction of coenzyme NAD^+ to NADH using formate as an hydride source [2]. Interestingly, Ir(III) Cp* complexes can catalyse the reverse reaction, the conversion of NADH to NAD^+, and transfer hydride to substrates such as quinones [3,4]. These organometallic complexes thus have the potential to perturb the redox balance in cells, potentially a highly effective strategy for selectively killing cancer cells [5]. The aim of the present work was to establish if organometallic complexes can act as catalytic anticancer drugs by modulation of the $NADH/NAD^+$ levels in cells.

Results:

We have investigated the activity of $[(\eta^6\text{-arene})Ru(R\text{-En})Cl]$ complexes towards human ovarian cancer cells in the absence and presence of formate, as well as the effect on the $NAD^+/NADH$ ratio in cells, cellular accumulation of Ru, and mitochondrial membrane potential [6]. Highly potent Cp* Ir(III) anticancer complexes can generate H_2O_2 in cancer cells via catalytic hydride transfer [7].

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Acknowledgements. We thank ERC, EPSRC, BBSRC, IAS and EU COST CM1105 for support.

ORAL COMMUNICATIONS

Deprotonation of CH_3 groups of N-heterocyclic ligands in a rhenium tricarbonyl complex.

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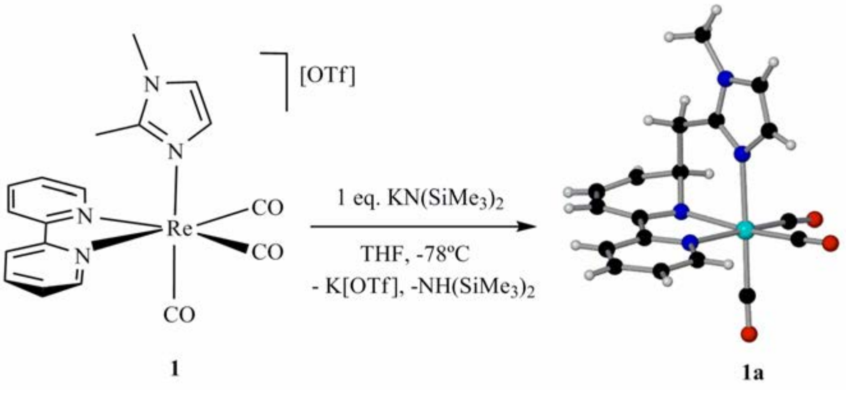
Work hypothesis and objective:

Previous results by our group have shown that α-CH groups of coordinated heterocycles (N-alkylimidazoles[1] and pyridines[2]), sulfides (*e.g.* SMe_2[3]) or phosphines (*e.g.* PMe_3) undergo intramolecular C-C coupling with cis-diimine chelates (2,2'-bipyridine or 1,4-diaza-1,3-butadienes) following C-H deprotonation. We set out to study if 2-methyl groups of N-heterocyclic ligands could display similar reactivity.

Results:

Compounds $[Re(bipy)(CO)_3(L)][X]$ (L= 1,2-Me_2Im (**1**), 2-methyloxazoline, X= OTf; L= α-picoline, X= $BAr^F{}_4$) instantaneously react with the strong base $KN(SiMe_3)_2$ at low temperature to afford single neutral products. In them, a C-C bond has been created between the deprotonated methyl group and C6 of the bipy ligand, which results in its dearomatization.



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The synthesis, structure and alcohol amination chemistry of ruthenium phosphino-amine complexes.

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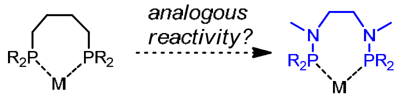
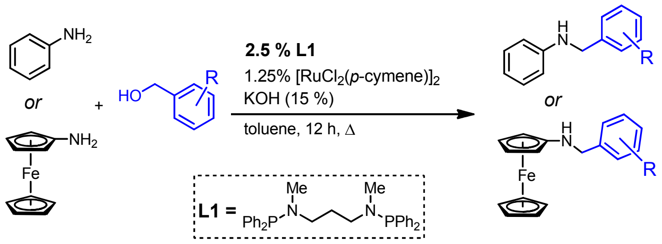
Work hypothesis and objective:

In a variety of catalytic processes, bisphosphines are used to modulate the reactivity of the catalytic metal centre. Unfortunately, their synthesis is work-consuming, becoming the bottle neck for rapid process discovery. This hurdle may be overcome by designing a rapid, robust and modular approach to bis-phosphines. Indeed, bis(aminophosphines) fulfil such requirements. They are obtained in one step by condensing a diamine with the corresponding chlorophosphine. The method is versatile and the abundance of amines allows for ample ligand sets to be quickly generated. These ligands have been used in selective ethene oligomerisations[1] and nitrile hydrations.[2] We recently discovered that bis(aminophosphines) are promising for Ru-catalyzed H_2 *autotransfer* processes. Amine alkylation with alcohols, as well as the conversion of nitriles to amides are examples.[3, 4]



Results:

Previously, we have developed a rapid and robust condensation of amines with chlorophosphines to obtain aminophosphines. Most ligands belong to either the PNP (two P bound to a nitrogen) or PNNP family. The PNNP-type ligand **L1**, promotes efficient Ru-catalyzed alkylation of amines, including aminoferrocene, by alcohols in an atom-economic H_2-*autotransfer* process. Interestingly, in the absence of ligand, an imine is obtained. The presence of the PNNP ligand seems crucial for the final step (the rehydrogenation of the imine).



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Using Arylspiroborate Metal Complexes for Borylation Reactions: To B-E or not to B-E?

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Work hypothesis and objective:

The metal catalyzed addition of B-H bonds has garnered a considerable amount of attention over the past few years as a simple, yet elegant, way of preparing a wide range of synthetically-relevant organoboron compounds.[1] The generation of air stable boronate ester derivatives is of singular interest for their use in the remarkable Suzuki-Miyaura cross-coupling reaction.[2] We have begun a systematic study to investigate the synthesis and reactivity of novel metal complexes containing weakly coordinating arylspiroborate ligands to be used as borylation catalyst precursors.[3]

Results:

Synthesis of arylspiroborate ligands is straightforward, economically-viable and environmentally-friendly using the appropriate catechol derivative and readily available metal borohydride salts. Stoichiometric studies with metal complexes are also being conducted to gain a further understanding into the nature of these species. We are examining these new metal complexes for the hydroboration, and related B-E addition reactions (E = main group element), of a wide range of substrates, the results of which will be disclosed.

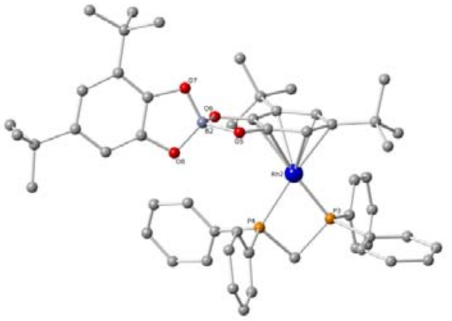

Figure 1. Molecular structure of a phosphinorhodium arylspiroborate complex.

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Aurophilic interactions as a route for supramolecular assemblies in water

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Work hypothesis and objective:

Gold(I) complexes with small ligands oligomerize to give dimers, trimers, tetramers, chain polymers, or layers with short Au···Au contacts (aurophilic interactions).[1,2]
In this work, we analyze how gold(I) derivatives can self-assemble spontaneously to give rise to the formation of supramolecular structures with different topologies.

Results:

We have recently observed the formation of supramolecular assemblies with the [Au(ethynyl-R)(phosph)] (phosph = PTA, DAPTA; R = pyridine, coumarin) water soluble complexes that lead to the formation of luminescent hydrogels.[3-5]
Moreover, we have also demonstrated that slight modifications on the chemical structure can induce significant changes on the supramolecular assemblies being able to obtain hydrogels, rods or vesicles (Figure 1).
Absorption and emission spectra analysis together with ^{1}H-NMR data shows that weak interactions are modulated by the presence of aurophilic intermolecular interactions.

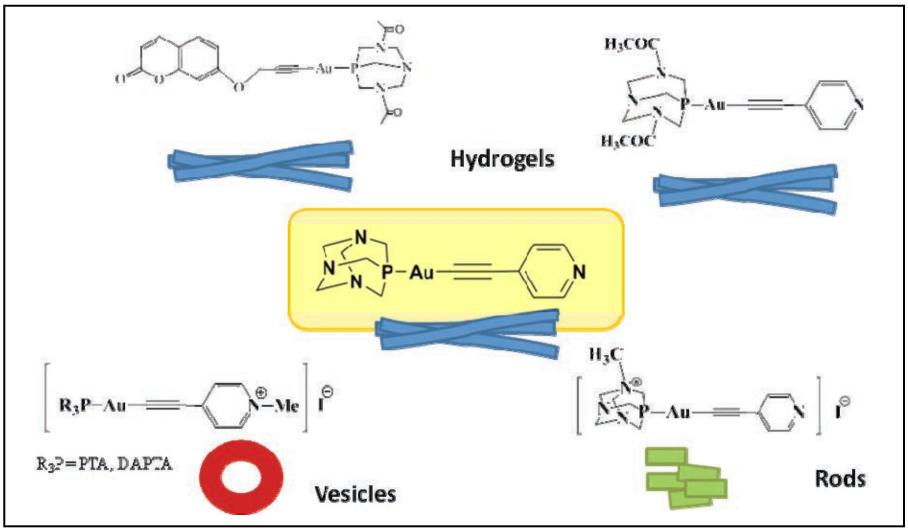

Figure 1. Supramolecular assemblies found with derivatives of [Au(4-ethynylpyridyl)(PR$_3$)] (PR$_3$ = PTA, DAPTA) complexes.

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[4] E. Aguiló, R. Gavara, J.C. Lima, J. Llorca, L. Rodríguez, *J. Mat. Chem. C.* **2013**, *1,* 5538.
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How to evidence the molecular coordination at the metallic surface of nanoparticles?

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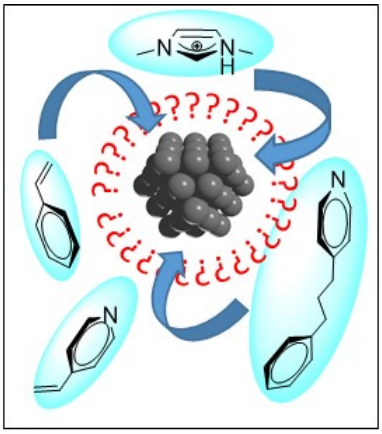
Work hypothesis and objective:

In the last years, metallic nanoparticles (MNPs) have been largely applied in catalysis due to their ability to present a dual reactivity, meaning a surface-like and a molecular behaviour.[1-3] The comprehension of the interaction at the metallic surface of reagents, stabilisers or solvents is crucial to understand their catalytic performance, mainly working in wet medium. We are interested in evidencing the coordination mode of those organic molecules at the nanoparticle shell. NMR tools appear as an appropriate way to help us, in particular for PdNPs [4] and RuNPs.[5,6]

Results:

RuNPs stabilised by the ligand 4-(3-phenylpropyl)pyridine represent a suitable colloidal system to develop NMR studies. MAS NMR and DOSY measurements permit to elucidate the coordination of the ligand [5] and NOE experiments, the interaction at the metallic surface of substrates such as styrene or 4-vinylpyridine, model reagents for catalytic hydrogenation purposes.[6] For instance, this kind of approach has permitted us to prove the bidentate π,π-interaction of the ligand to the MNP.



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[5] I. Favier, S. Massou, E. Teuma, K. Philippot, B. Chaudret, M. Gómez, *Chem. Commun.,* **2008**, 3296.

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Gold Allene Complexes

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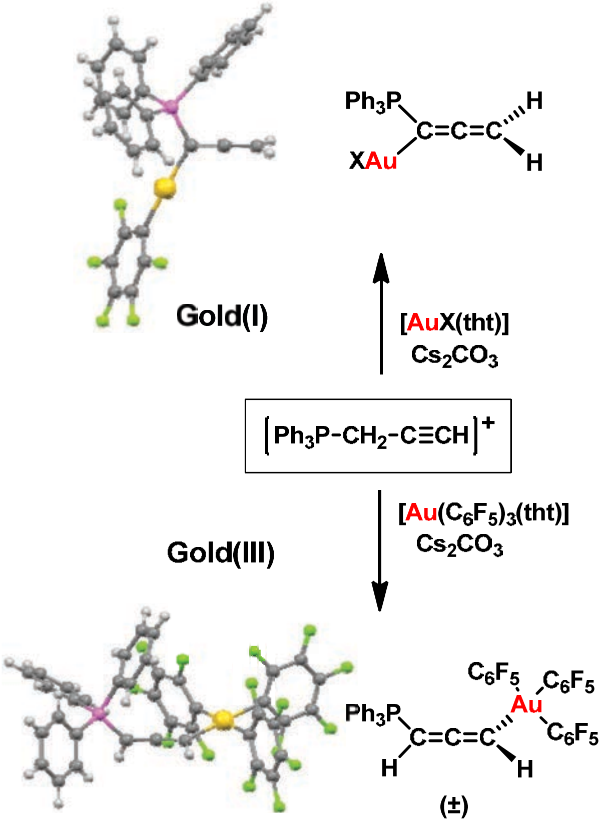
Work hypothesis and objective:

Whilst allenes are versatile substrates and gold allene complexes have frequently been proposed as intermediates in gold catalysed transformations, until now very few examples have been isolated or structurally characterised and hence the mechanisms of such transformations are poorly understood.[1][2] The use of triphenylpropargylphosphonium bromide, a stable source of the allene compounds, allows the possibility for the preparation of stable gold allene complexes including appealing axially chiral complexes.

Results:

Several unprecedented η^1-allene gold(I) and gold(III) complexes have been achieved starting from triphenylpropargylphosphonium bromide. A remarkable regioselectivity has been found depending on the gold oxidation state. For the gold(I)-allene derivatives the gold(I) centre coordinates to the α carbon atom, whilst for gold(III), coordination to the less substituted γ carbon was found, resulting in a highly unusual chiral gold complex. All the complexes have been structurally characterised by X-ray diffraction showing the characteristic distances for a C=C=C unit. This work opens the possibility for the preparation of a wide range of organogold derivatives, some of which could be key intermediates in catalytic transformations.



[1] W. Yang, A.S.K. Hashmi, *Chem. Soc. Rev.,* **2014**, *43*, 2941

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Synthesis and DFT studies of novel catalysts via (2+2) and (3+2) cycloadditions and their application as chiral ligands in metal-catalyzed reactions.

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[2]IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain
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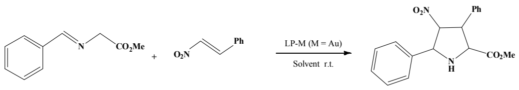
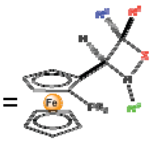
Work hypothesis and objective:

Thermal cycloaddition reactions (n + m) constitute a very convenient method for the chemical synthesis of different cycloadducts in a single preparative step, thus obtaining complex cyclic compounds. In this work, we have synthetized and evaluated the catalytic properties of novel a enantiopure family of hybrid ferrocene ligands. These catalysts were obtained via diastereocontrolled (3 + 2) or (2 + 2) cycloadditions. DFT studies on the cycloaddition reactions show that the presence of the ferrocenyl-phosphine moiety promotes the exclusive formation of one of the possible stereoisomers.[1] Moreover, these compounds were tested as catalyst on reactions such as 1,3-dipolar cycloadditions, C-H insertion reactions and (2+1) cyclopropanations, using Cu, Ag, Au and Rh as metallic coordinating centers (Scheme 1 and 2). Furthermore, DFT calculations on the reaction mechanisms were performed in order to understand the origins of the enantioselectivity observed when these new catalysts are used (Fig. 1).

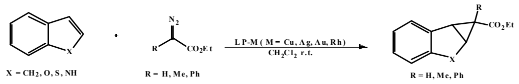


Scheme . 1

LP =



(a) X = CHR- CR^4(CO$_2$R^5)-
(b) X = CO



Scheme . 2

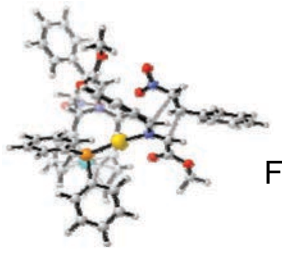


Fig. 1

Results:

We have tested the effect of these hybrid ferrocene ligands on gold catalyzed cyclopropanation and (3+2) cycloaddition reactions. As far as pyrrolidine ligands were involved, no enantioselection was observed on the reaction mixtures. On the other hand, the use of β-lactams on (3+2) cycloadditions implies a enantiomeric excess of about 50 %.

[1] E. Conde, D.Bello, A. de Cózar, M.Sánchez, M.A. Vázquez and F. P. Cossío. *Chem. Sci.*, **2012**, *3*,1486-1491

O08

Redox Catalysts for Selective Oxidation Processes and Energy Related Transformations

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Work hypothesis and objective:

The selective oxidation of both organic and inorganic molecules is fundamentally important to life and vastly useful in industry. Therefore, for instance, the efficient preparation of epoxides is of central importance in organic synthesis,[1] and the oxidation of water to dioxygen is a key transformation when a potential device for the generation of hydrogen through the splitting of water is envisaged.[2] Our research aims to contribute to this important challenges by means of preparing and mastering molecular, colloidal and heterogeneous redox catalysts.

Results:

With regards to the epoxidation of alkenes, this contribution will mainly deal with the work carried out in our laboratories exploring metal-metal cooperation, stereoselectivity and catalyst anchoring and recyclability by employing molecular systems and hybrid nanomaterials.[3] A second part will pay attention to the particularities of water oxidation catalysis, specially the identified O-O bond formation mechanisms, catalyst decomposition and high oxidation states stabilization (Figure 1), the covalent and electrostatic anchoring of both molecular and colloidal species, and the performance of the whole set of prepared systems.[4]

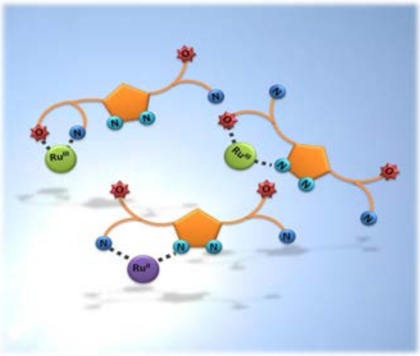

Figure 1. Redox Controlled Linkage Isomerization for Stabilizing High Oxidation States

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[4] (a) X. Sala, S. Maji, R. Bofill, J. García-Antón, L. Escriche, A. Llobet, *Acc. Chem. Res.* **2014**, 47, 504. (b) J. Aguiló, L. Francàs, H. Liu, R. Bofill, J. García-Antón, J. Benet-Buchholz, A. Llobet, X. Sala, *Catal. Sci. Technol.* **2014**, 4, 190. (c) J. Aguiló, A. Naeimi, R. Bofill, H. Mueller-Bunz, A. Llobet, L. Escriche, X. Sala, M. Albrecht, *New J. Chem.* **2014**, 38, 1980.

Polynorbornene supportted NHCs. Use in Pd catalyzed C-C cross coupling reactions.

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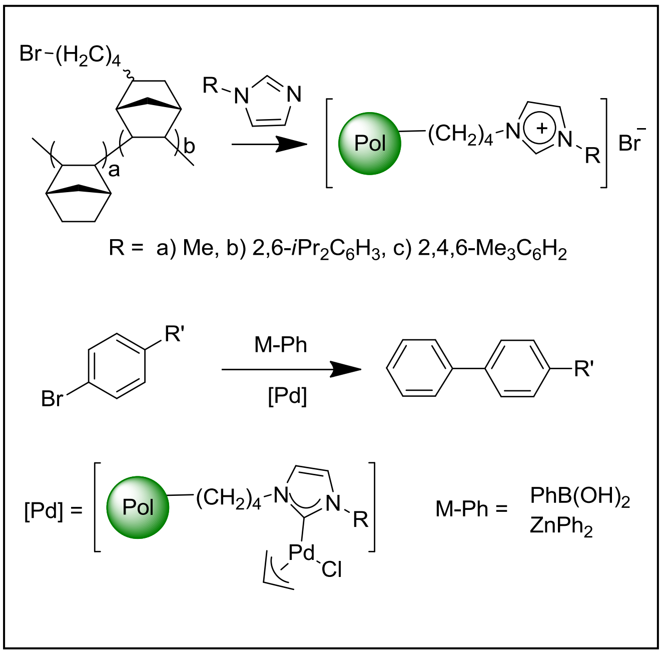
Work hypothesis and objective:

Over the last two decades N-Heterocyclic carbenes (NHCs) have been widely used as ligands in organometallic catalysis. Many different processes, especially C-C cross coupling reactions use palladium complexes with these ligands. On the other hand, attaching the complexes to some solid support allows the catalyst not only to keep the selectivity or steric and electronic control, but to add the recyclability of the catalysts achieving lower costs and waste. Recently our group has developed halogen functionalized vinyl-polynorbornenes with inert backbones [1]. From these polymers we have made different imidazolium salts, common precursors of NHCs, and some polymer-supported palladium complexes useful as catalysts in organometallic reactions.

Results:

We present here the synthesis of different polynorbornene-anchored imidazolium salts from a bromoalkylated-polynorbornene and diverse N-substituted imidazoles. We also describe the synthesis of some polymer-supported palladium complexes by generation of the NHCs from the imidazolium salts by treatment with a base. These complexes have been used as catalysts in different Suzuki and Negishi reactions. The recyclability of the catalysts has been evaluated.



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O10

P-stereogenic amino phosphines: Synthesis and its use in asymmetric catalysis.

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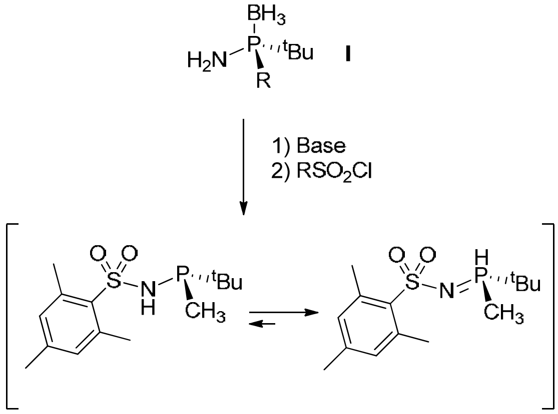
Work hypothesis and objective:

Chiral phosphines play a key role to attain high activity and selectivity in asymmetric catalysis. As a consequence a great effort has been devoted to develop efficient phosphine ligands for any catalytic process. Our group has developed a synthesis of novel P-stereogenic aminophosphine synthons (**I**) bearing a primary amino group.[1] These compounds are easily prepared in optically pure form on large scale using cis-1-amino-2-indanol as chiral auxiliary.[2]

Results:

The P-stereogenic aminophosphine building blocks **I** have proven to be useful in the preparation of several chiral ligands such as N-sulfonyl secondary iminophosphoranes (SIP) and the diphosphine MaxPHOS.[1,3] The presence of the NH group bounded to a bulky electron-rich phosphine brings about the opportunity for the NH/PH tautomerism to take place. The tautomeric equilibrium is shifted towards the P(V) form thus protecting the phosphorus atom from oxidation. We will present the use of our chiral ligands in Rh catalyzed asymmetric [2+2+2] cycloadditions of endiynes, asymmetric hydrogenations and Pauson-Khand cycloadditions.



Tautomeric equilibrium

[1] M. Revés, C. Ferrer, T. León, S. Doran, P. Etayo, A. Vidal-Ferran, A. Riera, X. Verdaguer, *Angew. Chem., Int. Ed.* **2010**, *49*, 9452.
[2] T. León, A. Riera, X. Verdaguer, *J. Am. Chem. Soc.* **2011**, *133*, 5740-5743.
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O11

Application of tethered aryl-diamine ruthenium catalysts for hydrogenation and transfer hydrogenations processes.

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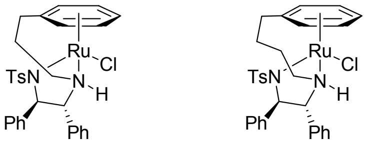
Work hypothesis and objective:

Tethered catalysts developed by Wills at el. [1] exemplify progressive, new generation Noyori type transfer hydrogenation catalysts. Due to the tether linking the arene ring to the diamine ligand, the catalysts exhibit enhanced stability and reactivity. Recently, they have been used for transformations towards pharmaceuticals such as antiepileptic drug Eslicarbazepine or anti-asthmatic drug Montelukast. [2] Such highly active and selective catalysts can meet the cost and efficiency targets for application in industrial processes.

[1] *J. Am. Chem. Soc.* **2005**, 7318; [2] WO2011131315A1, WO2009130056A1.

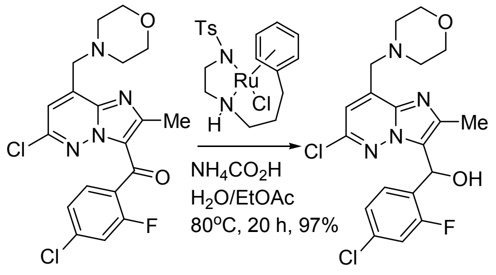
Results:

Application of tethered aryl-diamine ruthenium catalysts for hydrogenation and transfer hydrogenations processes, including examples of industrially relevant molecules which demonstrate homogeneous catalysts can provide solutions were heterogeneous catalysis fails due to chemoselectivity issues. [3] Discussions will include the development of an efficient two-step catalytic method for the reductive deoxygenation of ketone **1** (via **2**), providing a key building block in the preparation of LY2784544 (a JAK2 inhibitor currently under clinical investigations for the treatment of myeloproliferative disorders). [4, 5]



C3-[(R,R)-teth-Ts-Dpen RuCl]   C4-[(R,R)-teth-Ts-Dpen RuCl]

Wills' tethered DPEN catalysts



1 **2**

[3] *ChemCatChem* **2013**, 5, 120; [4] US Pat. Appl. Publ. US 20100152181A1 20100617; CAN 153:97762, AN 2010:753991.2010; [5] Org. Process Res. Dev. **2012**, 16, 70.

Development of New Small Bite-Angle Rhodium Phosphine Complexes for Hydroacylation Catalysis

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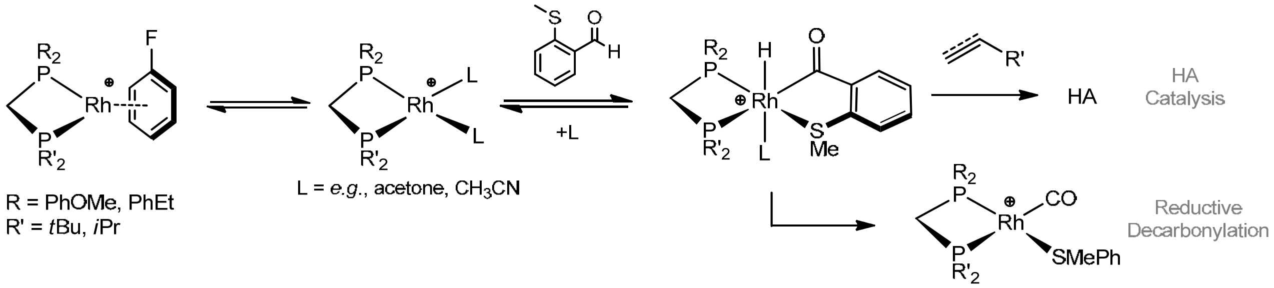
Work hypothesis and objective:

The atom-efficient coupling of aldehydes with alkynes or alkenes to form ketones, the hydroacylation reaction (HA), is a potentially powerful transformation for organic and materials synthesis.[1] Very recently our group (in collaboration with the Willis group, Oxford) have reported on small bite-angle rhodium phosphine complexes which are efficient and selective catalysts for this type of reaction.[2] The objective of the work presented here is the development of new Rh-complexes robust against the decarbonylation. This deleterious side-reaction, the main limitation against the widespread adoption of this coupling methodology, ultimately forms an inactive metal-carbonyl species.

Results:

We have developed a new family of rhodium bis-phosphine complexes containing small bite-angle ligands, which as have appended Lewis-Basic groups that can potentially stabilise the metal centre. These new complexes show excellent results in the HA reactions, they are remarkably resistant to decarbonylation, allowing for them to be recycled without loss in conversion. A detailed mechanistic study (rate, order and labelling studies) allows us to further understand the reaction mechanism and the reasons behind the high activity and selectivity of these catalysts.



[1] Willis M. C. *Chem. Rev.*, 110, (2010), 725-748.
[2] Chaplin A. B., Hooper J. F., Weller A. S. and Willis M. C. *J. Am. Chem. Soc.*, 134, (2012), 4885-4897. Pernik, I., Hooper J. F., Chaplin, A. B., Weller A. S. and Willis M. C. *ACS Catal.*, 2, (2012), 2779-2786.

POSTERS

Theoretical insights into the mechanism of oxodiperoxomolybdenum-catalysed sulphide oxidation using hydrogen peroxide.

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Work hypothesis and objective:

Green sulfoxidation is a topic of extraordinary importance due to the relevance of sulfoxides as useful intermediates in the preparation of chemically value-added compounds. A clear understanding of the reaction mechanism is necessary in order to improve their efficient usage. Even though computational chemistry is an optimal tool for studying the pathways and their energies, only a small number of theoretical studies of metal-catalysed oxidation of sulphides have been reported. In particular, for Mo-catalysed systems, DFT studies carried out by Sensato [1] and Calhorda [2] have been published.

Results:

The mechanism of the oxidation of organic sulphides using H_2O_2, catalysed by $[Mo(O)(O_2)_2(L)]$ complexes (L = 3-methylpyrazol, 3,5-dimethylpyrazol, and H_2O), was investigated by DFT calculations. A Sharpless type outer-sphere mechanism was considered as the most probable pathway, although the viability of a Thiel type mechanism was also analysed. The highest barrier of the catalytic profile, following a Sharpless mechanism, was the oxo-transfer step. In order to yield the sulfoxide product and the starting catalytic species, the oxidation of the resulting dioxoperoxo species with H_2O_2 was found to be the most favourable pathway, under catalytic conditions. Subsequently, the sulfoxide to sulfone oxidation was produced in a completely similar mechanism with the $[Mo(O)(O_2)_2(L)]$ catalyst, showing equivalent characteristics to the first oxidation process. Small energy differences in comparison with the first oxidation were computed in this second oxo-transfer step, which was in agreement with the experimental formation of the sulfone product in the reaction with an excess of oxidant. The experimental characterization of several octamolybdates in the stoichiometric reaction between dimethylsulfoxide and $[Mo(O)(O_2)_2(L)_2]$, in water, was indirect proof of the formation of the proposed intermediates.

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Towards Intermolecular Gold(I)-Catalyzed Cross-Couplings

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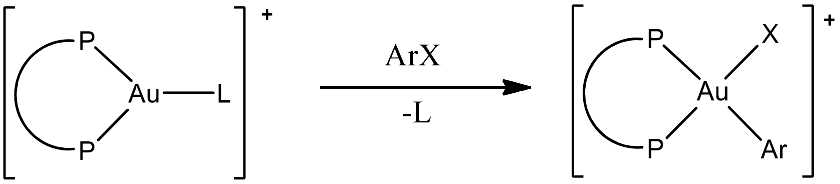
Cross-coupling reactions of C_{sp2} electrophiles (aryl and alkenyl halides) catalyzed by gold(I) are unknown.[1] Oxidative addition, which is a key step for these transformations, is not a facile process with gold(I) complexes. Interestingly, σ(Si-Si) or C_{sp3}-halide bonds undergo oxidative addition to gold(I).[2] The oxidative addition of C_{sp2}-halide bonds to gold(I) usually requires a high energy of activation,[3] and has only been achieved in an intramolecular fashion using specific systems which can form a phosphine chelate.[4] In the context of cross-coupling reactions catalyzed by gold, the intermolecular version could play an important role. We have decided to explore the synthesis of gold(I) complexes with distorted trigonal planar geometry that, according to DFT calculations, could favor the formation of a square planar gold(III) complexes by an oxidative addition.



Several bidentate phosphines, such as MeDuphos, PrDuphos and Xantphos, have been examined in order to obtain a distorted trigonal planar geometry around the gold atom.

Acknowledgments: We thank MICINN (project CTQ2010-16088/BQU), the European Research Council (Advanced Grant No. 321066), and the ICIQ Foundation for financial support.

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Organocatalytic diboration of mixed diboron reagent.

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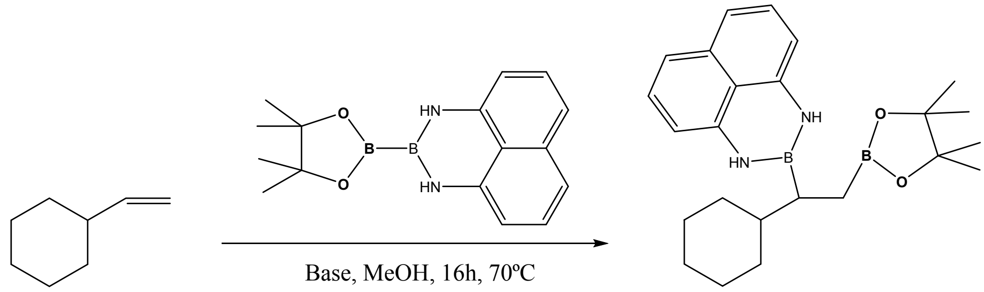
Work hypothesis and objective:

Efficient organocatalytic diboration reactions of alkenes have received much attention and are valuable synthetic methods for the preparation of organoborane intermediates. The activation of symmetrical diboron reagents in the absence of metals have already been demonstrated recently,[1] by the aid of alkoxide groups.

The aim of this organocatalytic study is to explore the diboration reaction of alkenes with Bpin-Bdan (pin: pinacolato, dan: naphthalene-1,8-diaminato) reagent in the presence of Lewis base and methanol. It was previously reported, in our group, the plausible mechanism in which methoxide is able to activate mixed diboron Bpin-Bdan reagent being able to transfer both the Bdan boryl unit to α,β-unsaturated carbonyl compounds.[2]

Results:

The last experimental results show that the excess of MeOH favours the MeO^- anion formation which quaternizes the Bpin moiety and provides the Lewis-acid $[BdanBpin{\cdot}MeO]^-$ adduct that is responsible for the catalysis. Further computational studies support this result.



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Selective oxidation of sulphides with H_2O_2 using oxodiperoxomolybdenum species immobilized on supported ionic-liquid-phase (SILP) as catalyst.

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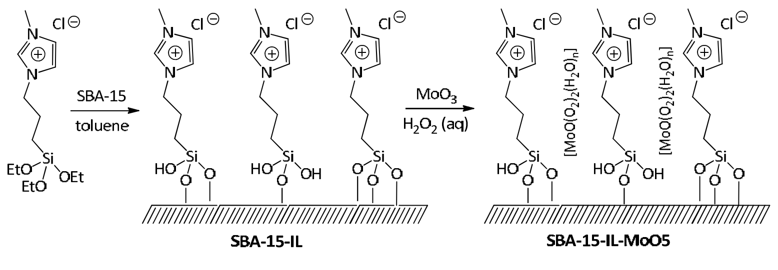
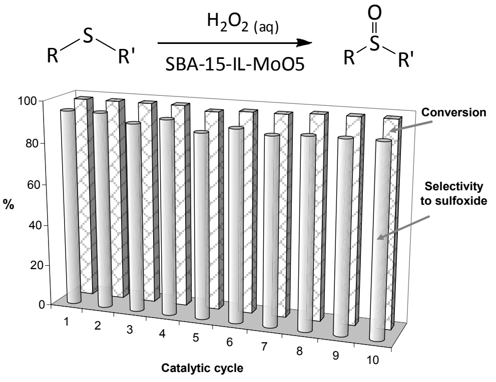
Work hypothesis and objective:

There is an increasing requirement for selective and environmentally-benign synthetic methods for the oxidation of sulphides to sulfoxides, due to their importance as synthetic intermediates. Significant drawbacks include: (i) the nature of the catalyst, namely the fact that its complicated syntheses and/or its metal price often leads to processes being expensive; (ii) the overoxidation to sulfones is frequently difficult to prevent; and (iii) recycling the catalyst is difficult. The knowledge that has been acquired with regard to oxodiperoxomolybdenum complexes and their activity in olefin epoxidation with hydrogen peroxide in ionic liquids (ILs) [1], prompted us to extend its use as catalysts in the oxidation of sulphides.

Results:

The oxodiperoxomolybdenum complex, $[Mo(O)(O_2)_2(H_2O)_n]$, was immobilized on a supported ionic-liquid-phase (SILP), in which the imidazolium IL is covalently anchored to a mesoporous SBA-15 silica. The resulting catalyst was tested in the oxidation of methylphenylsulphide, as model reaction, using hydrogen peroxide in order to select the best reaction conditions. The activity was very good (conversion of 95 % after 1h at 25 ºC) with a high selectivity towards sulfoxide (98 %). The results obtained for other sulphide substrates and the catalyst recycling will be discussed in this communication.





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P05

Reacción del complejo insaturado $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ con óxido nítrico

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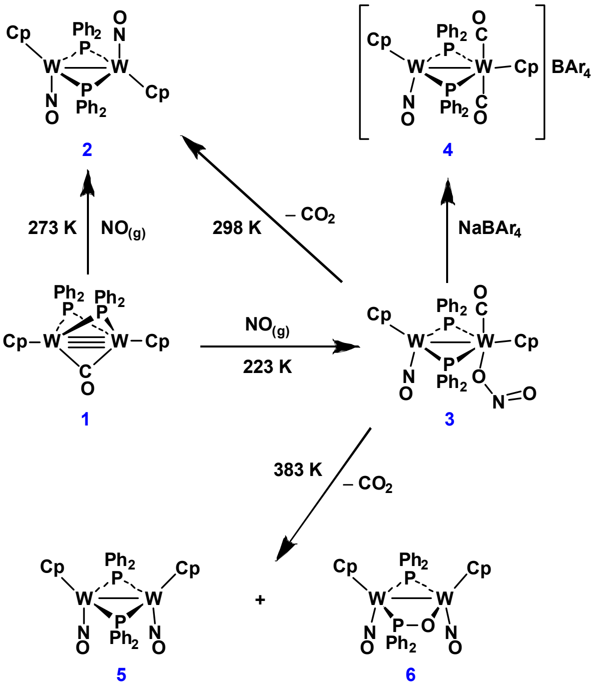
Antedentes y Objetivos:

Los procesos de escisión del enlace N-O de ligandos nitrosilo resultan de interés para el desarrollo de nuevos catalizadores para la descomposición o reducción de óxidos de nitrógeno. Recientemente, nuestro grupo de investigación descubrió que los aniones insaturados $[M_2Cp_2(\mu\text{-}PR_2)_2(\mu\text{-}CO)]^-$ (R = Ph, M = Mo;[1] R = Cy, M = Mo, W)[2] eran capaces de promover la ruptura a bajas temperaturas del enlace N-O en ligandos nitrosilo coordinados. Con estos precedentes, se decidió estudiar el potencial del compuesto isoelectrónico de wolframio $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ en los procesos de activación de enlaces N-O a través de sus reacciones con monóxido de nitrógeno.

Resultados:



La reacción del monocarbonilo $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ con NO da lugar a la formación de dos productos diferentes, el complejo trans-$[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$ o el complejo nitrito $[W_2Cp_2(\mu\text{-}PPh_2)_2(ONO)(CO)(NO)]$, dependiendo de las condiciones experimentales. Este último compuesto tiene un ligando nitrito que se puede desplazar con facilidad mediante reacción con $NaBAr_4$, lo que genera el complejo dicarbonilo $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2(NO)]BAr_4$ como único producto (Ar = 3,5-$C_6H_3(CF_3)_2$). La evolución térmica de este complejo, en cambio, supone la transferencia de oxígeno desde el ligando nitrito al monóxido de carbono o a un ligando fosfuro, dependiendo de las condiciones experimentales, para dar derivados dinitrosilo con puentes fosfuro o fosfinito.[3]

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[2] M. A. Álvarez, M. E. García, M. A. Ruiz, A. Toyos, M. F. Vega, *Inorg. Chem.* **2013**, *52*, 3942.

[3] M. A. Álvarez, M. E. García, D. García-Vivó, S. Melón, M. A. Ruiz, A. Toyos, *Inorg. Chem.* **2014**, (DOI: 10.1021/ic500498k).

P06

Pd-Catalyzed Double and Monocarbonylation of Aryl Iodides. Insights into the Mechanism and the Selectivity.

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Work hypothesis and objective: Our goals were to characterise the catalytic cycle for the first efficient phosphine-free Pd catalytic system for double carbonylation of aryl iodides,[1] where DBU is the ligand, to determine the role of the base, and to identify the factors that favour the origin of the monocarbonilation:dicarbonilation selectivity. We have studied three different substrates iodobenzene, (p-OMe)iodobenzene and (p-CN)iodobenzene, because their selectivity ratios are 76:24, 98:2 and 1:99, respectively.

Results: The mechanism was elucidated with full agreement with experimental results. The process consists of: i) oxidative addition of aryl iodide to the Pd(0) **1a‘** to form the Pd(II) **2a**, ii) migration of the aryl group on the CO to produce Pd-acyl **3a**, iii) replacement of a DBU by a CO to yield **4a**, iv) DBU-assisted attack of amine at a terminal CO to form the Pd-acyl-amide species **5a**, and v) reductive elimination of the amide and acyl ligands to yield the α-ketoamide and restore the catalyst (Figure 1). The monocarbonylation reaction can take place when the acyl ligand is not deactivated enough. In such cases, the CO and the acyl ligand compete for the amine and end the reaction before the second carbon-carbon bond is formed. In contrast, for substrates with electron withdrawing substituents (i.e. *p*-cyano), the aryl migration to the CO ligand becomes slower, allowing the amine base-assisted attack to CO early in the cycle.

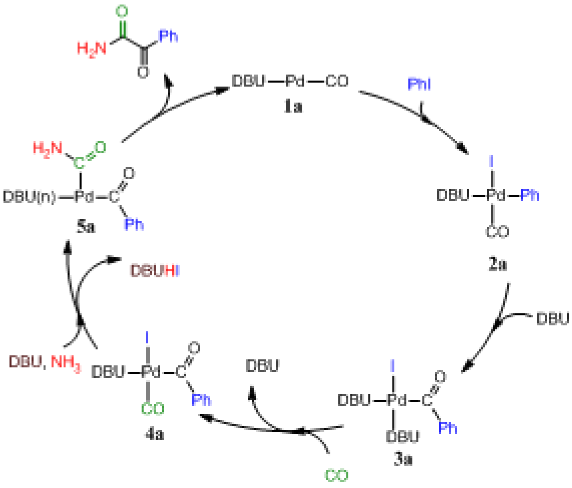

Figure 1. Scheme of the calculated mechanism.

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Síntesis y reactividad de complejos ciclopentadienílicos con enlaces triples M≡W

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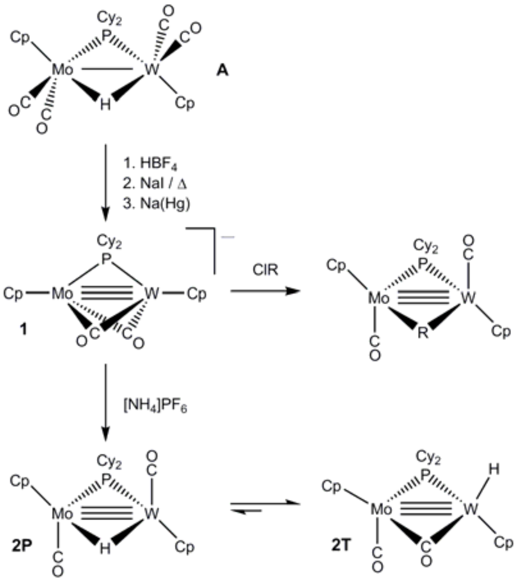
Origen y Objetivos del Trabajo:

Recientemente nuestro grupo de investigación ha desarrollado vías sintéticas eficaces para la preparación de los complejos $[M_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ y $[M_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2]$ (M = Mo, W).[1] Estudios de reactividad de estas especies demostraron que la presencia conjunta de un enlace M≡M y de una carga negativa o un ligando hidruro, respectivamente, les confiere una gran versatilidad química, convirtiéndose en intermedios sintéticos clave en la preparación de nuevos compuestos insaturados con diversas funcionalidades (p.e. alquilos, carbinos, etc.).[2] Como extensión natural de estos estudios, en este trabajo nos planteamos la síntesis y el estudio de reactividad de los correspondientes complejos heterometálicos $[MoWCp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ (**1**) y $[MoWCp_2(H)(\mu\text{-}PCy_2)(CO)_2]$ (**2**). Ello nos ha permitido establecer que la presencia de dos metales diferentes tiene un efecto sustancial sobre la reactividad y estructura de esta familia de compuestos.

Resultados:

La ruta sintética empleada para preparar los compuestos **1** y **2** es similar a la desarrollada para los compuestos homólogos de W.[1b] Así, el complejo hidruro saturado $[MoWCp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (**A**) se transforma en el anión insaturado **1** en un proceso en tres etapas de reacción [protonación, adición de I^- y reducción con Na(Hg)]. La posterior protonación del compuesto **1** con $[NH_4]PF_6$ da lugar al hidruro insaturado **2**, que en disolución está presente como una mezcla de dos isómeros (**2P** y **2T**). A su vez, el anión **1** permite la preparación de distintos complejos alquilo, $[MoWCp_2(\mu\text{-}R)(\mu\text{-}PCy_2)(CO)_2]$, por reacción con diferentes electrófilos hidrocarbonados. Finalmente, también se discutirán algunas reacciones del hidruro **2** que ponen de manifiesto su elevada reactividad frente a diferentes tipos de moléculas.



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Novel Dimerization of Maleic Anhydride Induced by a Strongly Nucleophilic Phosphinidene Mo_2 Complex.

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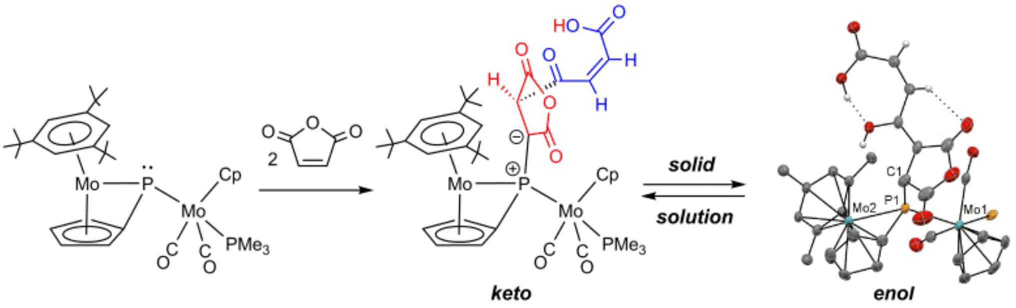
Work hypothesis and objective:

Maleic anhydride (MA) is a highly functionalized molecule used in nearly every sector of chemical industry. However, no studies appear to have been reported on the reactions of MA or related molecules with the particular family of P-donor species represented by the phosphinidene (PR) metal complexes, which is surprising, since the latter complexes are known to react with alkenes and carbonyl compounds.[1] Related reactions previously reported are limited to the trapping of a transient diradical diphosphinidene complex with MA, a process involving the carbonyl group of the latter.[2] We have now examined the reactions of MA and related species with the novel phosphinidene complex $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2(PMe_3)]$ (**1**), a molecule displaying a strongly nucleophilic character (Mes* = 2,4,6-$C_6H_2{}^tBu_3$).

Results:

Complex **1** is readily obtained from the reaction of PMe_3 with $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$, and its basicity is proven by its rapid reaction with $BH_3{\cdot}THF$ to give the borane adduct $[Mo_2Cp\{\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}(BH_3)PC_5H_4\}(\eta^6\text{-}HMes^*)(CO)_2(PMe_3)]$. Its reaction with MA gives the phosphinidenium-ylide $[Mo_2Cp\{\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}(C_8H_4O_6)PC_5H_4\}\text{-}(\eta^6\text{-}HMes^*)(CO)_2(PMe_3)]$, an unusual complex derived from a novel dimerization of MA involving olefinic to carbonyl C–C coupling and an [1,7]-H shift, to yield a carbene which is stabilized by coordination of the P atom. The carbene moiety undergoes reversible *keto* to *enol* tautomerization from solution to the solid state, a rearrangement accompanied by a strong pyramidalization of the ylidic carbon atom.



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Covalent immobilization of Pd-NHC complexes onto various inorganic supports; activity and reusability in a range of C-C coupling reactions.

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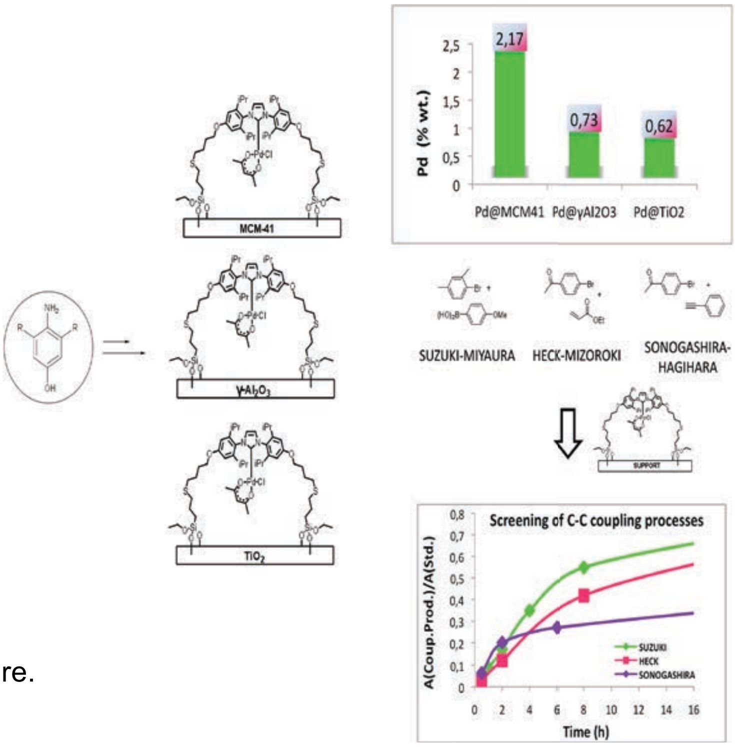
Work hypothesis and objective:

Recent reports have described the successful use of *para*-alkoxy-functionalised N-heterocyclic carbenes as ligands in Pd-catalyzed cross-coupling reactions.[1,2] In this work we describe a very general and straightforward procedure for the attachment of Pd-NHC complexes onto the surface of MCM-41, γ-Al_2O_3 and TiO_2.

Results:

Alkoxy functionalization at the aryl *para* positions of the imidazolium preligands is used as a handle to introduce triethoxysilyl groups, suitable for condensation with hydroxyl groups present on the surface of the inorganic solids. Characterization of the solid-supported Pd complexes of these ligands was followed by the study of their catalytic performance in Suzuki-Miyaura, Heck and Sonogashira couplings.
Recyclability studies are also presented here.



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Terminal-Phosphanido Rhodium Complexes

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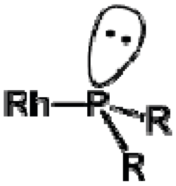
Work hypothesis and objective:

Complexes with a terminal phosphanido (M–PR_2) functionality bound to a single late transition metal center have been proposed as intermediates in relevant processes such as dehydrocoupling[1] and hydrophosphanation[2] reactions. From a mechanistic point of view, both, outer- and inner-sphere mechanisms have been considered. Nonetheless, the most widely established pathway involves the nucleophilic attack of the phosphanido ligand to an uncoordinated olefin. Consequently, an in-depth understanding of the reactivity of phosphanido ligands may aid in the development of the above mentioned and new catalytic transformations.

Results:

We will showcase reactions that give isolable rhodium complexes with a terminal phosphanido ligand, which result from the oxidative-addition of the P–H bond in secondary phosphanes to rhodium. Such type of complexes has been spectroscopically detected in very few instances, but there are not isolated examples up to date, despite the key role of this activation reaction in dehydrocoupling and hydrophosphanation processes. Moreover, we have found that the nucleophilicity of the phosphanide ligand promotes the formation of P–C bonds with activated substrates, which results in effective catalytic hydrophospanation reactions. In addition, we will describe catalytic dehydrocoupling of secondary phosphanes in the presence of ethylene as hydrogen acceptor and the X-ray structure of the resting state of the catalyst. We will also discuss the formation of an unusual rhodaphosphetane under stoichiometric conditions, which involves an alternative mechanism for P–C bond formation.



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P11

Copper-catalyzed *ortho*-C̃H functionalization of protected anilines

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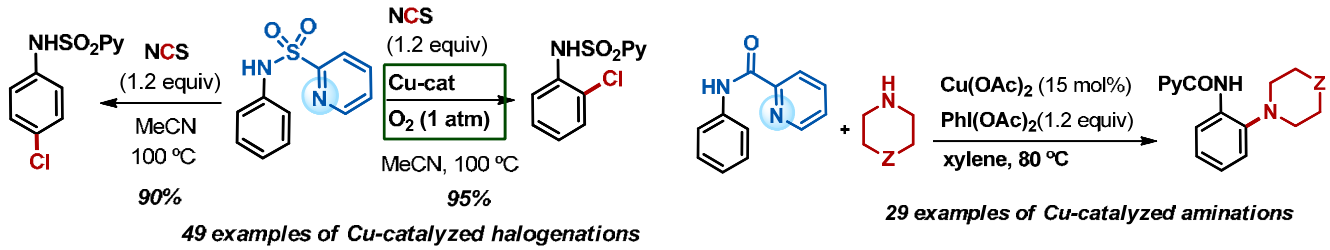
The direct functionalization of C̃H bonds using an inexpensive, low-toxic metal catalyst such as Cu is emerging as a cutting edge field of synthetic organic chemistry due to its attractiveness from a green and sustainable chemistry perspective.[1] In this context, our group has recently reported *a practical protocol for the ortho-halogenation of aniline derivatives that combines Cu-catalysis and the use of molecular oxygen as terminal oxidant*.[2] This method relies on a readily removable *N*-sulfonyl directing group and displays high regio- and mono-halogenation selectivity, as well as excellent functional group tolerance, especially to halogen substituents.

Likewise, we have also developed a *regioselective Cu-catalyzed ortho-C–H amination process assisted by a removable N-COPy group that provides a straightforward means for the preparation of ortho-aminoaniline derivatives*.[3] This direct cross-dehydrogenative coupling between arenes and R_2NH represents an appealing approach that complements standard procedures for *N*-aryl bond formation relying on pre-activated substrates



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[1] For reviews, see: (a) Wendlandt, A. E.; Suess, A. M.; Stahl, S. S. *Angew. Chem. Int. Ed.* **2011**, *50*, 11062; (b) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R.; Kozlowski, M. C. *Chem. Rev*. **2013**, *113*, 6234.

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P12

Designing Ru(IV) catalysts for the selective hydration of nitriles to amides under mild aqueous conditions.

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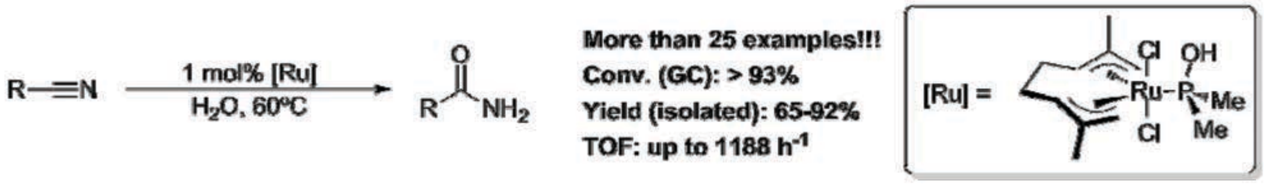
Amides constitute one of the most employed building blocks in synthetic organic chemistry, and can be found as raw materials in a variety of industrial processes for the large-scale manufacture of polymers, detergents and lubricants. Many drugs and biologically active molecules also contain such functional group. Accordingly, the preparation of amides is of high current interest. During the last years metal-catalyzed hydration of nitriles has emerged as one of the most promising tools for the synthesis of primary amides with atom economy.[1]

In this context, ruthenium has proved to be an excellent choice regarding the development of new active catalysts for such transformation in aqueous media, and many examples can be found in literature so far.[2] Tyler and co-workers recently reported the outstanding catalytic activity of a new Ru(II) catalyst bearing the phosphinous acid PMe_2OH as ligand.[3] This ligand, which is also found in the structure of the well-known Parkin's hydration catalyst $[PtH\{(PMe_2O)_2H\}(PMe_2OH)]$,[4] seems to facilitate the hydration of the metal-coordinated nitrile through the activation of the nucleophilic water molecule by H-bonding with the OH group (bifunctional catalysis).

In this contribution, we present the synthesis of a new Ru(IV) catalyst based on PMe_2OH able to promote the selective hydration of nitriles to amides in water, at low metal loadings, and under mild reaction conditions (see Scheme 1).



Scheme 1: Hydration of nitriles catalyzed by a Ru(IV) catalyst in water under mild conditions.

[1] García-Álvarez, R., Crochet, P., Cadierno, V. *Green Chem*. **2013**, *15*, 46-66, and references therein.

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Polycarbonates and cyclic carbonates by Mn(III) haloporphyrines-catalysed coupling of CO_2/epoxides

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Rua Larga 3004-535 Coimbra (Portugal)

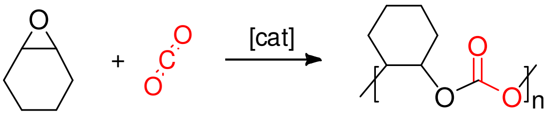
Work hypothesis and objective:

Organic carbonates and polycarbonates are valuable compounds due to their wide applications in many industrial areas [1]. An environmental benign route to carbonates is the reaction of epoxides with carbon dioxide (Scheme 1) as an inexpensive, widely available, non-toxic and renewable carbon source [2]. Inoue and col. discovered that Mn-porphyrinate complexes, without any co-catalyst, are active for the copolymerisation of cyclohexene oxide (CHO) with carbon dioxide [3].

We thought that the introduction of electron withdrawing groups, such as halides, in the porphyrin backbone may increase the Lewis acidity of the catalyst, favoring the opening of the epoxide, and providing more active catalysts. Thus, Mn-porphyrinate complexes with halide substituents (**1** and **2**, Figure 1) were prepared and its catalytic activity in the CO_2/epoxide coupling was checked.

Results:

Complex **1** is highly active in the copolymerization of CHO/CO_2 employing a very low catalyst loading at 80 ºC under 50 atm (84 % conversion at 0.036 molar % catalyst, TOF 90 h^{-1}). The introduction of several halide atoms may be the responsible for the improved activity in respect to the non-substituted system (**3**, Figure 1). Complex **1** was also supported in carbon nanotubes (**4**, Figure 1) and recycling experiments were also performed. Acyclic epoxides afforded selectively the cyclic carbonates in good to high yields.



Scheme 1

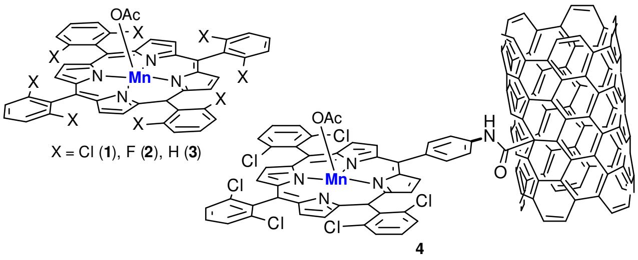


Figure 1

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Hydroformylation as central tool for sustainable sequential reactions under microwave irradiation

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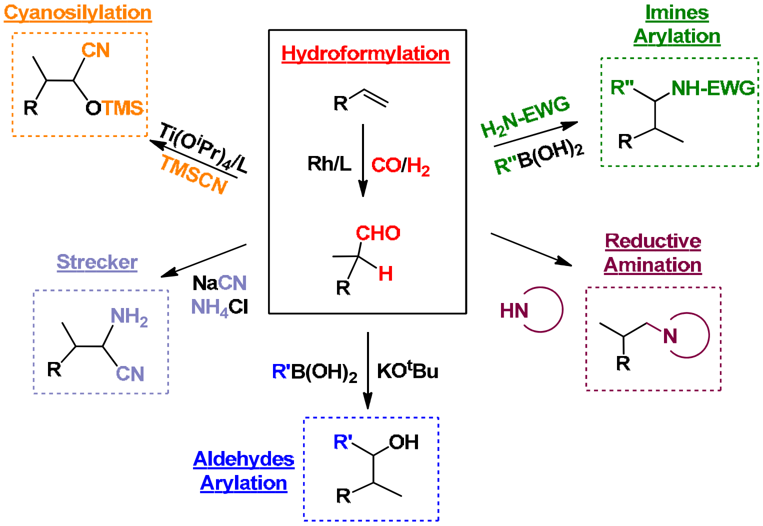
Work hypothesis and objective:

Based on the growing interest of modern organic chemistry in the design of highly efficient sequential chemical reactions, which allows the maximization of structural complexity and diversity, with just a minimum number of synthetic isolated steps, hydroformylation can be considered one of the most powerful synthetic tool to be incorporated in multi-step reactions. [2]

Results:

So, in this communication we present our recent results for the implementation of rhodium catalysed hydroformylation of olefins, followed by different sequential transformations,namely hydroformylation/aldehyde arylation, [2] - imine arylation; cyanosilylation, reductive amination and -Strecker reaction (Figure 1).



FFigure 1: Sequential reactions involving hydroformylation

Acknowledgements: The authors thank for financial support to Programa Compete and QREN/FEDER/FCT (PTDC/QUI-QUI/112913/2009). A.R. Almeida also thanks to FCT for PhD grant SFRH/BD/73190/2010.

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Phosphoroamidite-oxazoline/thiazole ligands for enantioselective Ir-catalyzed hydrogenation of unfunctionalized olefins.

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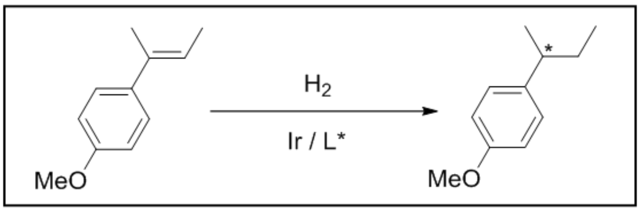
Work hypothesis and objective:

The asymmetric hydrogenation of olefins is one of the most powerful transformations for preparing chiral compounds. Whereas the reduction of olefins containing an adjacent polar group has been successfully achieved, the hydrogenation of unfunctionalized olefins is less developed and the search for more efficient ligands is still needed.[1] Our group found that the introduction of π-acceptor moieties in ligands is highly advantageous.[2] So having this in mind, herein a set of new phosphoroamidite-oxazoline/thiazole ligands has been designed to the title reaction (Scheme 1).



Scheme 1. Asymmetric Ir-catalyzed hydrogenation of unfuctionalized olefins.

Results:

Excellent ligands have been identified for a range of substrates providing enantioselectivities comparable to the best one reported in the literature.[1] A simple quadrant model has also been elaborated to rationalize the hydrogenation results.

[1] See, for example: a) X. Cui, K. Burgess, *Chem. Rev.* **2005**, *105*, 3272; b) S. J. Roseblade, A. Pfaltz, *Acc. Chem. Res.* **2007**, *40*, 1402; c) T. L. Church, P. G. Andersson, *Coord. Chem. Rev.* **2008**, *252*, 513; d) O. Pàmies, P. G. Andersson, M. Diéguez, *Chem. Eur. J.* **2010**, *16*, 14232; e) D. H. Woodmansee, A. Pfaltz, *Chem. Commun.* **2011**, *47*, 7912; f) Y. Zhu, K. Burgess, *Acc. Chem. Res.* **2012**, *45*, 1623.

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Rhodium catalysed hydroformylation reaction under microwave irradiation

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Rui. M. Carrilho, Gonçalo N. Costa[1] Lucas D. Dias,[2] and
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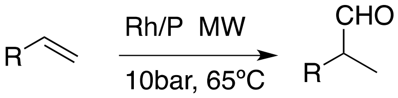
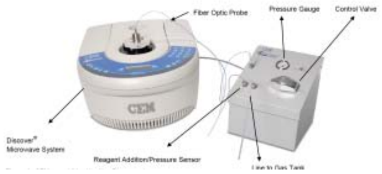
Work hypothesis and objective:

Rhodium catalysed hydroformylation of alkenes is one of the most powerful methods to transform, in just one step, a carbon-carbon double bond into an aldehyde with an extra carbon atom.[1] There are in the literature just few examples of the use of microwave irradiation in hydroformylation reactions. [2] In this work we intend to join the atom efficiency of hydroformylation with the energy economy of microwave irradiation to increase the sustainability of these type of processes.

Results:

In this communication we present a pioneer work to promote the optimization of hydroformylation reactions of aryl and long chain alkyl olefins using Rh/P as catalysts and microwave irradiation. The experiments were carried out on a 10 mL microwave vessel charge with CO and H_2, We study the effect of the solvent, temperature and irradiation power on the activity and selectivity of rhodium catalysed hydrofromylation of olefins, observing a significant effect of time irradiation and temperature on the activity and selectivity.
We conclude that under microwave irradiation the solvent and irradiation power are crucial issues to be considered.





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Synthesis of new NHC-based ligands with pyrene tags for the generation of Pd (II) complexes. Study of their catalytic aplications

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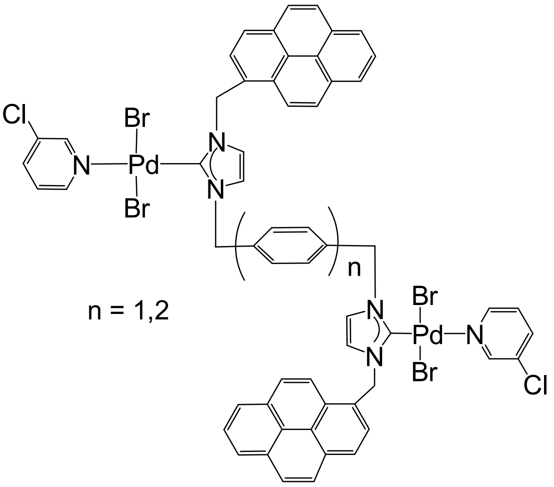
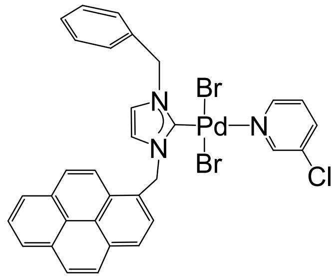
Work hypothesis and objective:

The synthesis of new ligands that can do more as contribute as spectator ligands, have demonstrated to be a promising tool in a wide range of applications, including homogeneous catalysis. We have recently shown that NHC-based ligands containing rigid polyaromatic systems have provided significant benefits in the activity of their related homogenous catalysts.[1] Also we have been very interested in comparing the activities of polymetallic catalysts with the ones provided by their monometallic analogues.

Results

Based on this finding, we now describe the synthesis of three pyrene-containing NHCs and their coordination to palladium. The catalytic properties of these complexes have been compared toward the Suzuki-Miyaura coupling and the acylation of aryl halides with aldehydes.





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Selevtividad en las reacciones de formación de acilcomplejos de rodio (III) con diaminas alifáticas

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Hipótesis de trabajo y objetivos:

Los complejos organometálicos de rodio que contienen ligandos fosforados o nitrogenados pueden desempeñar un importante papel en la transformación de muchos compuestos orgánicos [1]. La síntesis estereoselectiva de este tipo de complejos puede facilitar el diseño de sistemas catalíticos regio y/o enantioselectivos [2]. Se pretende sintetizar selectivamente complejos de Rh(III) que contengan un ligando P-acilo y una diamina alifática.

Resultados:

La reacción del acilcomplejo $[Rh(H)Cl(PPh_2(o\text{-}C_6H_4CO))(piridina)_2]$ (**1**) con diaminas alifáticas (NN') conduce a la formación de los derivados $[Rh(H)(Cl)(PPh_2(o\text{-}C_6H_4CO))(N,N')]$ con elevada estereoselectividad dependiendo de la diamina empleada. Con N,N'-dimetil- o N,N'-difeniletilendiamina se obtiene un único isómero, que evoluciona, en diclorometano o cloroformo, por intercambio del hidruro por un cloro del disolvente, originando el correspondiente compuesto $[Rh(Cl)_2(PPh_2(o\text{-}C_6H_4CO))(N,N')]$. Con las diaminas N,N,N'-trimetil- y N,N,N',N'-tetrametiletilendiamina, la primera reacción origina una mezcla de dos isómeros de los correspondientes hidrurocomplejos, que muestran menor tendencia al intercambio de hidruro por cloro. Con derivados de etilendiamina que poseen algún grupo amino primario no es posible aislar los hidrurocomplejos análogos. Así con N-metiletilendiamina o 1,2-difeniletilendiamina se obtienen dos isómeros de los correspondientes diclorocomplejos. El ligando N,N-dimetiletilendiamina (N,N-Me_2-en), con un grupo amino disustituido y otro primario, presenta un comportamiento especial. La reacción de este ligando con **1** en presencia de ácido tetrafluorobórico conduce a la obtención del dímero catiónico $[Rh_2(\mu\text{-}Cl)(Cl)_2(PPh_2(o\text{-}C_6H_4CO))_2(N,N\text{-}Me_2\text{-}en)_2]BF_4$.

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Hydroxymethylpyridine Containing Half-sandwich Complexes of Rh(III), Ir(III) or Ru(II)

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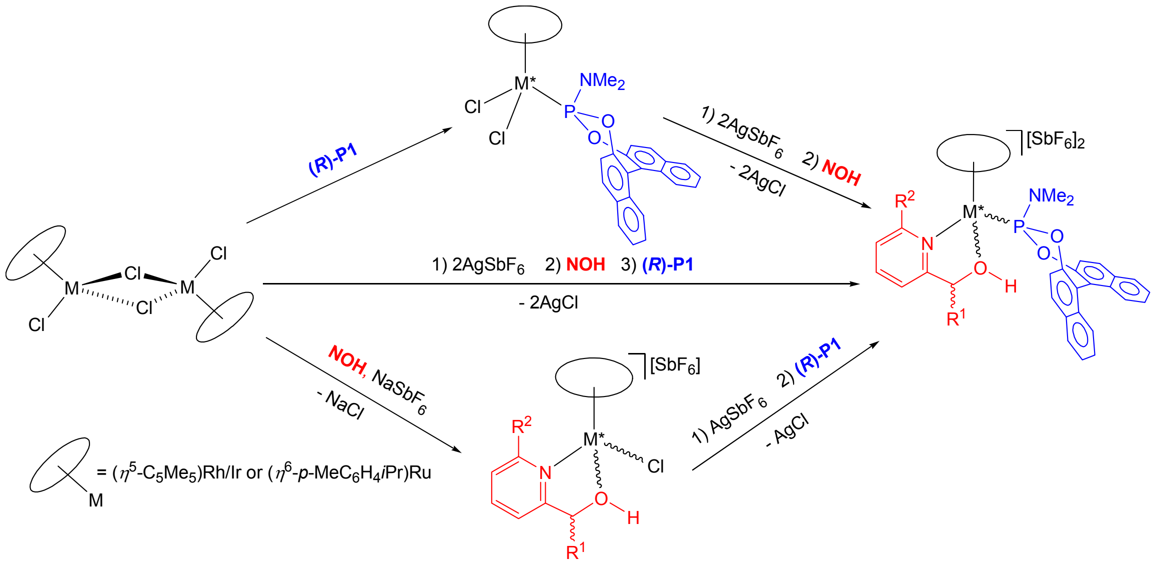
Work hypothesis and objective: Recently, we have reported that water[1a] or a ligand with an OH functionality[1b] coordinated to a metallic fragment can act as a Brønsted acid electrophile activator for Diels-Alder[1b] and Friedel-Crafts[1] reactions. Our aim is to prepare chiral complexes containing hydroxymethylpyridine ligands. We anticipate that they would be adequate candidates to act as asymmetric Brønsted acid catalysts.

Results: Complexes of formula $[(\eta^n\text{-ring})M(\mathbf{NOH})\{(\boldsymbol{R})\mathbf{\text{-}P1}\}][SbF_6]_2$ containing an OH functionality coordinated to a metallic cation have been prepared following three different routes (Scheme). The preparative reactions are highly diastereoselective. The absolute configuration of the new complexes has been determined by NMR spectroscopy and diffractometric studies. In spite of the expected enhancement of the acidity of the hydroxypyridine OH group, the hydroxyl proton remains bonded to the oxygen atom when coordinated to the metal.



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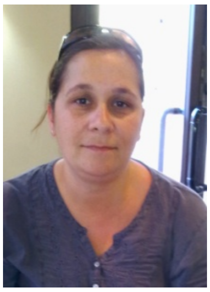
Selective Catalytic Deuterium Labelling of Alcohols and amines during a Transfer Hydrogenation Process of Ketones or Imines Using D_2O as Deuterium Source.



M. Carmen Carrión,[a,b] **Margarita Ruiz-Castañeda,**[a] **Lucía Santos,**[c] **Ana M. Rodríguez,**[d] **Blanca R. Manzano,**[a] **Félix A. Jalón**[a] **and Agustí Lledós.**[e]

[a]Departamento de Química Inorgánica, Orgánica y Bioquímica, [c]Dpto. de Química-Física. UCLM. Fac. de Ciencias y Tecnologías Químicas-IRICA, Avda. C. J. Cela, 10, 13071 Ciudad Real, Spain. [b]Fundación PCYTA, Paseo de la innovación, 1, 02006 Albacete, Spain. [d]E.T.S. Ing. Industriales, UCLM. [e]Departament de Química, Univ. Autònoma de Barcelona, Edifici Cn, 08193 Cerdanyola del Vallés, Spain.

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Work hypothesis and objective:

Increasing interest in chemical research has been focused on the development of methodologies for the selective preparation of deuterium-labelled molecules and biomolecules, with a wide range of applications. α-Deuterated alcohols can be obtained by reduction of aldehydes or ketones in stoichiometric reactions with deuterated reagents, or by means of catalytic procedures that may involve either a reduction or a CH/D exchange between alcohols and an appropriate deuterium source. Similarly, deuterated amines could be catalytically obtained from imines.

Results:

The new complex [(η^6-*p*-cym)RuCl(κ^2-N,N-dmbpy)](BF_4) is water-soluble and active in the catalytic transfer hydrogenation (TH) of different ketones to the corresponding alcohols using aqueous HCOONa/HCOOH as the hydrogen source at pH 4.4. When the catalytic reaction was carried out in D_2O, selective deuteration at the Cα of the alcohols was observed due to a rapid Ru−H/D$^+$ exchange, which was also deduced theoretically. Imines were hydrogenated in the same conditions, but negligible deuterium labelling was observed, possibly due to the high activity in the TH process.[1] However, deuteration was achieved in different experimental conditions.

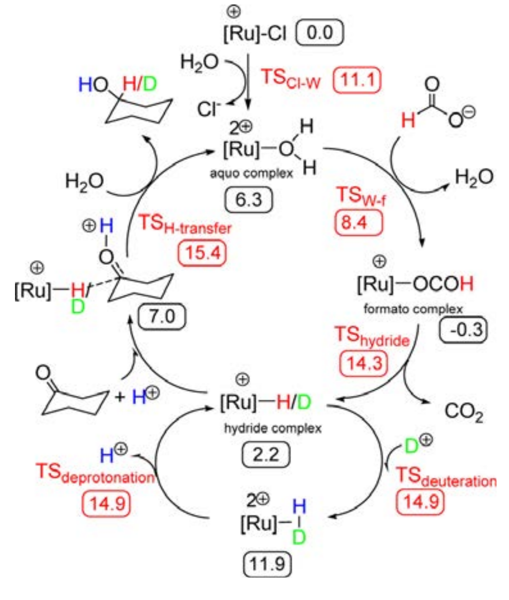

Fig. 1. Mechanism of the Coupled TH/Deuteration Catalytic Cycle.

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Deep Eutectic Solvents as New Green and Biorenewable Reaction Media for Au(I)-Catalyzed Cycloisomerization of (*Z*)-Enynols into Furans

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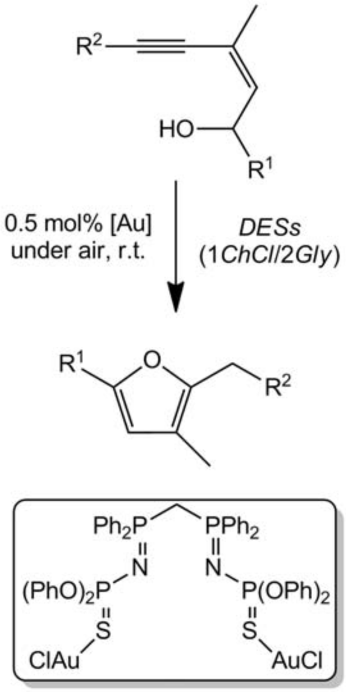
Work hypothesis and objective:

Despite that the problems associated with conventional volatile organic solvents (*VOCs*) are well established, the use of green and biorenewable solvents still remains a lasting challenge. In this sense, the advantages of using Deep Eutectic Solvents (*DESs*) as reaction media are highlighted from the fact that they are biodegradable, non-toxic, recyclable and could be easily prepared using inexpensive raw materials [mixture of a hydrogen bond donor (*i.e.*, glycerol (*Gly*) or urea) with a simple halide salt (choline chloride, *ChCl*)] [1]. Although *DESs* have been explored in a variety of applications including metal deposition, purification of biodiesel, biotransformations and different synthetic processes, their application in metal-mediated organic reactions has been barely noticed [2].

Results:

In this communication, we will present the use of different *DESs* as green and biorenewable solvents for the Au(I)-catalyzed cycloisomerization of (*Z*)-enynols into furans, proceeding with efficiency, selectivity, atom economy, at room temperature, under air and in short reactions times. It is important to note that the catalyst could be recycled up to 10 consecutive times.



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Functionalized polynorbornenes via palladium catalyzed cross coupling reactions.

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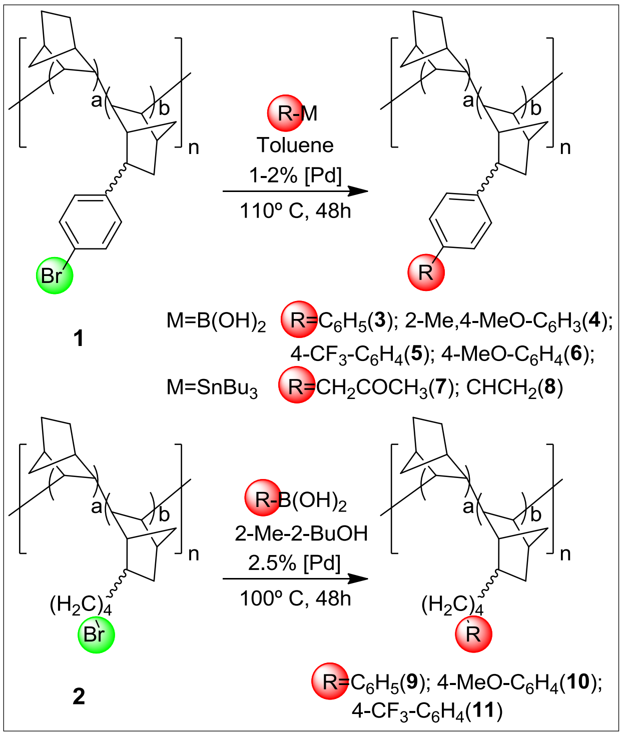
Work hypothesis and objective:

Vinylic addition polymerization of norbornene (NB) leaves the bicyclic structural unit intact. This leads to a robust material (V-PNB) with an all aliphatic backbone suitable as support of reagents or functional groups that carry out a specific property. The vinylic addition polymerization of functionalized norbornenes is difficult to achieve and most catalytic systems fail to do so. We devised a different route to synthesized these materials by direct vinylic polymerization of bromoalkylnorbornenes followed by reaction with nucleophiles.[1] We report here the synthesis of unprecedented bromoaryl V-PNBs and the subsequent functionalization of these polymers and also the bromoalkyl V-PNBs using palladium-catalyzed cross coupling reactions.

Results:

Polymer **1** was synthesized by copolymerization of NB and NB-C_6H_4Br catalyzed by $[Ni(C_6F_5)_2(SbPh_3)_2]$. Suzuki reactions have been carried out on **1** and also on the more challenging bromoalkyl polymer **2** obtaining the substituted biaryl or aryl V-PNBs **3-6** and **9-11**. The Stille reaction allows the introduction of other groups different from aryl as shown for **7** and **8**. In all cases the bromo substitution ranges from 75 to 100%. The presence of the new groups in these polymers has been confirmed by ^{13}C NMR and IR spectroscopy. This work shows that Pd-catalyzed couplings can be applied efficiently to the functionalization of polymers of interest.



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Outer-Sphere Mechanisms for the Hydrosilylation of Terminal Alkynes

Manuel Iglesias, **Pablo J. Sanz-Miguel, Francisco J. Fernández-Álvarez, Jesús J. Pérez-Torrente and Luis A. Oro.**

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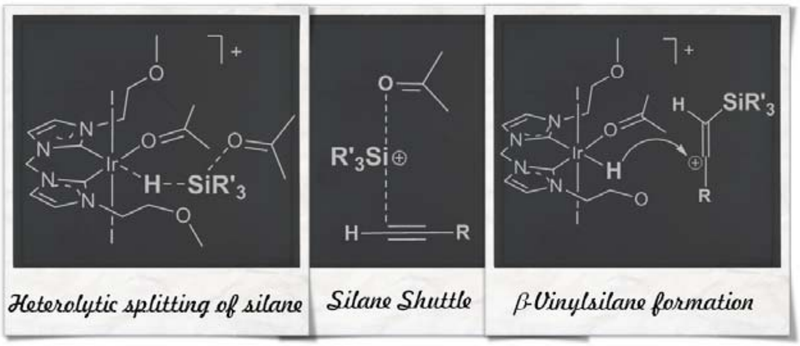
Work hypothesis and objective:

The major issue concerning the hydrosilylation of terminal alkynes arises from its selectivity, reports on selective preparation of β-(Z) and especially α-vinylsilanes being particularly scarce.[1] We aim at the selective preparation of vinylsilanes employing Rh and Ir(III) catalysts and the study of the reaction mechanisms involved.

Results:

In this presentation we show the synthetic route to rhodium and iridium(III) biscarbene complexes that selectively catalyze the hydrosilylation of terminal alkynes. Experimental data and DFT calculations strongly suggest that these catalysts operate by outer-sphere mechanisms based on the oxophilicity of the oxygen atom and the Lewis acidity of the metal center.[2] These results represent the first example of an outer-sphere mechanism for the hydrosilylation of terminal alkynes and are in agreement with studies by Brookhart on hydrosilylation of carbonyl compounds by Ir(III) catalysts.[3]



Heterolytic splitting of silane

Silane Shuttle

β-Vinylsilane formation

[1] I. Ojima, Z. Li, J. Zhu, *The Chemistry of Organic Silicon Compounds;* S. Rappoport, Y. Apeloig, Eds; Wiley: New York, 1998; Chapter 29.

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Mechanistic Insights into Rhodium- and Iridium Mediated Alkene Oxidation with O_2

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[b] Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, Oslo, Norway
[c] Departamento de Química Inorgánica, ISQCH-CSIC-Universidad de Zaragoza

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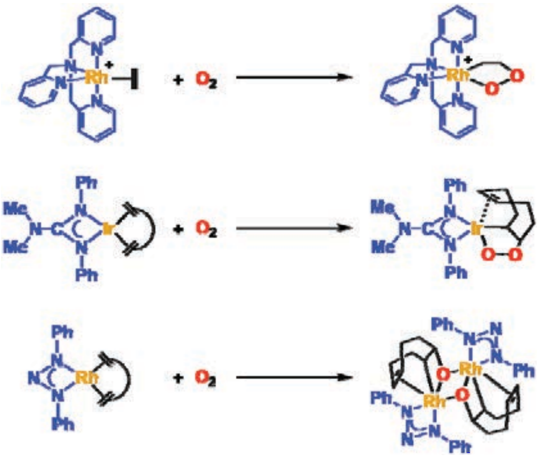
The addition of O_2 to a coordinated olefin is an effective strategy for the functionalization of organic molecules. Metal-catalyzed oxidation of olefins can give rise to a whole variety of organic products. However, the mechanistic details on how dioxygen binds to the olefin and forms the C-O bond are still not fully understood.[1] We focused on the oxidation of olefins coordinated to Rh and Ir complexes that are known to promote C-O bond formation.[2]



The computational study has revealed that the three complexes evolve through different reaction pathways, despite the similarities between them. The electronic nature of both the metal and the ligand are crucial in the coordination of O_2 and its addition to the C=C bond.

[1] L. Boisvert, K. I. Goldberg, *Acc. Chem. Res.*, **2012,** *45,* 899.

[2] **(**a) M. R. Kelley, J.-U. Rohde, *Chem. Commun*., **2012,** *48*, 2876; (b) C. Tejel, M. A. Ciriano, E. Sola, M. P. del Río, G. Ríos- Moreno, F. J. Lahoz, F. J., L. A. Oro, *Angew. Chem. Int. Ed.*, **2005,** *44,* 3267; (c) M. Krom, R. G. E. Coumans, J. M. M. Smits, A. W. Gal, *Angew. Chem. Int. Ed.*, **2001**, *113*, 2164.

Bidentate Coordination of Amidinate Germylenes and Silylenes on Carbonyl Dicobalt Complexes: The Importance of a Slight Difference in Ligand Volume

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In the last few years, new generations of cyclic heavier tetrylenes (HT), particularly silylenes and germylenes stabilized by amidinate fragments,[1] have allowed a significant advance of the HT coordination chemistry, including applications in catalysis[2]. Working with such hot-topic ligands, we have recently discovered an unprecedented coordination mode for amidinate-HTs, since the germylene Ge(*i*Pr_2bzam)(HMDS) (*i*Pr_2bzam = *N*,*N*'-bis(*iso*propyl)benzamidinate; HMDS = $N(SiMe_3)_2$), which is armed with just one accessible lone pair of electrons on the Ge atom, can be transformed into a 4-electron-donor κ^2*Ge*,*N*-ligand when treated with $[Co_2(CO)_8]$.[3]

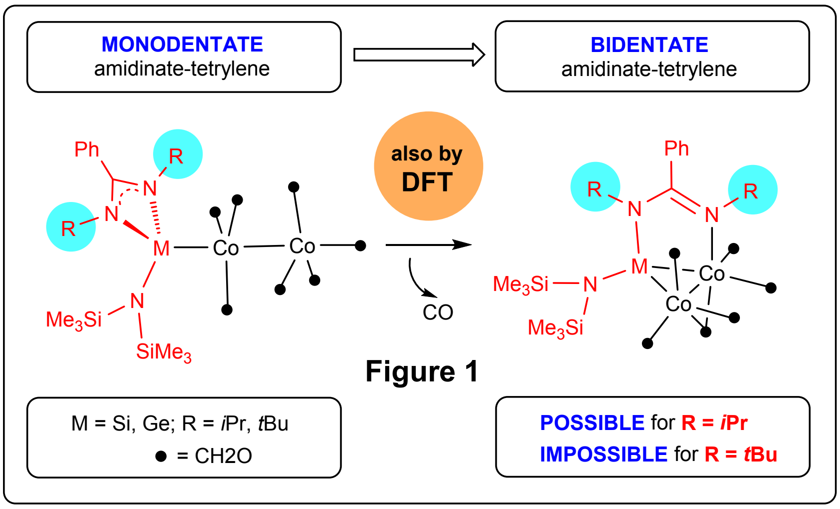

Figure 1

In this contribution, we provide experimental and DFT theoretical data that shed light on (a) the crucial importance that the volume of the amidinate N–R groups has on the terminal-to-bridging transformation of ligands of the type M(R_2bzam)(HMDS) on dicobalt complexes, (b) the mechanism of that transformation, and (c) the effect that the use of a different M atom (Si or Ge) has on the final outcome of the reactions of $[Co_2(CO)_8]$ with M(R_2bzam)(HMDS) ligands. This study has shown that such a transformation (Figure 1) is negligibly influenced by the nature of M (Si or Ge) but is strongly dependent upon the steric hindrance exerted by the amidinate N–R groups.[4]

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Amido and alkyl complexes of calcium and strontium containing highly fluorinated Tp' ligands.

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Work hypothesis and objective:

The chemistry for the heavier group 2 metals (Ae) is underdeveloped. The main challenge of this chemistry is to control the Schlenk equilibrium that scrambles the ligands in heteroleptic complexes ($2\ AeXX' = AeX_2 + AeX'_2$). Several heteroleptic complexes {L}Ae-Nu (L = β-diketiminate; tris(pyrazolyl)borates, etc.;[1] Nu = NR_2, OR) proved to be good catalysts in ROP and hydroelementation reactions. Few examples of heteroleptic alkyl complexes are known.[2]

Results:

Highly fluorinated hydrotris(indazolyl)borate proligands Tp^F with tunable electronic and steric properties have been developed in our group.[3] We describe herein our initial attempts at unravelling the chemistry of Tp^FAe complexes. The very electron poor ligand $F_{21}\text{-}Tp^{4Bo,CF3}$ failed to coordinate to Ca^{2+}, whereas adding two equiv. of $Tl(F_{12}\text{-}Tp^{4Bo,Ph})$ to CaI_2 gave the homoleptic $[(F_{12}Tp^{4Bo,Ph*})_2Ca]$ with a sterically induced 1,2-borotropic shift in the ligand.[4]
The heteroleptic amido complexes $[(F_{12}\text{-}Tp^{4Bo,Ph})AeNR_2]$ (Ae = Ca, Sr; R = $SiMe_3$, $SiMe_2H$) were synthesized. Agostic distortions, especially strong for Sr, stabilize the structures (Figure 1). $[(F_{12}\text{-}Tp^{4Bo,Ph})Ca\{N(SiMe_3)_2\}]$ is a very active catalyst for the cyclohydroamination reaction. The rare heteroleptic alkyl complexes $[(F_{12}\text{-}Tp^{4Bo,Ph})CaR]$ (R = $CH(SiMe_3)_2$, C≡CPh) have also been characterized

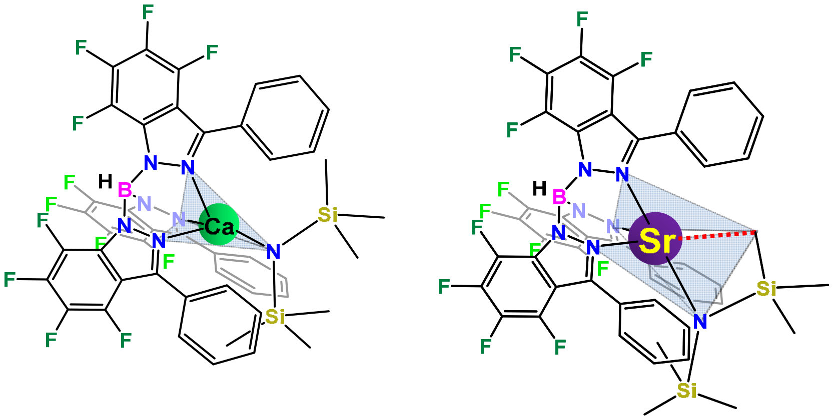

Figure 1: $[(F_{12}\text{-}Tp^{4Bo,Ph})Ae\{N(SiMe_3)_2\}]$ (Ae = Ca, Sr) complexes.

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Pd-catalysed Urea Synthesis in Ionic Liquid.

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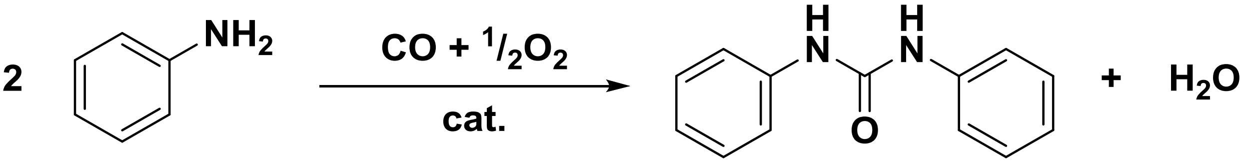
Work hypothesis and objective:
Ureas are indispensable compounds commonly found in the structures of a large number of biologically active compounds. Ureas are widely used as agrochemicals, dyes, antioxidants and HIV inhibitors, and are, furthermore key intermediates in organic synthesis.[1] Palladium catalysts are widely used for carbonylation reactions and have previously been applied for the carbonylation of amines, but the best results have been obtained at high pressure, high temperature and under an explosive gas mixture,[2] making the system unsafe. It is thus desirable to develop a system which is active under milder conditions. Ionic liquids are reported to have a beneficial effect in many reactions[3] and it is our hypothesis that, the combination of ionic liquid and a new palladium catalysts can lead to an efficient, robust, versatile catalytic system for the carbonylation of both aliphatic and aromatic amines, at low pressures and temperatures. The objective is, to find a new palladium/IL based catalytic systems that will afford the carbonylation of a wide range of amines under mild reaction conditions.



Scheme 1. Carbonylation of aniline to form diphenyl urea

Results:
We have developed a system which operates mild conditions, is fully recyclable, is 100% selective and have a TOF of 325, which is 2 orders of magnitude higher than published results obtained at comparable pressure.[4]

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Catalytic hydrodehalogenation versus C-C coupling in benzyl halides

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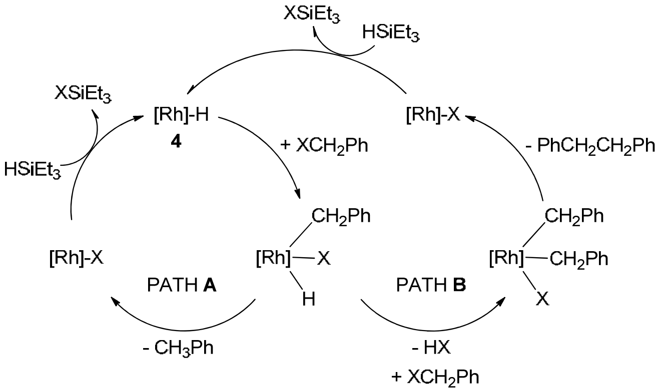
Work hypothesis and objective:

The application of hydrosilanes as hydrogen source in catalysis constitutes one of our research aims. We have recently reported that $[Rh(Cl)(COD)(R\text{-}NHC\text{-}(CH_2)_3Si(O^iPr)_3)]$ (R = 2,6-$^iPr_2Ph$ (**1a**), ^nBu (**1b**)) complexes are active hydrosilylation catalysts.[1] On the other hand, the development of effective catalytic systems for hydrodehalogenation of Csp^3-X (X = Cl, Br) bonds of organic halides is of current interest.[2] Thus, we decided to explore the potential application of our Rh-catalysts in hydrodehalogenation processes using $HSiEt_3$ as hydrogen source.

Results:

The reaction of benzyl chloride with $HSiEt_3$ in presence of species **1** (2.0 mmol %) affords toluene and $ClSiEt_3$. Interestingly, if the reaction is carried out in the presence of one equivalent of a Lewis base the selective formation of the C-C coupling product, $PhCH_2CH_2Ph$, is achieved. Analogous behaviour was observed with benzyl bromide. However, in this case the reaction in absence of base gives mixtures (70/30) of toluene and $PhCH_2CH_2Ph$.



Scheme 1

[1] G. Lázaro, F. J. Fernández-Alvarez, M. Iglesias, C. Horna, E. Vispe, R. Sancho, F. J. Lahoz, M. Iglesias, J. J. Pérez-Torrente, L. A. Oro, *Cat. Sci. Technol.* **2014**, *4*, 62-70. [2] F. J. Fernández-Alvarez, M. Iglesias, L. A. Oro, V. Passarelli, *Comprehensive Inorganic Chemistry II*, **2013,** Vol 8,. p. 399-432.

SBA-16 doped with Zr: valorization of glycerol

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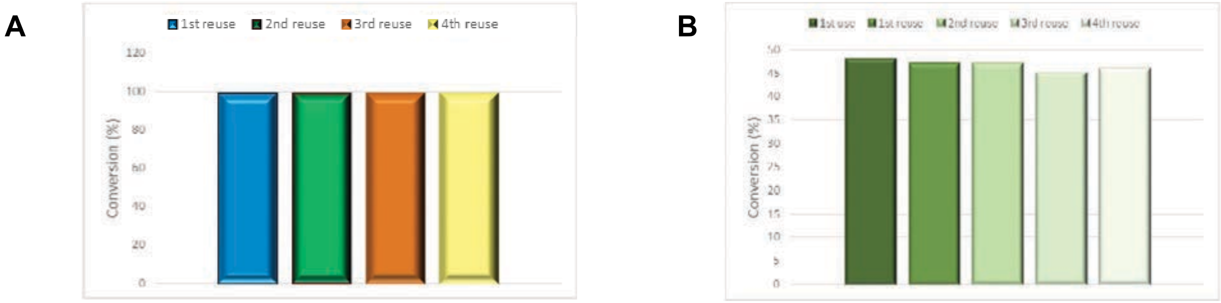
Glycerol has the potential to be a versatile building block in biorefineries[1], it is a nontoxic, biodegradable compound, it will provide important environmental benefits to new platform products. In the present work, Zr-containing SBA-16 materials with varying Si/Zr ratios were utilized in glycerol valorization for the production of esters, via reaction with levulinic acid, which is a biomass-derived platform molecule, like glycerol, and glycerol formal via acetalisation with paraformaldehyde.

Materials were found to be highly active and selective for the production of valuable compounds from glycerol using benign by design solventless protocols which employ mild reaction conditions. Quantitative conversion was achieved in the esterification of glycerol with levulinic acid with moderate selectivites to diacetylglycerides, being Zr-SBA-16(25) most active in the reaction as expected by its large concentration of acid sites. Comparably, Zr-SBA-16(100) exhibited optimum activities under optimized conditions in the acetalisation of glycerol with paraformaldehyde[2].

Investigated catalysts were generally highly stable and reusable under the investigated conditions, with a particularly outstanding recyclability of Zr-SBA-16(25) in glycerol esterification, the catalyst could be successfully reused up to four times, without any decrease in activity and selectivity. Gratifyingly, Zr-SBA-16(50) could also be succesfully used in the acetalisation without loss of activity and selectivity.



Expertiments of catalyst recycling in **A:** esterification using 50 mg of Zr-SBA-16(25), 1 mmol glycerol, 5 mmol levulinic acid, 140 ºC, without solvent for 15 h reaction. **B:** acetalisation 100 mg of Zr-SBA-16(50), 1 mmol glycerol, 1 mmol of paraformaldehyde, 100ºC, without solvent for 8h

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Diamine Catalyzed Addition of $ZnEt_2$ to $PhC(O)CF_3$: Two Mechanisms, and Autocatalytic Asymmetric Enhancement

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Work hypothesis and objective:

The asymmetric addition of dialkylzinc compounds ZnR_2 to aldehydes and ketones is one of the most powerful methodologies to access to optically active secondary and tertiary alcohols.[1] The asymmetric synthesis of chiral trifluoromethyl-substituted tertiary alcohol is nowadays of special relevance,[2] mainly because of the interest to introduce CF_3 groups in chiral reagents and in biologically active compounds (Figure 1).[3]

Results:

Mechanistic studies of the catalytic addition reaction of $ZnEt_2$ to $PhC(O)CF_3$ in the presence of three very efficient catalysts (TMEDA, ^{t}BuBOX, and **L**; **L** is a chiral diamine synthesized from optically pure (*R*,*R*)-1,2-diphenylethylenediamine and (*S*)-dibromomethyl-1,1'-binaphthalene) revealed strong differences in their behavior. Furthermore, the ^{19}F NMR signals of the main product of the reaction ($[Zn(Et)\{OC^*(CF_3)(Et)Ph\}]_2$) allow for the estimation *in situ* of the enantioselectivity of the process for the chiral ligands without the assistance of chiral chromatography. For the ligands TMEDA and ^{t}BuBOX the catalysis shows no unusual features and goes through $[(N–N)Zn(Et)\{OC(CF_3)(Et)Ph\}]$. For N–N = **L**, the observation of an autocatalytic asymmetric enhancement during the catalysis and an unusual inverse concentration dependence on the reaction rate gave us the clue to propose an additional novel catalytic cycle.

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Detection and Isolation of Species from the Reaction of Diazocompounds and Tp^{x}Cu Complexes.

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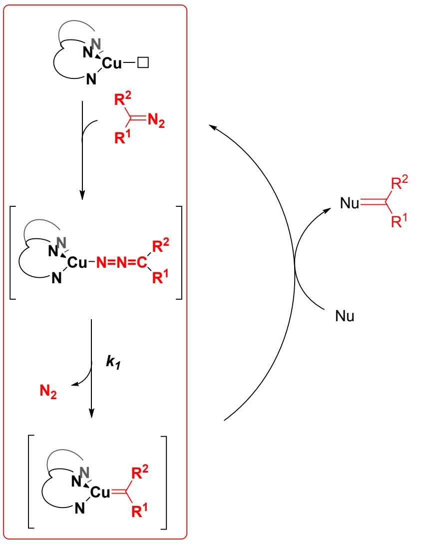
Work hypothesis and objective:

The metal catalyzed carbene transfer from diazocompounds is a very useful tool in many organic transformations, including X-H insertion reactions.[1] This contribution focuses on the detection of the different intermediates, such as metalo-carbene and diazoester complexes, which have been proposed in the reaction mechanism of that process, using Tp^{x}Cu compounds (Scheme 1).[2]

Results:

We have carried out the characterization of different copper carbene species Tp$^{R,R'}$Cu=CPhCO$_2$Et (R = Ms, ^{i}Pr, Me, and R' = H, ^{i}Pr, Me, respectively) by ^{13}C NMR spectroscopy, using N$_2$^{13}CPhCO$_2$Et. There is a very good correlation between the chemical shifts of the carbene carbons and the IR carbonyl stretching frequencies of the corresponding adducts, Tp$^{R,R'}$Cu(CO). On the other hand, we have isolated the diazo complex Tp^{Ms}Cu(η^1-N$_2$CPhCO$_2$Et). The structure proposed by NMR spectroscopy has been confirmed by a study of single-crystal X-ray diffraction. In addition, the isolation of this compound has allowed us to carry out a kinetic study by variable temperature NMR spectroscopy and by monitoring the N$_2$ evolution.



Scheme 1

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Synthesis and characterization of Rh nanoparticles stabilized by NHC ligands and their application in selective hydrogenation reactions.

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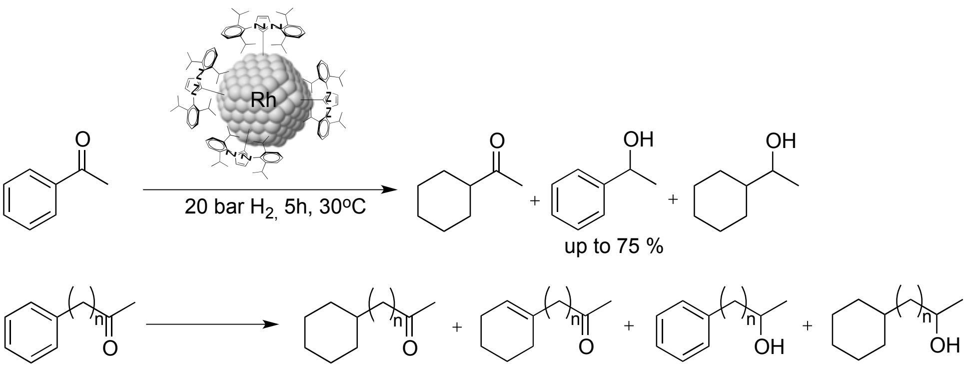
Work hypothesis and objective:
The application of metal NPs as catalysts is receiving an ever-increasing interest.[1] Indeed, metal NPs present the advantages of both homogeneous and heterogeneous catalysts, since they are extremely active, their reactivity can be modulated and they can be recovered and reused. [2] The influence of various stabilizers have been recently reported and significant efforts have been made in the synthesis of ligand-stabilized nanoparticles to achieve control of their properties. [3] In this context, the use of NHC ligands is of high interest as their strong coordination was shown to direct the selectivity of these catalysts. [4] The objective of this work is the synthesis and characterization of Rh NPs stabilized by NHC ligands and the study of their application in hydrogenation reactions.

Results:
In this work, we describe the synthesis of Rh NPs stabilized by N-Heterocyclic carbene ligands following the "organometallic approach" and their application in selective hydrogenation of aromatic ketones.[5] These NPs have been characterized by TEM, IR, TGA, XRD and liquid and solid state NMR using isotopically labelled ligands in order to facilitate the location and characterisation of these stabilizers at the surface of the NPs.



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CCC-Pincer-NHC Osmium Complexes: New Types of Blue-Green Emissive Neutral Compounds for Organic Light-Emitting Devices

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[a] Departamento de Química Inorgánica – Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza – CSIC, 50009 Zaragoza (Spain) and [b] Universal Display Corporation, 375 Phillips Blvd., Ewing NJ08618, USA

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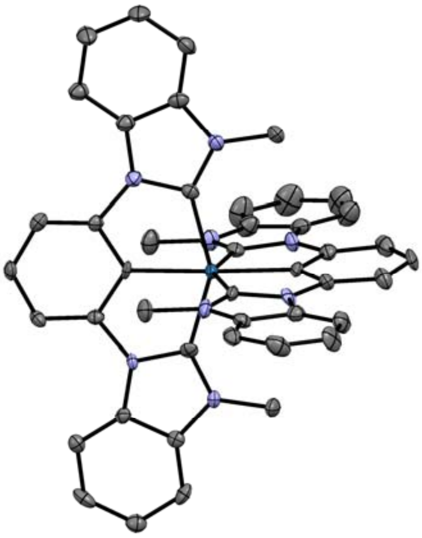
Work hypothesis and objective:

An important class of N-heterocyclic carbene ligands is that introducing a donor atom between two carbene edges. This type of ligands provide pincer coordination, and although a diverse array of pincer ligands bearing the NHC motif have been employed, those based on an NHC-aryl-NHC framework are attracting special interest, since the transition metal complexes bearing these ligands, mainly iridium and platinum, have interesting photophysical properties [1]. The objective of this research has been the synthesis and characterization of Osmium derivatives with pincer ligands of the type NHC-aryl-NHC, and the study of their photophysical properties.

Results:

We show here the results of the reactivity of the complex $OsH_6(P^iPr_3)_2$ towards $C_{benzimidazolium}C_{aryl}C_{benzimidazolium}$ and $C_{imidazolium}C_{aryl}C_{imidazolium}$ salts. Neutral Os(CCC)-pincer derivatives, including Os(IV)- and Os(II)-hydride species and homoleptic and heteroleptic bis(tridentate) Os(II) complexes have been prepared. Some of them have interesting photophysical properties, and moderate to high photoluminescence quantum yields are observed in the solid state.



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Study of the mechanim of isoprene telomerisation

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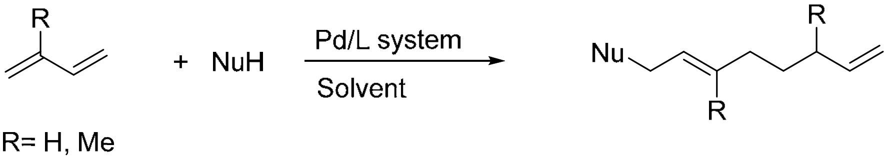
Work hypothesis and objective:

The telomerization reaction refers to the transition metal-catalyzed oligomerization of 1,3-dienes in the presence of nucleophiles. The telomerisation of butadiene (R=H) and isoprene (R=Me) have been the most widely studied (Scheme).



In the butadiene telomerisation, the control of the selectivity towards the lineal telomer is successfully achieved by using several Pd/L systems, and its catalytic cycle has been studied [1]. However, the isoprene telomerization presents a challenging problem of selectivity since up to 8 different telomeres can be formed. A mechanism similar to that described for butadiene has been proposed. This mechanism involves the initial coordination of two diene units to palladium with concomitant formation of a bond between the dienes and a π-allyl system [2]. However, a mechanism starting from a Pd-H has been also proposed [3]. In this communication we present our studies of isoprene telomerization. Species that can be originated from Pd-H species were detected by NMR.

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Temperature Dual Stereocontrol for the Reaction between *N*-Methyl-2-methylindole and Nitrostyrenes Catalyzed by (S_{Rh},R_C)-[(η^5-C_5Me_5)Rh{(*R*)-prophos}(H_2O)][SbF_6]$_2$

Isabel Méndez,[a] **Ricardo Rodríguez**,[a] **Daniel Carmona**,[a] **Víctor Polo**,[b] **and Luis. A. Oro**[a]

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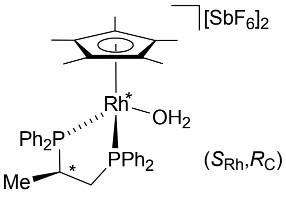
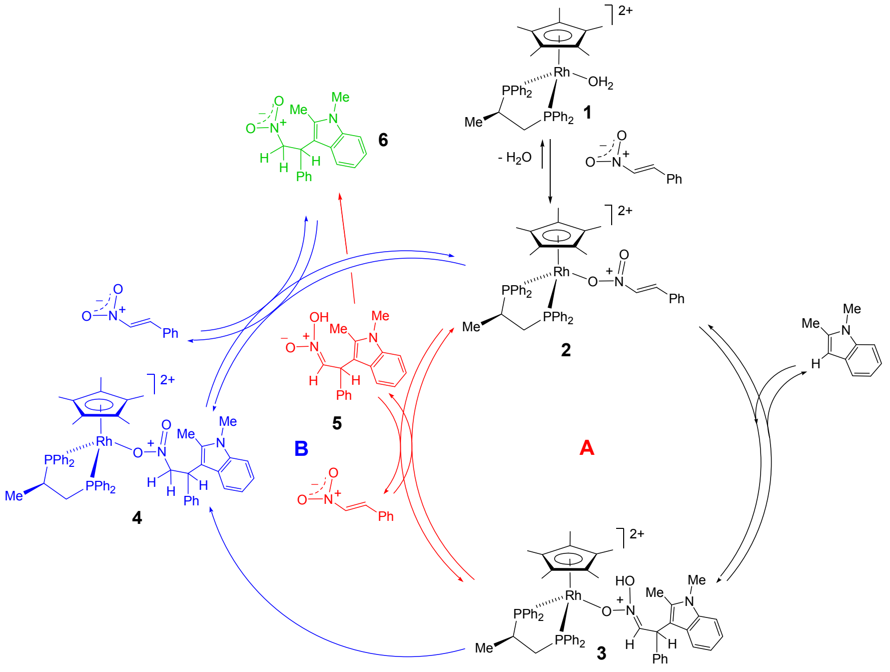
Work hypothesis and objective: The synthesis of both enantiomers of a chiral molecule usually requires the preparation of both enantiomers of the chiral catalyst. However, many catalysts are only readily available in a single configuration. Here, we report the highly enantioselective preparation of both enantiomeric products of the Michael-type Friedel-Crafts (FC) reaction between indoles and *trans*-*β*-nitrostyrenes by simply changing the reaction temperature.[1] The rhodium complex **1** is employed as the catalyst precursor.



1

Results: The enantiomeric excesses obtained in the asymmetric FC Reaction of *N*-methyl-2-methylindole with *trans*-*β*-nitrostyrene at different temperatures are listed in the Table. The origin of the enantioselectivity is rationalized on the basis of two competitive catalytic cycles, A and B, supported by spectroscopic experimental data and theoretical calculations.



T (K)	*e. e.*
313	97 (*S*)
298	98 (*S*)
283	99 (*S*)
273	98 (*S*)
263	96 (*S*)
253	2 (*S*)
243	84 (*R*)
233	96 (*R*)

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Synthesis and substitution reactions of [FeFe]-hydrogenase model complexes with P=O functionality at the bridgehead

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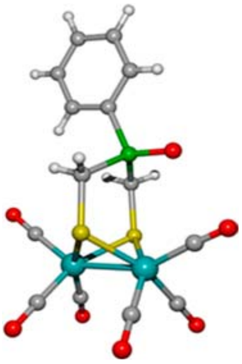
Work hypothesis and objective:

The global fossil fuels reserves are diminishing and they are harmful to the environment. One of the alternative renewable fuels is hydrogen which causes no deleterious products for the environment [1]. In nature, hydrogen is produced from protons and electrons by a catalytic process (taking place in certain microorganisms) using [FeFe]-hydrogenases [2] These enzymes attracts continuous interest because of their potential biotechnological applications as hydrogen producers. Biomimetic catalysts based on the active site of [FeFe]-hydrogenases have been synthesized, characterized and their ability to catalyze the reduction of weak acids to hydrogen have been demonstrated by different groups all over the world.

Results:

Novel types of [FeFe] hydrogenase model complexes containing phosphine oxide in the bridgehead**,** namely $[Fe_2(CO)_6][(\mu\text{-}SCH_2)_2P(R)=O]$ (R= Ph (**1**) and R= Et (**2**)) have been synthesized and characterized [3]. Treatment of acetonitrile solution of **1** with one equivalent of $Me_3NO.2H_2O$ followed by PPh_3 or $P(OEt)_3$ afforded $[Fe_2(CO)_5(PPh_3)][(\mu\text{-}SCH_2)_2P(R)=O]$ **4** or $[Fe_2(CO)_5(P(OEt)_3][(\mu\text{-}SCH_2)_2P(R)=O]$ **5** in quantitative yield. Complexes **1-4** have been characterized by spectroscopic techniques, elemental analysis, mass spectrometry and X-ray structure determination. The electrochemical behavior of **1** has been investigated along with its ability to catalyze the reduction of acetic acid to form dihydrogen



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Iridium hydride complexes with κ- *P,P,Si* pincers

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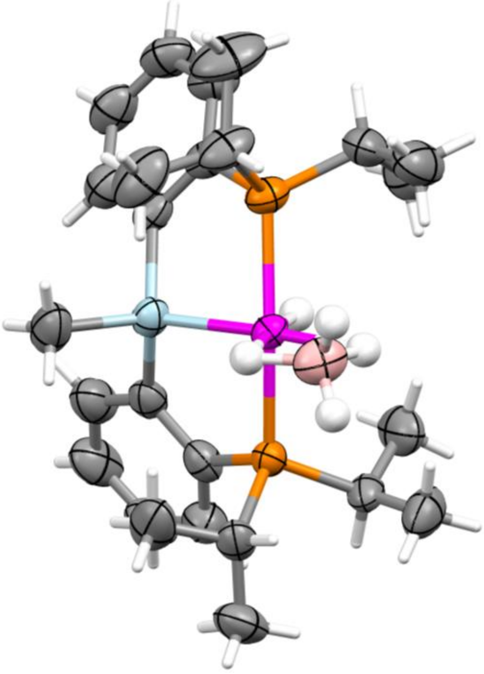
Work hypothesis and objective:

The large trans influence and effect of the silyl function of κ-*P,P,Si* pincer ligands make the difference in the chemistry of late transition metals complexes, favouring unusual structures and new reactions.[1,2] We are interested in exploring possible positive consequences of such peculiarities in the context of catalytic hydrogenation/dehydrogenation processes.

Results:

The contribution describes the preparation of new iridium hydrides containing the pincer ligand {κ-*P,P,Si*-Si(Me)(C_6H_4-2-P*i*Pr_2)$_2$, and discusses the impact of the silyl function in their structures, behaviour in solution and reactions.



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P38

Betaine Adducts of Imidazolidenes and Carbodiimides, Promising Electroneutral Amidinate-Type Ligands

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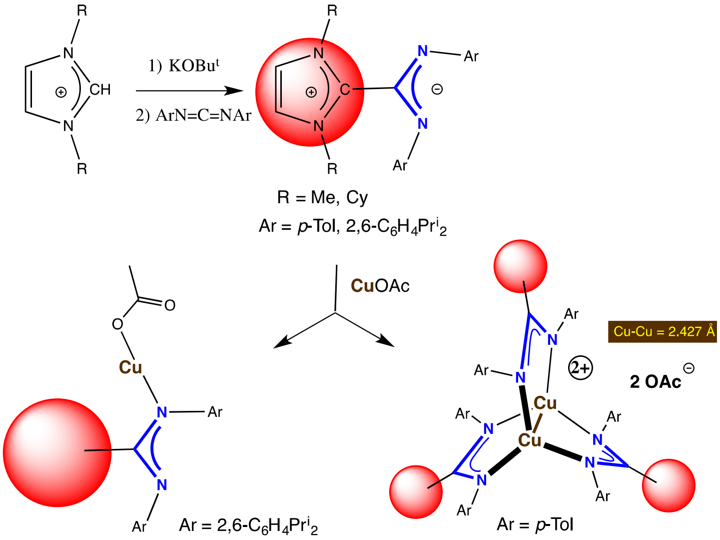
Betaines are zwitterionic compounds that are usually generated reacting electroneutral nucleophilic and electrophilic reagents. A number of interesting betaines can be readily accessed from the reaction of heterocyclic carbenes with heterocumulenes X=C=Y, such as CO_2, CS_2, etc [1]. These betaines can act as ligands towards transition metal centres, but this potential remains largely unexplored. Specifically, the interaction of imidazolium carbenes with carbodiimides gives rise to betaines that can be regarded as neutral analogues of the well-known imidinate ligands. However, no complexes containing this cabene-carbodiimide betaines have been reported so far.

A simple one-pot procedure has been developed for the synthesis of carbodiimide adducts of imidazolium-based carbenes. The new molecules have been fully characterized, and a series of Cu(I) complexes have been prepared. Both terminal (κ^{i}-*N*) and bridging (μ-*N,N'*) coordination modes of the betaine ligand have been identified.



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Sulfonated, trifluoromethylated and carboxylated triarylphosphines. Application in biphasic hydroformylation.

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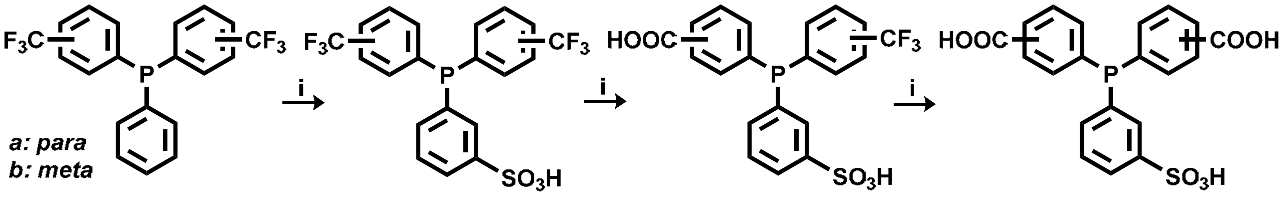
We have designed a methodology to obtain triarylphosphines containing sulfonic and carboxylic groups, and in some cases also trifluoromethyl groups. This methodology is based on the reaction of trifluoromethylated phenyldiarylphosphines with oleum and boric acid [1, 2]:



i: a) $H_3BO_3/SO_3/H_2SO_4$; b) H_2O **1a-b** **2a-b** **3a-b**

We have also developed an efficient method to separate and purified these phosphines when they are obtained as mixtures. Appropriate substitution allows to prepare phosphines with modulated water soluble properties (sulfonic groups), with variable acidity (CF_3 groups), as well as different amphiphilicity (through modification of the carboxylic functionality).

Some of these phosphines have been used in rhodium catalysed biphasic hydroformylation (organic solvent/ water) of vinyl acetate. The rate of hydroformylation depends on the number of trifluoromethylated groups. Hence, phosphines type **1** are more active (tof $\approx$ 7 min^{-1}) than type **2** (tof $\approx$ 4 min^{-1}) , and type **3** are nearly no active under biphasic conditions (P = 30 bar CO + H_2 at 80°C; 5 ml water/ 4 ml Et_2O , vinyl acetate/phosphine/Rh =2500/20/1). Separation of the aqueous catalytic mixture allows efficient recycling of the catalyst.

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Discrete Mixed-Valence Metal Chains: Generation of Iridium Pyridonate Blues by Protonation

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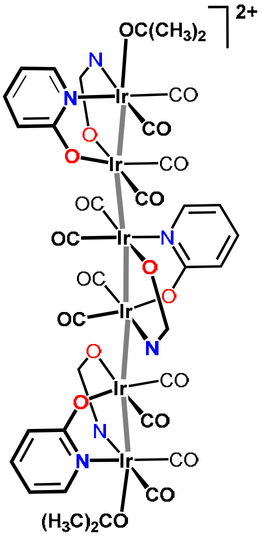
Work hypothesis and objective:

Compounds containing discrete chains of metal-bound atoms are interesting because of their potential applications in nanoscale devices. In this context, a molecular wire generally refers to molecules able to undergo electronic delocalization along the backbone and to be connected to other electroactive components.[1] Mixed-valence metal chains can be considered molecular wires because they fulfil both requirements. Despite the interest of this field, the rational design of molecular metal wires is still in its infancy, so that a progress in precise synthetic procedures to provide such type of compounds is needed. Some preparative approaches involve the reduction of d^7-species or the oxidation of dinuclear complexes with d^8 square-planar metal centres.[2]

Results:

In this communication we will show some alternative procedures to synthesize discrete mixed-valence iridium chains. Thus, addition of protic acids such as HBF_4, HCl or trifluoroacetic acid to the dinuclear complex $[Ir_2(CO)_4(\mu\text{-}Opy)_2]$ (Opy = 2 pyridonate) promotes the formation of metallic oligomers with control of the length (nuclearity), allowing the isolation of a new family of iridium pydidonate blues. These results contrast with the typical outcome from reactions of mononuclear iridium(I) complexes with protic acids, which produce the protonation of either anionic ligands or the metal to give hydride complexes.



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Iminophosphine nickel complexes with polar olefins.

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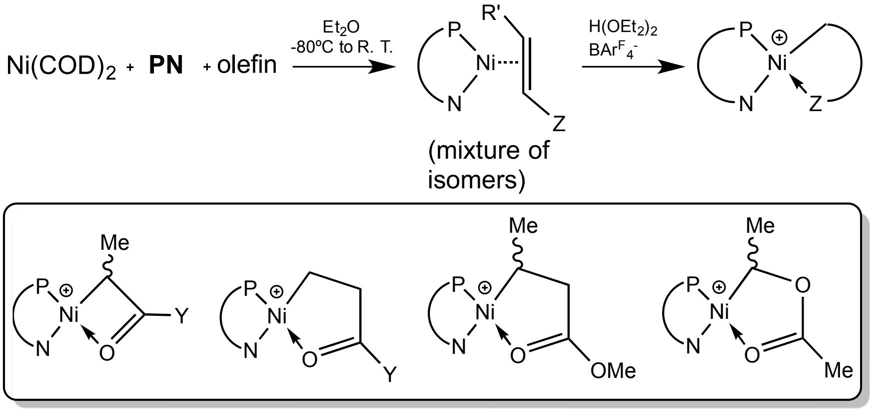
The synthesis of organometallic complexes useful as catalyst precursors for the polymerization of olefins without the presence of cocatalyst continues to attract much interest[1,2], due to their compatibility polar monomers and usefulness in mechanistic studies. The objective of our research is the synthesis of new nickel complexes potentially active as single-component catalysts for ethylene polymerization and copolymerization. To this purpose we selected hybid phosphine-imino ligands derivatives, since they are known to give rise to robust polymerization catalysts, but their organometallic chemistry is still underdeveloped.
To accomplish our research goals, three iminophosphine ligands were synthetized differing in the nature of the phosphorous substituents. The interaction of these ligands with $Ni(COD)_2$ in the presence of polar olefins (methyl acrylate, vinyl acetate, methyl vinyl ketone or methyl crotonate) leads to the corresponding Ni(0) olefin complexes, which upon protonation with Brookhart's acid afford cyclic cationic alkyl complexes which exhibit four- or five membered chelate rings, depending on the choice of iminophosphine ligand and olefin. It is known that similar chelate rings play an important role in the copolymerization of ethylene and polar olefins catalyzed by Pd or Ni complexes [3 – 5]



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Chemoselective Deuteration of CH Bonds Catalysed by Ag(I) or Zn(II) salts. Mechanistic Theoretical Modelization.

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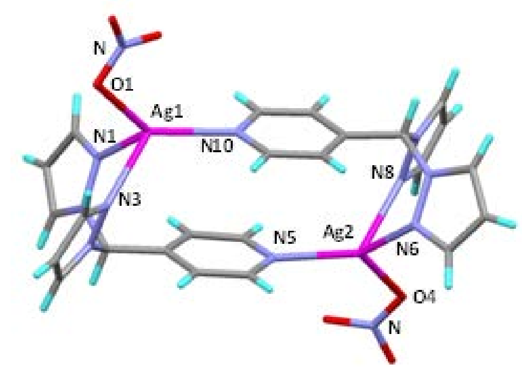
Work hypothesis and objective:

The obtention of isotopically labeled compounds shows an increasing interest due to the use of these substrates in fields such as kinetics, mass spectrometry, biomedicine and materials science. The deuteration of CH bonds with attached electro-acceptor groups, as heterocycles or arenes, is an easy process both in acid or basic medium. However, to achieve a chemoselective deuteration of only some types of such CH groups is a complicated task.



Proposed precatalyst species

Results:

In this work, we present results on the chemoselective deuteration of the methinic group of compounds of the type bis(pyrazol-1-yl)-R-methane in deuterated methanol or water, without the addition of acid or base. The deuteration labeling is highly dependent on the nature of the R group, so that, among the tested substrates, only in the case where R = 4-pyridyl and the pyrazoles are not methylated this deuteration takes place with a 100% yield in less than one hour. When R = H or Ph no deuteration is observed. The reaction does not occur with the free ligand and takes place only in the presence of Ag(I) or Zn(II) salts and it is catalytic.

Based on our previous experimental knowledge and theoretical studies performed, a mechanism has been proposed. This implies the formation of dimeric species (Figure) in solution and a heterolytic O–D bond activation of CD_3OD, assisted by the 4-pyridyl. The formation of M-OMe intermediates promotes the methynic CH activation through a stereoselective step.

Amine Gold(III) Complexes with Catalytic Activity as Precursors of Novel Bidentate Acyclic Carbene Derivatives

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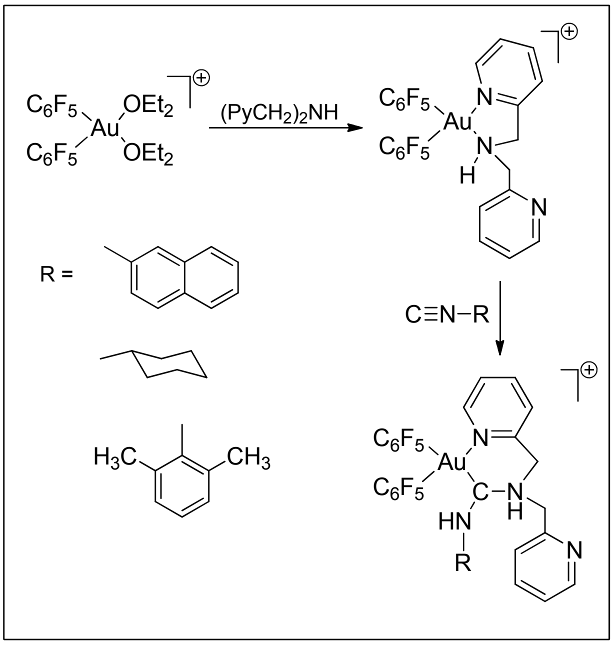
Work hypothesis and objective:

There is now an increasing interest in gold(III) derivatives mainly because of their potential applications in diverse fields such as medicine in which they present cytotoxic activity, as luminescent materials or as catalysts for a great variety of organic reactions. The most promising derivatives are those with N-heterocyclic carbene ligands, whereas the acyclic carbene complexes have been far less studied. We have developed and interesting methodology to prepare asymmetric bidentate acyclic gold(III) carbenes, starting from a gold(III) derivative with a heterofunctional amine by reaction with isocyanides.[1]

Results:

The complex $[Au(C_6F_5)_2(PyCH_2NHCH_2Py)]\ ClO_4$ has been synthesised and structurally characterized. In the solid state the complex has chiral nitrogen, but in solution is fluxional with a dynamic exchange between the nitrogen atoms of the pyridine. This behaviour allows their use as an active catalyst in several organic transformations involving the activation of alkynes to the nucleophilic attack. This complex reacts with isocyanides forming novel gold(III) derivatives with bidentate acyclic carbene ligands, with biological properties.



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Design and study of the photophysical properties of cyclometalated Pt^{IV} complexes.

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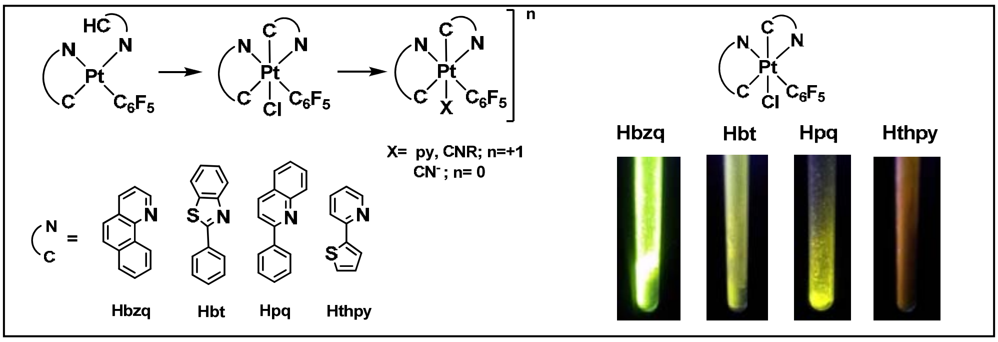
Work hypothesis and objective:

Luminescent Pt^{II} cyclometalated complexes have attracted great interest in recent years because they have shown extraordinary potential in highly efficient organic light-emitting diodes (OLED) devices, as molecular sensors, in biological labeling and photocatalysis. However, the photoluminescence properties of Pt^{IV} complexes have received a very limited attention, which contrasts with the extensive luminescence studies carried out on complexes of other d^6 ions, such as Re^{I}, Ru^{II}, Os^{II} and Ir^{III}.

In the last years, our research group has reported several contributions related to luminescent mono and polymetallic Pt^{II} materials, studying the influence of the cyclometalated ligands and coligands on their photophysical properties[1,2].We have also described some Pt^{IV} derivatives obtained by oxidative reactions to Pt^{II} compounds, but they have resulted to be non-emissive [3].

Results:

With the aim to obtain luminescent Pt^{IV} complexes, we have designed a new synthetic route by oxidation of cyclometalated Pt^{II} complexes of the type $[Pt(C\text{^}N\text{-}\kappa C,N)(HC\text{^}N\text{-}\kappa N)(C_6F_5)]$. Herein, we present a series of homoleptic bis-cyclometalated Pt(IV) derivatives $[Pt(C\text{^}N)_2(C_6F_5)Cl]$ using C-deprotonated 2-(2‘-thienyl)pyridine (Hthpy), 2-phenylbenzo[d]thiazole (Hbt), 2-phenylquinoline (Hpq) and 7,8-benzo[h]quinoline (Hbzq) as ligands. Substitution of the chloride ligand by neutral (py, NCR) or anionic (CN^-) ligands allow us to modify the electronic characteristics, thus tuning their emissive properties. Detailed photophysical studies of these Pt^{IV} derivatives and their Pt^{II} precursors have showed that the emissive properties depend on the type of cyclometalated ligand, the Pt oxidation state and the coligand.



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P45

Nuevas herramientas *on-line* : Técnicas Avanzadas en el Laboratorio de Química (TALQ)

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En estos últimos años, un grupo de profesores de la Universidad de Barcelona, *grupo GIDOLQUIM*, hemos desarrollado un proyecto de innovación docente para su utilización en el aprendizaje de las técnicas avanzadas en el laboratorio de química (TALQ) (www.ub.edu/talq). Consideramos el proyecto como la segunda parte del ya desarrollado Operaciones Básicas en el Laboratorio Químico (www.ub.edu/oblq).

El objetivo del proyecto es dar a conocer al alumno, de forma sencilla y gráfica, las operaciones que podríamos definir como "avanzadas" que se llevan a término en un laboratorio de química. Por otro lado se pretende proporcionar al profesor una herramienta de apoyo efectiva en el trabajo de descripción de estas operaciones que se pueda llevar a cabo en el aula, previamente a introducir al alumno en el laboratorio. Se trata por tanto de una herramienta dirigida tanto al estudiante como al profesor.

El contenido se ha distribuido en 5 amplios apartados :

Tema 1. Disolventes y reactivos. Conceptos y tratamiento previo.
Tema 2. Trabajar con gases. Generación de gases. Reacciones con gases a presión.
Tema 3. Activación de reacciones químicas por métodos físicos: agitación, temperatura, microondas, ultrasonidos, fotoquímica.
Tema 4. El proceso de la liofilización. Conceptos y procedimientos.
Tema 5. Reacciones en atmósfera inerte. Técnicas de creación, materiales y procedimientos.

Creemos que el material desarrollado puede ser muy interesante para toda la comunidad educativa involucrada en el aprendizaje práctico del trabajo en Química Organometálica y es por ello que nuestra intención es que sea un material libre en su utilización, dentro de los términos habituales de registro de autor de material electrónico.

TEMA 1. DISOLVENTES Y REACTIVOS
Conceptos y tratamiento general.

TEMA 2. TRABAJAR CON GASES
Generación de gases. Gases a presión.

TEMA 3. ACTIVACIÓN DE REACCIONES QUÍMICAS
Activación de reacciones químicas por métodos físicos.

TEMA 4. EL PROCESO DE LA LIOFILIZACIÓN
Conceptos y procedimientos.

TEMA 5. REACCIONES EN ATMÓSFERA INERTE
Técnicas de creación, materiales y procedimiento.

P46

Application of pyranoside phosphite-pyridine ligands to enantioselective metal-catalyzed allylic substitutions and conjugate 1,4-additions

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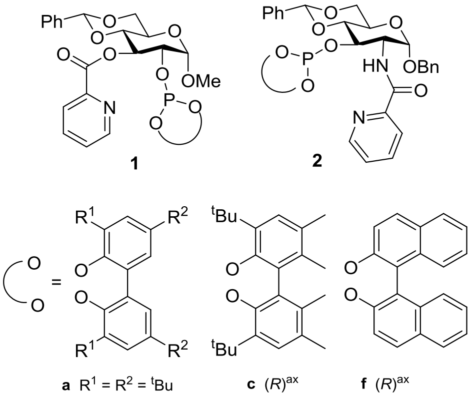
Work hypothesis and objective:

Metal-catalyzed allylic substitution[1] and conjugate 1,4-addition[2] are two of the most powerful carbon-carbon bond forming reactions for the construction of enantioriched synthons for both biologically active and natural compounds. Sugar-derived ligands are interesting building blocks for these processes since their low cost and high modular nature.[3] On the other hand, P-N ligands have been succesfully applied in several asymmetric processes[4] since they present the benefits of bearing a soft and a hard coordinating function. In this context, we have prepared glucopyranoside ligands **1** and **2** containing a phosphite and a pyridine moiety, in order to be applied in the Pd-catalyzed allylic alkylation and Cu-catalyzed 1,4-conjugate addition.

Results:

We have investigated the effects of varying the position of phosphite group at both C-2 (ligand **1**) or C-3 (ligand **2**) of the pyranoside backbone, as well as the effects of different substituents and configurations in the biaryl phosphite moiety (**a**-**f**). By varying the position of the phosphite moiety and the substituents/configuration at the biaryl phosphite moiety we have been able to identify ligands that provided high enantioselectivities in the Pd-catalyzed allylic substitution of cyclic substrates (ee's up to 86%) and desymmetrization of *meso*-cyclopent-2-ene-1,4-diol (ee's up to 94%) and in the Cu-catalyzed conjugate 1,4-addition of dialkylzinc reagents to a challenging aliphatic enone *trans*-3-nonen-2-one (ee's up to 90%).



[1] (a) Z. Lu; S. Ma, *Angew. Chem. Int. Ed.,* **2008**, *47*, 258. (b) M. Diéguez; O. Pàmies, *Acc. Chem. Res.*, **2010**, *43*, 312.
[2] (a) A. Alexakis; J. E. Bäckvall; N. Krause; O. Pàmies; M. Diéguez, *Chem Rev.*, ***2008,*** 108*, 20796.* (b) C. Hawner; A. Alexakis, *Chem. Commun.,* **2010**, *46*, 7295.
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Experimental and DFT study of the synthesis of acetals catalyzed by gold(I) compounds.

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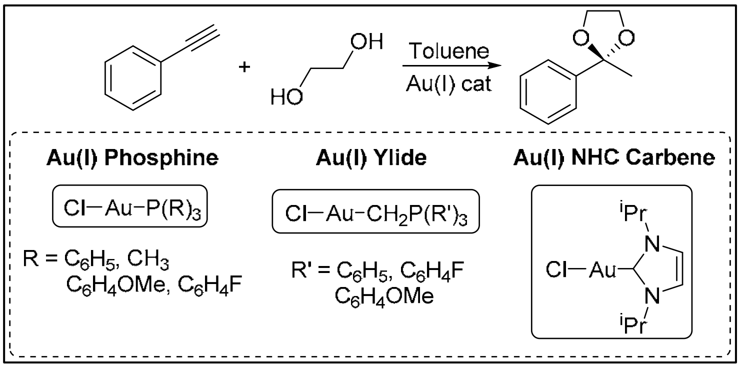
Work hypothesis and objective:

Cyclic acetals are important molecules for protecting carbonyl groups in organic synthesis [1] and for the generation of chiral auxiliaries. Transition metal compounds catalyze the reaction of many alkynes with different nucleophiles. In the case of gold, it has been described that cationic Au(I) complexes, for example, catalyze the formation of dimethyl acetals from alkynes by addition of methanol. [2]

We decided to study, experimentally and theoretically, the behaviour of different Au(I)-phosphine ([AuClP(R)$_3$]; R=C_6H_5, CH_3, C_6H_4OMe, C_6H_4F), Au(I)-ylides ([AuCl(CH$_2$P(R')$_3$)]; R'=C_6H_5, C_6H_4F, C_6H_4OMe) and Au(I)-NHC ([AuCl(^{i}Pr)]) complexes as catalysts in the reaction of phenylacetylene with ethyleneglycol for the formation of acetals.

Results:

Catalytic tests under strong conditions (100 ºC, 4 h) allowed to achieve up to 100% conversion. Meanwhile, under softer conditions (75 ºC, 1 h), NHC carbene Au(I) complex reaches the highest conversion followed by phosphine and finally the ylide Au(I) catalyst.



We tried to explain this trend constructing the energy profile through DFT calculations and studying several properties of the system, such as the NBO charge of the metallic centre or the energy barriers. The main conclusions we point out to three factors affecting to the catalyst efficiency: the energetic barriers, the gold electrophilicity and the stability of the catalysts.

[1] P. G. M. Wuts, T. W. Greene, *Greene's Protective Groups in Organic Synthesis*, Wiley, **2006**.

[2] J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem. Int. Ed.*, **1998**, *37*, 1415.

Novel complexes of nickel with dialkyl terphenyl phophines

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[b]*Departamento de Química Inorgánica, Universidad de Sevilla*-Consejo Superior de Investigaciones Científicas, Avenida Américo Vespucio 49, 41092 Sevilla (Spain)
Email: marmargom4@alum.us.es

Work hypothesis and objective:

The extraordinary success of palladium as catalyst in cross-coupling chemistry is closely linked to the use of bulky phosphines as ligands.[1] Nickel represents a cost-effective alternative to replace palladium in this type of processes. Given the scarce number of active catalytic systems based on nickel[2] for C-C and C-N bond formation via cross-coupling, we focus on the preparation of nickel complexes stabilized by monodentate bulky phosphine ligands.

Results:

A family of dialkyl terphenyl phosphines (Fig. 1), recently prepared in Carmona's group, have been the ligands chosen to carry out this study. These ligands are structurally related to Buchwald's dialkyl biaryl phosphines.[3]

We account here for the synthesis and the structural characterization of nickel compounds bearing this type of ligands. A preliminary study on the catalytic properties of the newly synthesized complexes in the Buchwald-Hartwig amination reaction is also presented.

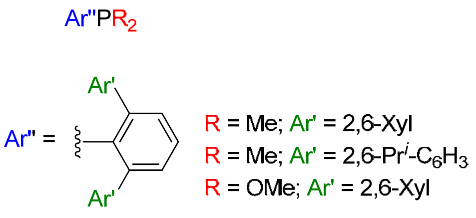

Figure 1. Ligands used in this work

[1] (a) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. A. de Meijere, F. Diederich, Eds.; Wiley-VCH: Weinheim, Germany, **2004**.
[2] (a) N. H. Park, G. Teverovskiy, S. L. Buchwald, *Org. Lett*., **2014**, *16*, 220; (b) S. Ge, R. A. Green, J. F. Hartwig, *J. Am. Chem. Soc.*, **2014**, *136*, 1617.
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Gold Carbenoids: Synthesis, Structure and Reactivity.

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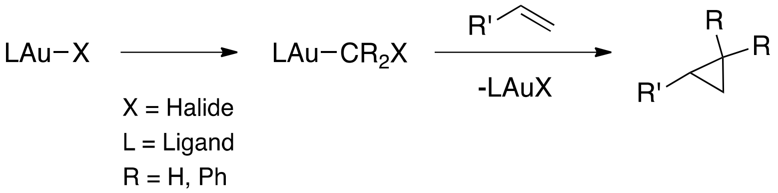
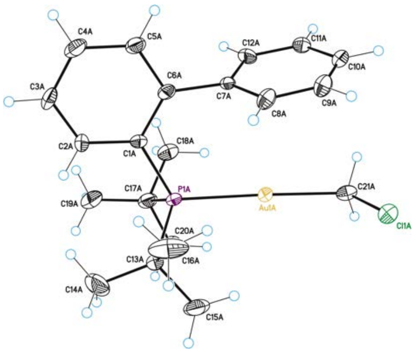
Many of the gold-catalyzed transformations of 1,n-enynes and other substituted alkynes proceed via gold(I) carbene intermediates.[1] We have synthesized a series of α-halogenated alkylgold complexes since α-haloorganometallic compounds (carbenoids) are known to function as latent carbenes.[2] The formal insertion of a carbene moiety into an Au(I)-X bond was achieved by the reaction with diazo compounds, or the transmetallation from α-haloorganolithium compounds. The structure and reactivity towards olefin cyclopropanation of carbenoid gold complexes will be presented.





Acknowledgments: We thank MICINN (project CTQ2010-16088/BQU), the European Research Council (Advanced Grant No. 321066), and the ICIQ Foundation for financial support.

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Structure-selectivity relationships in the Hydrogenation of Aromatic Ketones Using as Catalysts Ruthenium and Rhodium Nanoparticles Stabilized by Phosphorus Ligands.

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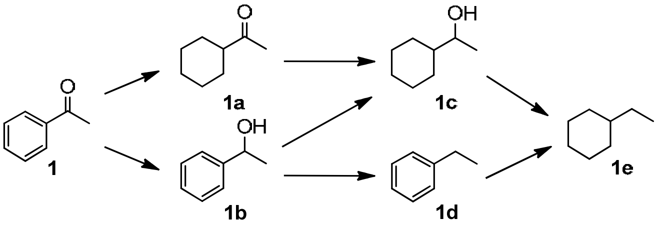
[3]Laboratoire de Physique et Chimie des Nano-Objets, Institut National des Sciences Appliquées, 31077, Toulouse, France
Email: emma.breso@urv.cat

Work hypothesis and objective:

The hydrogenation of arenes is an important area of research ought to the interesting industrial application in the production of cyclohexanes or in the partial arene hydrogenation to cyclohexenes.[1] Nowadays, the reduction of an arene in substrates containing other hydrogenable functional groups has become a really important process.[2] The objective of this work is to study the structural factors in substrate and nanoparticles influencing the selectivity in the hydrogenation of aryl ketones.

Results:

We present the preparation of Ru and Rh NPs stabilized by mono- and bidentate phosphines and their use as catalysts in the hydrogenation of aromatic ketones. The effect of the nature of the metal and the stabilizing agent on the chemoselective hydrogenation of the aryl groups vs the ketone is also studied. Taking acetophenone (**1**) as model substrate, different aryl ketones modified in the aryl moiety and in the alkyl chain, as well as non-conjugated aryl ketones, are also studied.



[1] a) Roucoux, A. ; Schulz, J. ; Patin, H. Chem. Rev. 2002, 102, 3757-3778; b) Widegren, J. A.; Finke, R. G. J. Mol. Catal. A: Chem. 2003, 102, 187-207. [2] a) Snelders, D. J. M.; Yan, N.; Gan, W.; Laurenczy, G.; Dyson, P. J. ACS Catal. 2012, 2, 201-207. b) Gonzalez-Galvez, D.; Lara, P.; Rivada-Wheelaghan, O.; Conejero, S.; Chaudret, B.; Philippot, K.; van Leeuwen, P.W.N.M. Catal. Sci. Technol. 2013, 3, 99-105. c) Gonzalez-Galvez, D.; Nolis, P.; Philippot, K.; Chaudret, B.; van Leeuwen, P.W.N.M. ACS Catal. 2012, 2, 317–321.

COMPLEJOS FOTOCRÓMICOS DE IRIDIO(III) DERIVADOS DE AZOBENCENO

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[2] *IKERBASQUE, Basque Foundation for Science, 48011, Bilbao*
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Hipótesis de trabajo y objetivo:

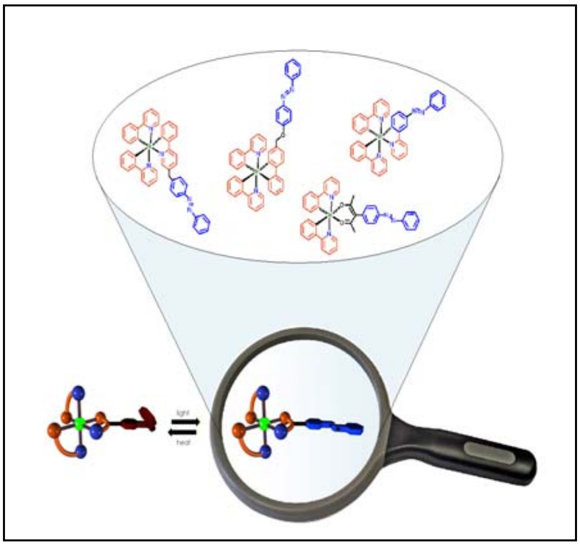
En la actualidad, el desarrollo y síntesis de nuevos complejos ciclometalados de iridio(III) es un área de investigación en auge debido a sus múltiples aplicaciones: OLEDs, marcadores bilógicos, sensores químicos... [1] Hasta donde nosotros sabemos, no se conocen ejemplos de este tipo de complejos que incorporen unidades fotocrómicas orgánicas en la estructura de sus ligandos.

Una de las unidades fotocrómicas más utilizadas, el fragmento azobenceno, experimenta una fotoisomerización reversible de la forma *trans* a la forma *cis,* producido evidentes cambios estructurales y electrónicos en la molécula. [2]

La obtención de complejos ciclometalados de iridio fotosensibles que incorporen dicha unidad, es un reto interesante debido a que las propiedades y/o funcionalidad de dichos complejos podrían ser controladas por estímulos externos: irradiación de luz, temperatura.

Resultados:

En nuestro grupo de investigación hemos sintetizado una amplia familia de complejos ciclometalados de iridio neutros con ligandos derivados de azobenceno (tipo fenilpiridina y acetilacetonato), destinados a investigar la transferencia de fotocromismo del grupo azobenceno al complejo organometálico. En este trabajo se discutirá cómo afecta la naturaleza del ligando que incorpora el fragmento azobenceno al comportamiento fotocrómico de los complejos organometálicos.



Familia de complejos fotocrómicos de iridio con ligandos derivados de azobenceno.

[1] Z. Liu, Z. Bian, C. Huang, *Top. Organomet. Chem.*, **2010**, 28, 113-142
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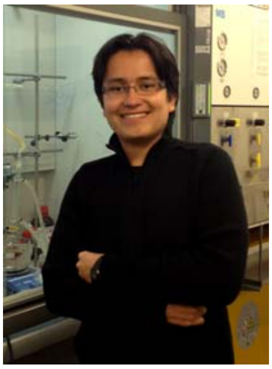
A Pyrene-Based N-Heterocyclic Carbene: Study of Its Coordination Chemistry and Stereoelectronic Properties



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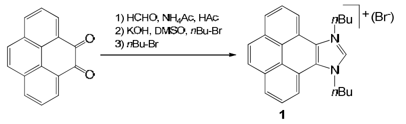
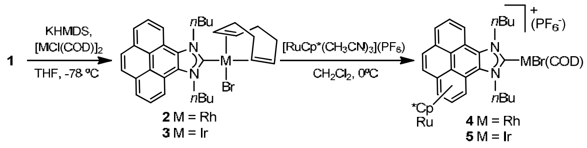
Pyrene is the chromophore of choice in fundamental and applied photochemical research, due to its fluorescence properties.[1, 2] Thus, its incorporation into N-heterocyclic carbene (NHC) ligands may add interesting photophysical applications to their derived complexes. For these reasons, our main goals are the development of a new pyrene-based NHC ligand, and the study of its coordination capabilities and photophysical properties.

As depicted in Scheme 1, pyrene-based imidazolium bromide **1** was synthesized in three steps. Compound **1** shows fluorescence properties with emissions ranging from 350 to 450 nm, and quantum efficiency of 0.31. The new pyrene-imidazolylidene was coordinated to Rh(I) and Ir(I), yielding compounds **2** and **3**, respectively. The presence of a pyrene backbone was used as a platform for the coordination of a $[RuCp^*]^+$ fragment, which allowed us to obtain heterometallic complexes of Rh/Ru (**4**) and Ir/Ru (**5**) (Scheme 2). The electronic properties of the pyrene-NHC ligand, and of the ligand bound to the cationic ruthenium fragment, were studied by means of IR spectroscopy and cyclic voltammetry.[3]



Scheme 1



Scheme 2

[1] T. M. Figueira Duarte, K. Müllen, *Chem. Rev.* **2011**, *111*, 7260.

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[3] H. Valdes, M. Poyatos, E. Peris, *Organometallics* **2014**, *33*, 394.

We gratefully acknowledge financial support from MEC of Spain (CTQ2011-24055/BQU) and UJI (P1.1B2011-22). We also would like to thank the Santiago Grisolía (H.V.) and Ramón y Cajal (M.P.) programs.

Experimental Study of the Mechanism of the Pd-catalyzed Aryl-alkyl Negishi Coupling using Hybrid Phosphine-Electron Withdrawing Olefin Ligands

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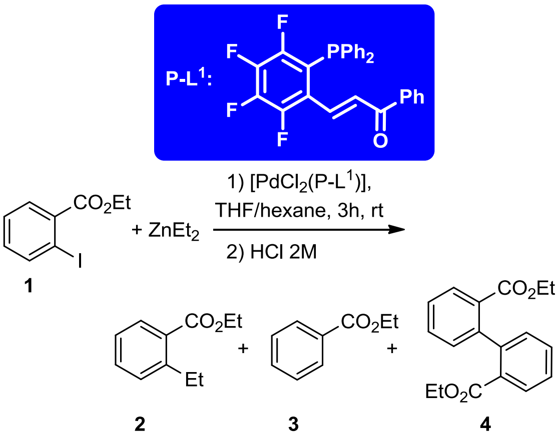
Work hypothesis and objective:

A few years ago Lei *et al.*[1] reported an efficient Pd-catalyzed Negishi-coupling of aryl halides with alkylzinc reagents using the hybrid phosphine/olefin ligand $PPh_2(2\text{-}RC_6H_4)$ (R = CH=CHCOPh). Similar results were reported recently by our group using the related phosphine/olefin $PPh_2(2\text{-}RC_6F_4)$ ligand in the figure (R = CH=CHCOPh) and other $PPh_2(2\text{-}RC_6F_4)$ ligands with different R groups.[2] The selectivity toward C–C cross-coupling products was highly improved with the former phosphine, nicknamed P-L^1, but decreased substantially with ligands without the electron withdrawing olefin fragment (EWO), and important proportions of Ar–H are formed. In this work we undertake further studies on the coupling in the figure to definitely confirm or discard the involvement of β-H elimination in the formation of the undesired reduction product **3**, and to better understand the effect of the $ZnEt_2$/ArI ratio on the reaction outcome.

Results:

The success of the reaction was attributed to the enhancement of the cross coupling reductive elimination rate favored by our ligand, as expected from our previous study of EWO as promoters of C–C coupling. Furthermore, Ar-H byproduct comes mainly from hydrolysis of ZnArEt species formed by undesired retrotransmetallation processes. An additional and synthetically interesting observation was that diminishing the Zn:**1** proportion of zinc reagent from 2.5 to 0.65 produced a notable increase of (**2**)/(**3**) (Ar–Et/Ar–H) selectivity towards the coupling product (97/3, instead of 90/10), although with formation of some homocoupling biphenyl product (**4**).



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(1) Luo, X.; Zhang, H.; Duan, H.; Liu, Q.; Zhu, L.; Zhang, T.; Lei, A. *Org. Lett.* **2007**, *9*, 4571−4574.
(2) Gioria, E.; Martínez-Ilarduya, J. M.; García-Cuadrado, D.; Miguel, J. A.; Genov, M.; Espinet, P. *Organometallics* **2013**, *32*, 4255−4261.

Detection and Isolation of Intermediates in Reactions Catalyzed by Nickel and Palladium Complexes Bearing N-Heterocyclic Carbenes Ligands

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Tomás R. Belderrain[a,*]

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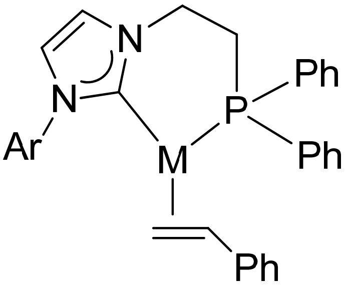
Work hypothesis and objective:

In most of the catalytic systems based on nickel and palladium complexes bearing N-heterocyclic carbenes ligands (NHC), precursor compounds such as $Pd(AcO)_2$ and $Ni(COD)_2$ have been used, with the catalytically active species formed *in situ*.[1] Although there exist mechanistic proposals for those catalytic transformations, few examples of the detection or isolation of some of the proposed intermediates have been described (i.e. palladium(0) and nickel(0) compounds). Our group recently have reported the synthesis of $IPrNi(sty)_2$ and $IPrPd(sty)_2$, and the use of those compounds as catalyst precursors in several catalytic systems.[2] With all these precedents in mind, we initiated the study of the isolation of reaction intermediates, using nickel(0) and palladium(0) complexes bearing monodentate and bidentate NHC ligands (Figure 1) as starting compounds.

Results:

Herein we report the isolation and characterization of the compounds obtained by the reaction of the nickel(0) and palladium(0) complexes with aryl halides and diazocompounds, respectively.



M = Ni, Pd

Figure 1

[1] See for example: (a) L. Ackermann, R. Sandmann, W. Song, *Org. Lett.* **2011**, *13*, 1784. [2] (a) C. Martín, F. Molina, E. Alvarez, T. R. Belderrain, *Chem. Eur. J.* **2011**, *17*, 14885. (b) M. J. Iglesias, J. F. Blandez, M. R. Fructos, A. Prieto, E. Álvarez, T. R. Belderrain, M. C. Nicasio, *Organometallics* **2012**, *31*, 6312.

Reactivity of the Chiral Metallic Brønsted Acid [(η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru(κ^3*P,O,O'*-POH)][SbF$_6$]$_2$ (POH = (S_{C1},R_{C2})-Ph$_2$PC(Ph)HC(OH)HCH$_2$OMe) toward Aldimines

Pilar Pardo, **Daniel Carmona, Pilar Lamata, Ricardo Rodríguez, Fernando J. Lahoz, Pilar García-Orduña, and Luis A. Oro**

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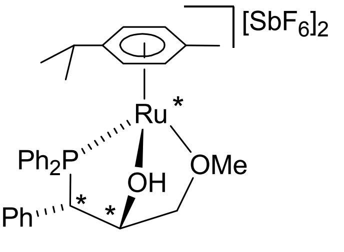
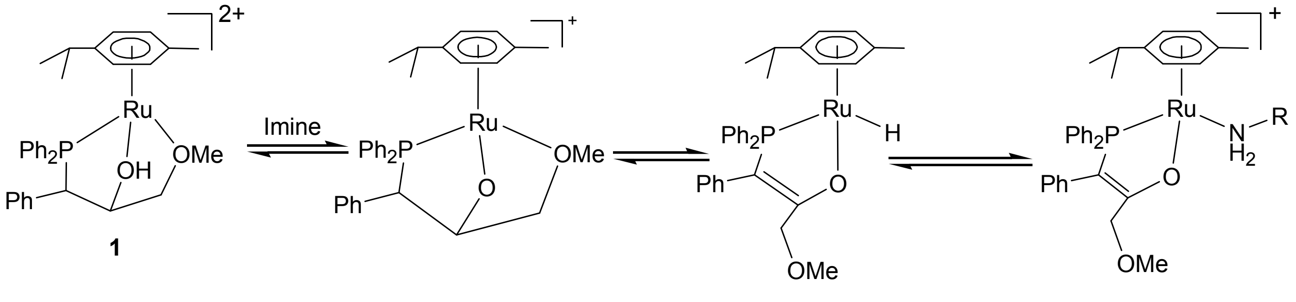
Work hypothesis and objective: Metallic catalysts usually activate organic substrates acting as a Lewis acid. Recently, we have reported the preparation of the 18 electron ruthenium complex [(η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru(κ^3*P,O,O'*-**POH**)][SbF$_6$]$_2$ (**1**, **POH** = (S_{C1},R_{C2})-Ph$_2$PC(Ph)H C(OH)HCH$_2$OMe).[1] The acidic properties of the OH group are enhanced by coordination to the metallic cation resulting in a Lewis acid assisted Brønsted-acid catalyst (LBA).[2] Here, we report the results obtained when attempting activation of the C=N bond of imines by **1**.



(R_{Ru},S_{C1},R_{C2})-**1**

Results: At RT, complex **1** catalyzes the Aza-Diels-Alder (ADA) reaction of aldimines with cyclopentadiene as well as the Aza-Friedel-Crafts (AFC) reaction between aldimines and indoles. In general, good conversions were obtained after some hours at RT with *endo*/*exo* molar ratios up to 94/6 for the ADA reaction. Important amounts of bisindole derivatives were obtained for the AFC reaction. In spite of **1** being enantiopure, racemic adducts were obtained in all cases. NMR solution studies under catalytic conditions explain the catalytic results obtained and reveal an unexpected stoichiometric reactivity of the ruthenium catalyst.



[1] Carmona, D.; Lamata, M. P.; Pardo, P.; Rodríguez, R.; Lahoz, F. J.; García-Orduña, P.; Alkorta, I.; Elguero, J.; Oro, L. A. *Organometallics* **2014**, *33*, 616-619.

[2] Yamamoto, H.; Futatsugi, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1924-1942.

P56

Reacciones de competición entre diferentes alcanos. Estudio de los efectos electrónicos y estéricos en la reactividad de los enlaces C-H

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A. Caballero,[a] **G. Asensio,**[b] **M. Etienne,**[c] **P. J. Pérez**[a]

[a] Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible y Departamento de Química y Ciencia de los Materiales, Universidad de Huelva 21007-Huelva. [b] Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, Burjassot 46100-Valencia. [c] Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France.

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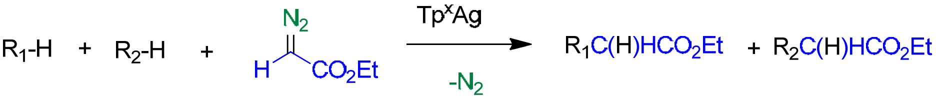
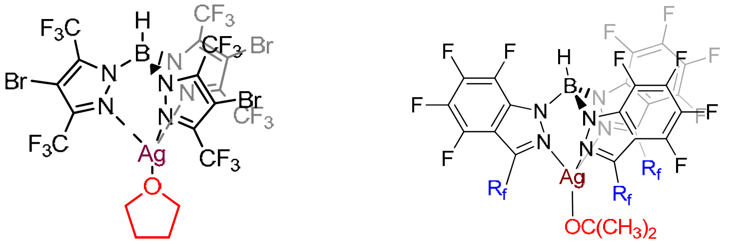
La gran inercia química de los hidrocarburos, debida principalmente a las altas energías de disociación de sus enlaces C-H, es el principal motivo de que se conozcan muy pocos ejemplos de funcionalización catalítica de alcanos, a pesar de la gran importancia de esta reacción.

Nuestro grupo de investigación ha desarrollado una familia de complejos de metales del grupo 11 capaces de catalizar de manera eficaz la inserción de grupos carbenos, procedentes de diazocompuestos, en los enlaces C-H de alcanos ligeros.[1,2] El objetivo de este trabajo es construir una escala de reactividades relativas de diferentes enlaces C-H, con entornos electrónicos y estéricos dispares, mediante experimentos de competición entre distintos alcanos frente a la reacción con EDA.





$R_f = CF_2CF_3$ $(F_{27}\text{-}Tp^{4Bo,3CF_2CF_3})Ag(CH_3COCH_3)$
$R_f = (CF_2)_3CF_3$ $(F_{39}\text{-}Tp^{4Bo,3(CF_2)_3CF_3})Ag(CH_3COCH_3)$

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[1] Pérez, P. J. *Alkane C-H Activation by Single-Site Metal Catalysis, Springer*, Dordrecht, 2012.
[2] Caballero, A.; Despagnet-Ayoub, E; Díaz-Requejo, M. M.; Díaz-Rodríguez, A.; González-Núñez, M. E.; Mello, R.; Muñoz, B. K.; Solo Ojo, W.; Asensio, G; Etienne, M.; Pérez, P. J. Science, **2011**, *332*, 835–838.

New acylrhodium(III) complexes derived from $PPh_2CH(Ph)CH_2CHO$

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Work hypothesis and objective:

It is known that $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) reacts with aldehyde-phosphane ligands like $PPh_2(o\text{-}C_6H_4CHO)$ to give acyl hydrido species, which can further react with bidentate N-donor ligands to afford cationic derivatives [1]. The aim of this work is to prepare new rhodium(III) complexes derived from $PPh_2CH(Ph)CH_2CHO$, with a chiral chain that can lead to a mixture of diastereoisomers, and to study their reactivity with aromatic diimines or amino-imines.

Results:

The reaction between $[RhCl(COD)]_2$ and $PPh_2CH(Ph)CH_2CHO$ (Rh:P = 1:1) in the presence of pyridine gives the acyl hydrido complex $[RhCl(H)(\kappa^2\text{-}PPh_2CH(Ph)CH_2CO)(Py)_2]$ (**1**), in which the hydride is exchanged by chloride in chlorinated solvents, to afford $[RhCl_2(\kappa^2\text{-}PPh_2CH(Ph)CH_2CO)(Py)_2]$ (**2**). Coordination of a second phosphane is achieved by the same reaction by using a Rh:P ratio of 1:2, to form complex $[RhCl(H)(\kappa^2\text{-}PPh_2CH(Ph)CH_2CO)(\kappa^1\text{-}PPh_2CH(Ph)CH_2CHO)(Py)]$ (**3**), where the phosphane is coordinated both as PC-bidentate (κ^2) and as P-monodentate (κ^1).

A similar species is prepared via reaction of the aromatic acyl complex $[RhCl(H)(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CO)(Py)_2]$ (**4**) with the aliphatic aldehyde-phosphane, to give $[RhCl(H)(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CO))(\kappa^1\text{-}PPh_2CH(Ph)CH_2CHO)(Py)]$ (**5**). Reaction of **5** with aromatic diimines such as 2,2'-bipyridine (bipy) and phenanthroline (phen) gives cationic complexes, isolated as a diastereomer mixture of $[RhCl(H)(NN)(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CO))(\kappa^1\text{-}PPh_2CH(Ph)CH_2CHO)]X$ (NN = bipy (**6**), phen (**7**); X = BF_4^-, BPh_4^-). When X = BPh_4^- diastereomers become separable by solubility. Reaction of **5** with amino-imines such as 8-aminoquinoline and 2-(aminomethyl)pyridine affords the formation of terdentate PNN ligands by condensation reaction of amine and aldehyde groups, in complexes $[RhCl(H)(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CO))(\kappa^3\text{-}PPh_2CH(Ph)CH_2CH{=}NN)]Cl$ (NN = NC_9H_6N (**8**), $NCH_2C_5H_4N$ (**9**)), also as a diastereomer mixture. In refluxing methanol, isomerisation occurs to afford a single diastereomer.

[1] M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M. R. Torres, M. Zarandona, *Organometallics* **2007**, 26, 5369-5376.

Síntesis y actividad antitumoral de nuevos metalodendrímeros de naturaleza carbosilano funcionalizados con complejos rutenio-areno.

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[b] *Dpto. Biomedicina y Biotecnología, Universidad de Alcalá de Henares. Alcalá de Henares, España.*
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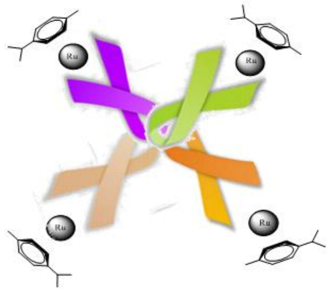
Según los datos proporcionados por la OMS, en 2030 se estima que haya 21.4 millones de nuevos casos de cáncer y 13.2 millones de muertes por esta enfermedad [1].

Recientemente, un nuevo grupo de macromoléculas, los metalodendrímeros, han sido estudiados como agentes anticancerígenos debido a que su multivalencia puede aumentar la posibilidad de que interaccionen con la diana molecular. En los últimos años varios grupos de investigación han sintetizado una serie de metalodendrímeros que contienen complejos de rutenio-areno funcionalizando la superficie del dendrímero tipo DAB [2].



Basándonos en estos resultados, nuestro grupo de investigación se ha centrado en la síntesis y en el estudio de las propiedades anticancerígenas de metalodendrímeros esféricos de naturaleza carbosilano, que contienen en su superficie complejos de rutenio con ligandos de tipo quelato N,O-, N,N- y N- de primera y segunda generación (G_1 y G_2), con 4 y 8 centros metálicos respectivamente, además de sus correspondientes complejos metálicos mononucleares (G_0). De todos ellos se ha medido la actividad antitumoral en diferentes líneas celulares cancerígenas: MCF-7, HeLa y HT-29 obteniéndose resultados muy prometedores.

[1] a) International Agency for Research on Cancer, World Health Organization. **2013**, Press Release N 223, 1-3. b) Global Cancer-Facts & Figures. *ACS*. **2007**, 2nd Edition, 1-58.

[2] a) P. Govender, A.K. Renfrew, C.M. Clavel, P.J. Dyson, B. Therrien, G.S. Smith. *Dalton Trans*. **2011**, 40, 1158-1167. b) P. Govender, L.C. Sudding, C.M. Clavel, P.J. Dyson, B. Therrien, G.S. Smith. *Dalton Trans*. **2013**, 42, 1267-1277.

Chiral Brønsted Acid Catalysts. Activation of Methyl 3,3,3-trifluoropyruvate by Hydroxymethylpyridine Containing Half-sandwich Complexes

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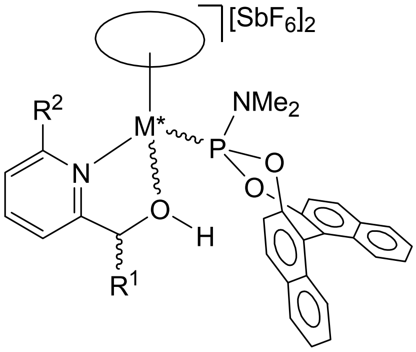
Work hypothesis and objective: Coordination of a hydroxyl group to a metallic Lewis acid strongly enhances its acidity. The resulting complexes potentially become Lewis acid assisted Brønsted-acid (LBA) catalysts.[1] We have recently prepared complexes of formula [(η^n-ring)M(**NOH**){**(*R*)-P1**}][SbF$_6$]$_2$ ((η^n-ring)M = (η^5-C$_5$Me$_5$)Rh, (η^5-C$_5$Me$_5$)Ir, (η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru) that contain the hydroxyl group of the hydroxypyridine ligand and the phosphoramidite (*R*)-monophos (**(*R*)-P1**, Scheme) coordinated to a cationic metal complex. Our aim is to apply these complexes as well as their analogues with other related phosphoramidite ligands (**P***) as enantioselective metallic Brønsted-acid catalysts.



Results: The hydroxyl group in complexes [(η^n-ring)M(**NOH**)**P***][SbF$_6$]$_2$ is deprotonated by soft mineral bases such as Na$_2$CO$_3$ rendering mono- and bi-nuclear compounds of formulae [(η^n-ring)M(**NO**){**(*R*)-P1**}][SbF$_6$] and [{(η^n-ring)M(κ^2*N*,*O*-μ-O-**NO**}$_2$][SbF$_6$]$_2$, respectively, showing the acidic properties of this group. The proton of the coordinated hydroxypyridine ligand is able to activate the carbonyl group of methyl 3,3,3-trifluoropyruvate towards the Friedel- Crafts addition of indoles. Quantitative conversion is achieved in a few minutes, at -70ºC, with e. e. up to 82 %. On the one hand, the chiral metallic cation enhances the acidity of the OH protons and, on the other it governs the stereochemistry of the catalytic process. The findings reported in this work may broaden the scope of Brønsted-acid catalysis: active Brønsted sites, such as OH, NH or SH functionalities, coordinated to appropriate metallic fragments could render new active Brønsted-acid catalysts. Notably, from chiral metallic fragments enantioselective catalysts could be derived.

[1] Yamamoto, H.; Futatsugi, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1924-1942.

Triphenylene-based metallomesogens: modulation of the mesogenic and electronic properties by metal fragments

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Bertrand Donnio,[2] **Pablo Espinet**[1]

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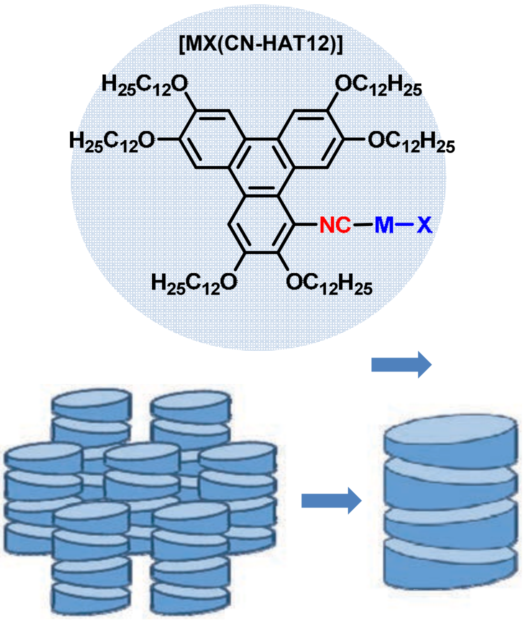
Work hypothesis and objective:

Discotic liquid crystals are useful systems for the synthesis of soft functional materials like nanoscale conductive devices, field-effect transistors or photovoltaic solar cells. Substituted triphenylenes have been widely used for this purpose. They are classical organic systems with many available procedures to modify and connect different groups to the aromatic core in order to modulate their properties [1]. Discotic liquid crystals based on triphenylene also are appropriate candidates for the synthesis of metallomesogens incorporating the characteristic properties of metal-containing molecules such as luminescence, conductivity or magnetism to obtain new materials. However, there are just a few examples of metallomesogens based on triphenylene reported in the literature [2].

[1] S. Kumar, *Chem. Soc. Rev.*, **2006**, *35*, 83-109; S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.*, **2007**, *36*, 1902-1929.
[2] E. Tritto, R. Chico, G. Sanz-Enguita, C. L. Folcia, J. Ortega, S. Coco, P. Espinet, *Inorg. Chem.*, **2014**, *53*, 3449-3455; J. L. Schulte, S. Laschat, R. Schulte-Ladbeck, V. von Arnim, A. Schneider, H. Finkelmann, J. *Organomet. Chem.*, **1998**, *552*, 171-176; S. Kumar, S. K. Varshney, *Liq. Crystals*, **2001**, 28, 161-163; A. N. Cammidge, H. Gopee, Chem. Comm., 2002, 966-967; B. Mohr, G. Wegner, K. Ohta, *Chem. Comm.*, **1995**, 995-996

Results:

We have prepared the ligand 1-isocyano-2,3,6,7,10,11-hexadodecyloxytriphenylene (CN-HAT12) and its corresponding organometallic complexes [AuX(CN-HAT12)] (X = Cl, C_6F_5, $C_6F_4OC_8H_{17}$, $C_6F_4OC_{10}H_{21}$), [(μ-4,4´-$C_6F_4C_6F_4$){Au(CN-HAT12)}$_2$], [PtI_2(CN-HAT12)$_2$] and [Ag(CN-HAT12)$_2$]BF_4. The free isocyanide ligand and the gold complexes exhibit hexagonal columnar mesophases. The coordination of the triphenylene-based ligand to the gold fragments produces an important increase of the range of existence of the mesophase. The electronic properties of all the compounds have also been studied. Cyclic voltammetric measures reveal a slight stabilization of the HOMO and the LUMO of these systems with the coordination of the isocyanide to the metallic fragment. The energy gap between the two frontier orbitals is smaller in the complexes respect to the free isocyanide ligand. All the compounds display luminescence in solution generated by π-π* transitions located in the triphenylene moiety.



Hydrogenation of N-heterocycles Catalyzed by Rh Nanoparticles Supported on Poliammino-borane

María L. Buil,[a] **Miguel A. Esteruelas**,[a] **Elisa Larraz**,[a] **Lynay Santacruz**,[b] **Alexandr Shafir**,[b] **Adelina Vallribera**.[b]
[a]Departamento de Química Inorgánica-Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain and [b]Department of Chemistry, Universitat Autònoma de Barcelona, Campus UAB,08193 Cerdanyola del Vallès, Barcelona, Spain.

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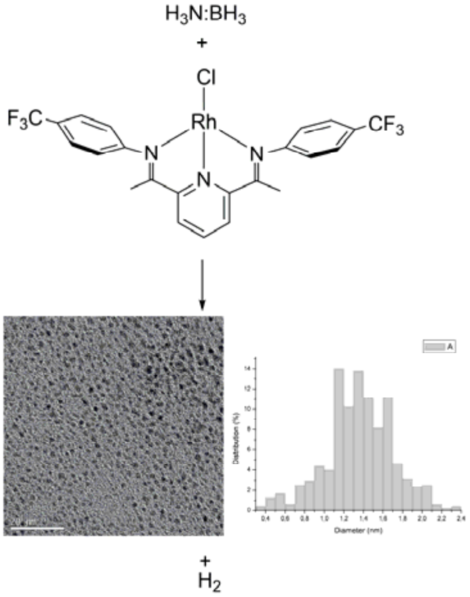
Work hypothesis and objective:

Catalytic hydrogenation of nitrogen heterocycles as a possible way to store hydrogen in organic liquids, and selective reduction of quinolones to 1,2,3,4-tetrahydroquinolines may lead to important intermediates for the synthesis of bioactive compounds.[1] Associated to this process is the use of hydrogen gas. The need for an easily transportable source of hydrogen has attracted considerable attention in the context of novel environmentally benign energy sources. Ammonia borane (H_3N-BH_3) appears attractive in view of its high thermal stability and hydrogen content (19.6 % by weight).[2] Unfortunately, the ammonia−borane dehydrogenation generally leads to polymeric materials, which are difficult to recycle.

Results:

A new catalyst composed of Rh nanoparticles supported on poliammino borane has been prepared by dehydropolimerisation of H_3N-BH_3 by RhCl[2,6-bis-{1-(4-trifluoromethylphenyl)iminoethyll}pyridine] under mild conditions, and characterized by TEM. This material has proved to be an efficient catalyst for the hydrogenation of N-heteroaromatic compounds under mild conditions in terms of pressure and temperature. Moreover this catalyst can be easily recovered and reused in 6 consecutives cycles in the hydrogenation of pyridine without loss of activity.



[1] (a) R. H. Crabtree, *Energy Environ. Sci.* **2008**, *1*, 134.(b) S.-L. Murahashi, Y. Imada, Y. Hirai, *Chem. Soc. Jpn.* **1989**, *62*, 2968.
[2] G. R. Whittell, I. Manners, *Angew. Chem. Int. Ed.* **2011**, *50*, 10288.

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Computational insights into copper-catalyzed trifluoromethylation of aryl iodides with CF_3SiEt_3

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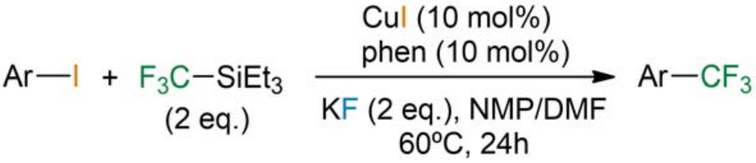
Work hypothesis and objective:

Trifluoromethylation has become a relevant topic in agrochemical and medicinal chemistry. Even so, mechanistic studies of the related metal-catalyzed CF_3 transfer processes are particularly scarce. In this report a plausible mechanism for the first copper-catalyzed trifluoromethylation of aryl iodides with triethyl(trifluoromethyl)silane (CF_3SiEt_3)[1] has been studied in detail with DFT calculations, aiming to improve the understanding of the reaction and leading to the proposal of new and more effective catalysts.



$$\mathrm{Ar{-}I} + \underset{(2\ \mathrm{eq.})}{\mathrm{F_3C{-}SiEt_3}} \xrightarrow[\substack{\text{KF (2 eq.), NMP/DMF} \\ \text{60}^{\circ}\text{C, 24h}}]{\substack{\text{CuI (10 mol\%)} \\ \text{phen (10 mol\%)}}} \mathrm{Ar{-}CF_3}$$

Results:

The main issues in this reaction, namely the trifluoromethyl transmetalation and the substrate activation, have been addressed and the obtained results clearly agree with the experimental observations, which state that electron-poor aryl iodides react faster than the electron-richer analogues.

Many different possible pathways were investigated for the fluorine-triggered trifluoromethyl transfer from CF_3SiEt_3 to the copper (I) catalyst. The computed results indicate that this process is, in truth, not a transmetalation but a ligand substitution process where the CF_3^- anion displaces the iodide on the active catalyst. Once the Cu–CF_3 complex is formed the reaction proceeds by following the typical oxidative addition/reductive elimination sequence through the corresponding copper (III) intermediates. Other substrate activation pathways *e.g.* σ-bond metathesis, often proposed in the literature, were ruled out since the energy requirements were found to be much higher. The rate-limiting step of the whole catalytic cycle corresponds to the oxidative addition stage, which is indeed more energy demanding for electron-rich aryl iodides.

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Nuevo Sistema Catalítico de Cobre Inmovilizado para las Reacciones de Transferencias de Carbenos en Flujo Continuo.

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[a]Laboratorio de Catálisis Homogénea. Dpto. de Química y Ciencia de los Materiales, Unidad Asociada al CSIC, Centro de Investigación en Química Sostenible (CIQSO), Universidad de Huelva, Campus de El Carmen, 21007-Huelva. [b]Instituto Catalán de Investigaciones Químicas (ICIQ), Avda de los Países Catalanes 16, 43007 Tarragona.

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La catálisis heterogénea presenta como ventaja en comparación con la homogénea la posibilidad de reciclar y reutilizar la especie metálica activa, lográndose así, procesos más sostenibles con el medio ambiente. En el caso que este proceso se lleve a cabo en flujo continuo, se consigue además, disminuir los costes y reducir el tiempo de operación.

En la actualidad existen bastantes ejemplos de catalizadores soportados que son activos en la transferencia de carbenos a olefinas,[1] aunque son muy escasos los ejemplos conocidos para la transferencia a otro tipo de sustratos saturados o insaturados[2], ni en batch ni en condiciones de flujo continuo.

Recientemente, uno de nuestros grupos, ha desarrollado un nuevo sistema catalítico heterogéneo basado en cobre[3] mediante la unión a un polímero orgánico con ligandos de tipo tris(triazolil)metano [Pol-Cu$^+$] (Fig. 1).

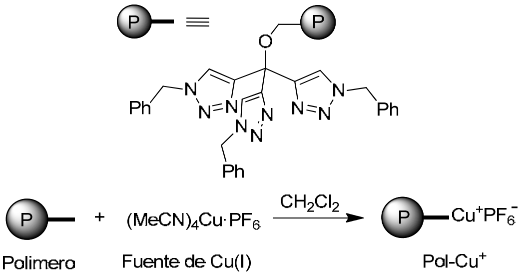


Figura 1

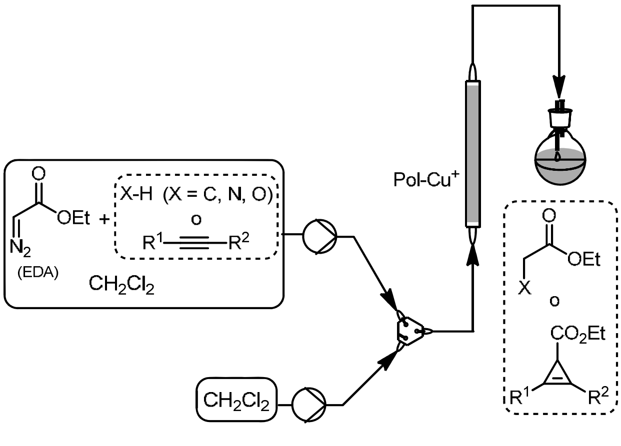


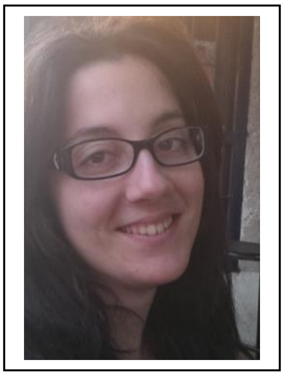
Figura 2

En esta comunicación se presentarán los resultados obtenidos (conversiones, selectividades, tiempos de operación, etc) en la reacción de transferencia de carbenos desde EDA a diferentes sustratos (Alcanos cíclicos, THF, Aminas, Alcoholes, y Alquinos) catalizada por este sistema de cobre soportado en el polímero e inmovilizado en una columna, de modo que es posible operar en flujo continuo.

En la Figura 2 se muestra un esquema del procedimiento experimental utilizado.

[1] Lim, J.; Riduan, S. N.; Lee, S. S.; Ying, J. Y. *Adv. Synth. Catal.* **2008**, *350*, 1295. [2] Fraile, J. M.; García, J. I.; Mayoral, J. A.; Roldán, M. *Org. Lett.* **2007**, *9*, 731. [3] Ozkal, E.; Özçubukçu, S.; Jimeno, C.; Pericàs, M. A. *Catal. Sci. Technol*. **2012**, *2,* 195.

Synthesis and characterization of copper-amine adducts. Reactivity toward small molecules.



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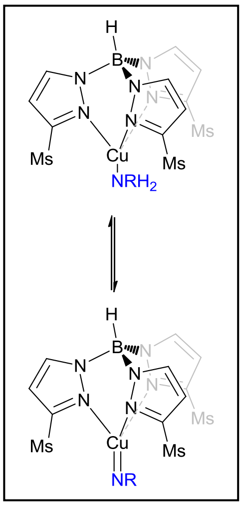
Work hypothesis and objective:

Late transition metals complexes bearing imido ligand has attracted the attention of the chemists in recent years due to these kinds of complexes are involved in a range of nitrene [NR] transfer reactions to unsaturated substrates and C−H bonds.[1] Among the late transition metals, catalysts based on copper show high activities.[2] However, few examples of isolation or detection of copper-nitrene species have been reported.[3]

Our work has been focused on the preparation of $Tp^xCu(NRH_2)$ amine adducts (Tp^x = bulky trispirazolylborate ligand), which can be used as starting material for the synthesis of copper-nitrene complexes.

Results:

In this contribution we describe the isolation and fully characterization of different copper-amine adducts. In addition, the study of the reactivity of these complexes with diazocompounds toward other N-H functionalized products.[4]



[1] J. F. Berry. *Comments Inorg. Chem.* **2009**, *30*, 28.

[2] L. Maestre, W. M. C. Sameera, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez, *J. Am. Chem. Soc.* **2013***, 135,* 1338.

[3] Y. M. Baidei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari, T. H. Warren, *Angew. Chem. Int. Ed.* **2008**, *47*, 9961.

[4] J. L. Klinkenberg, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2011**, *50*, 86.

Quantitative relationship between the structure and the nucleophility of trivalent boron compounds

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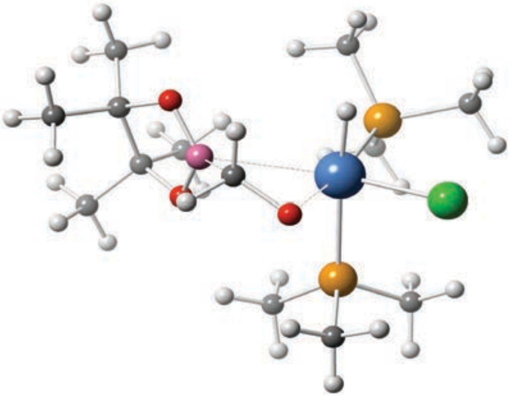
Work hypothesis and objective:

Most trivalent boron compounds are electrophiles due to the lack of two electrons to fill the outer orbital of the boron atom. However, these compounds can change their reactivity from an electrophilic character to a nucleophilic behaviour by changing the nature of the substituents on the boron atom.[1] This tuneable reactivity show potential application in organic synthesis. Our group had defined computational descriptors to build a *tendency map* that classifies the boryl fragments according to their nucleophilic character.[2] In a step forward, we pursue to set a quantitative relationship between the structural and electronic properties of boryl compounds and their nucleophilic reactivity.



Results:

The study covers a full range of boryl fragments that are bonded to main-group metals and coordinated to transition-metals. To define a quantitative dependent variable that measures the nucleophilic activity, we made use of the boryl addition to formaldehyde and computed its free energy barrier. Using multivariate techniques, we were able to generate mathematical models that correlate well with computed reactivity and that show predictive ability ($q^2 > 0.7$). These models indicate that the polarity of the M-B bond is the key factor.

[1] J. Cid, H. Gulyás, J. J. Carbó, and E. Fernández, Chem. Soc. Rev. **2012**, *41*, 3558-3570.

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Multifunctional Iridium-Zr-MOF for N-alkylation of amines with alcohols and hydrogenation of arenes

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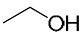
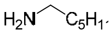
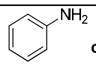
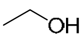
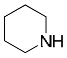
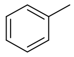
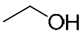
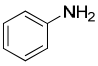
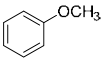
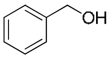
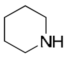
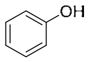
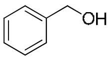
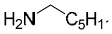
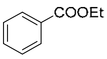
Work hypothesis and objective:

Zr-based MOF (UiO66-NH_2) has a large specific surface area and pore size as well as good chemical resistance to water and organic solvents, which result in desirable properties for catalytic applications. This highly stable material was selected as support.We have developed a simple and efficient method for new readily recoverable hybrid catalyst that combines the catalytic activity of transition-metal complexes with the architecture of metal organic frameworks (MOFs) and their application for cascade reactions [1], N-akylation of alcohols [2] and hydrogenation of arenes [3].

Results:

In the tested reactions, **UiO-66-LIr** can be recovered by simple filtration in air and reused without significant loss of catalytic activity, at least after 5 cycles while framework structures are maintained.

N-Alkylation			Hydrogenation		
Alcohol	**Amine**	**TOF (h^{-1})**	**Substrate**	**Conv. (%) (h)**	**TOF (h^{-1})**
		**940**	 c	**98 (10)^c**	**85**
		**450**		**100 (5)**	**98**
		**570**		**65 (24)**	**60**
		**202**		**85 (6)**	**110**
		**980**		**90 (5)**	**235**

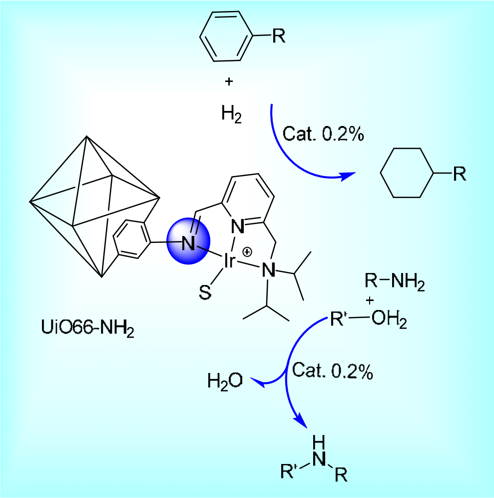


Figure 1.

[1] a) M. PINTADO-SIERRA, A. M. RASERO-ALMANSA, A. CORMA, M. IGLESIAS, F. SÁNCHEZ, *J. Catal.*, **2013**, *299*, 137. [2] A. M. RASERO-ALMANSA, A. CORMA, M. IGLESIAS, F. SÁNCHEZ, *ChemCatChem*, **2014**, DOI: 10.1002/cctc.201402101. [3] M. IGLESIAS, A. M. RASERO-ALMANSA, A. CORMA, F. SÁNCHEZ, *Green Chem,* **2014**, DOI: 10.1039/C4GC00581C.

Acknowledgment. The authors thank the MINECO of Spain (Projects MAT2011-29020-C02-02 and Consolider Ingenio 2010-MULTICAT.

Compuestos de oro(I) luminiscentes y/o mesógenos vía click chemistry.

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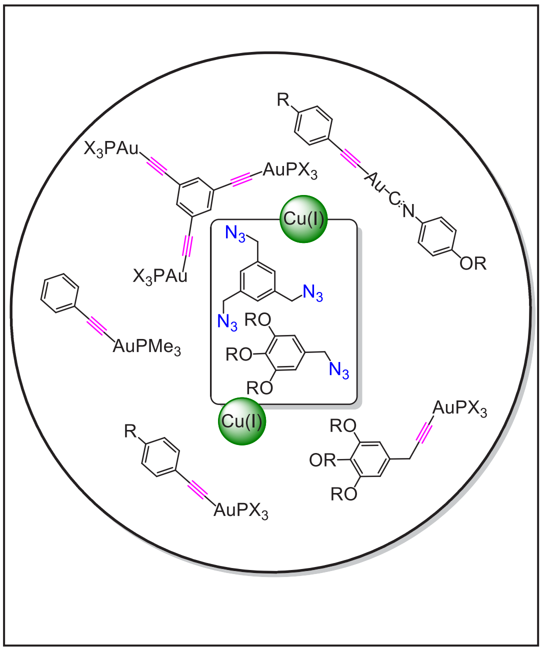
Hipótesis de trabajo y objetivos:

La reacción de cicloadición de azidas y alquinos de Huisgen catalizadas por cobre (I), ejemplo clásico de la “click chemistry”, se ha usado en ciencia de materiales para construir nuevas estructuras. Mediante esta reacción se han obtenido moléculas orgánicas calamíticas y discóticas con potenciales propiedades mesógenas, luminiscentes y optoelectrónicas [1]. Los acetiluros de oro(I) son moléculas bien conocidas, con propiedades luminiscentes en algunos casos, y que originan con facilidad materiales que muestran comportamiento de cristal líquido. Nos proponemos sintetizar nuevos compuestos de oro(I) combinando acetiluros o azidas de oro(I) con azidas o acetilenos orgánicos, que puedan presentar propiedades mesógenas y ópticas.

Resultados:

Se sintetizaron diferentes acetiluros de oro con y sin cadenas alifáticas que se hicieron reaccionar con una azida bencílica con y sin cadenas hidrocarbonadas para obtener estructuras calamíticas; además, con 1,3,5-(triazidometil) benceno para preparar compuestos discóticos. Por otro lado se sintetizaron azidas de oro(I) para hacerlas reaccionar con acetilenos y con acetiluros de oro(I).Todas las reacciones se llevaron a cabo usando $[Cu(NCMe)_4]PF_6$ como catalizador de la reacción.



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Agradecimientos: Comisión Interministerial de Ciencia y Tecnología (Proyecto CTQ2011–25137) y la Junta de Castilla y León (Proyecto VA302U13)

Face to face activation of phenylselenium boranes with α,β-unsaturated carbonyl substrates: facile synthesis of C-Se bonds

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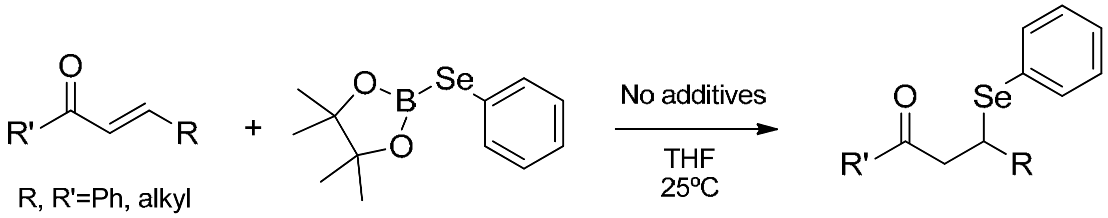
xavier.sanz@urv.cat

Work hypothesis and objective:
There has been recent considerable interest in the generation of organoselenium compounds for their extensive applications. Of particular significance is the synthesis of selenium substituted carbonyl compounds which are well known to act as enone β-anion synthons.[1] In this context, we decided to prepare new PhSeBpin (**1**) species and examine its reactivity with a scope of α,β-unsaturated carbonyl compounds from an experimental and computational point of view.

Results:

Quaternization of one boron atom in species containing B-B and B-E bonds (E= elements from group 14) facilitates the heterolytic cleavage of these stable bonds.[2] Now, we have found that the simple approach of the substrate α,β-unsaturated carbonyl compounds to the selenium boron species PhSeBpin (**1**), promotes the PhSe transfer from the reagent to the substrate, in a selective manner. Remarkably, the direct addition does not require the presence of any transition metal complex as catalyst or bases or even co-solvents such as MeOH, unlike other E-Bpin additions. A theoretical study supports the obtained results.



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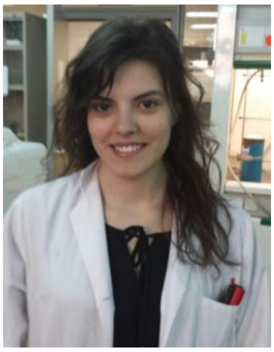
[1] a) C.-M., Chu, S. Gao, M. N. V. Sastry, C.-W. Kuo, C. Lu, J.-T. Liu, C.-F. Yao, *Tetrahedron*, **2007**, 1863; b) B. Srinivas, V. P. Kumar, R. Sridhar, V. P. Reddy, Y. V. D. Nageswar, K. R. Rao, *Helv. Chim. Acta*, **2009**, *92*, 1080; c) W. R. Leonard, T. Livinghouse, *J. Org. Chem.*, **1985**, *50*, 730.

[2] a) C. Kleeberg, L. Dang, Z. Lin, T. B. Marder, *Angew. Chem., Int. Ed.*, **2009**, *48*, 5350; b) C. Pubill-Ulldemolins, A. Bonet, C. Bo, H. Gulyás and E. Fernández, *Chem. Eur. J.*, **2012**, *18*, 1121; c) C. Kleeberg, A. G. Crawford, A. S. Batsanov, P. Hodgkinson, D. C. Apperley, M. S. Cheung, Z. Lin, T. B. Marder, *J. Org. Chem.*, **2012**, *77*, 785; d) C. Kleeberg, *Dalton Trans.*, **2013**, *42*, 8276; e) H. Braunschweig, A. Damme, R. D. Dewhurst, T. Kramer, T. Kupfer, K. Radacki, E. Siedler, A. Trumpp, K. Wagner, Ch. Werner, *J. Am. Chem. Soc.,* **2013**, *135*, 8702; f) H. Braunschweig, A. Damme, J. O. C. Jimenez-Halla, T. Kupfer, K. Radacki, *Angew. Chem., Int. Ed.*, **2012**, *51*, 6267; g) H. Braunschweig, A. Damme, T. Kupfer, T., *Chem. Commun*. **2013**, *49*, 2774.

Dendrones de naturaleza carbosilano con ferroceno en el punto focal. Síntesis y aplicaciones biomédicas.



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Biomateriales y Nanomedicina (CIBER-BBN) (España).
[2] *Departamento de Biomedicina y Biotecnología. Universidad de Alcalá.*
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El ferroceno es uno de los complejos organometálicos más utilizado debido principalmente a sus propiedades electroquímicas, aunque otras de sus características como su gran estabilidad o facilidad de funcionalización hacen que sea posible su aplicación en diversas áreas de la química. Dentro de la rama de la biomedicina, se conocen muchos ejemplos en los que este sistema mejora la actividad biológica de diversas moléculas orgánicas aumentando su capacidad antifúngica o antitumoral [1]. Por otro lado, los dendrímeros han mostrado interesantes propiedades como transportadores de material génico, fármacos o en su uso como antibacterianos, antivirales y anticancerígenos. Sin embargo, en la bibliografía hay pocos sistemas dendríticos solubles en agua, ninguno de ellos de naturaleza carbosilano, que contengan ferroceno y que aúnen las ventajas de ambos sistemas [2]. Los dendrímeros de naturaleza carbosilano han mostrado excelentes propiedades biomédicas [3], las cuales sería interesante combinar con las aportadas por el ferroceno mediante la formación de sistemas hidrosolubles.

Se ha llevado a cabo la síntesis y caracterización de nuevos sistemas dendríticos de generaciones 1-3 solubles en agua con ferroceno en el punto focal a partir de formilferroceno y cuñas dendríticas con un grupo amino en el punto focal (NH_2) y fragmentos alilo en la periferia. La incorporación de los grupos amonio se realiza siguiendo una metodología divergente, mediante reacciones de hidrosililación. Estos metalodendrímeros han mostrado resultados prometedores en ensayos de actividad antibacteriana frente a E.*Coli* y S. *Aureus* y ensayos de citotoxicidad mediante MTT en células cancerígenas MCF-7 y HT-29.

[1] A.M. Allahverdiyev, M. Bagirova, E.S. Abamor, S.C. Ates, R.C. Koc, M. Miraloglu, S. Elcicek, S. Yaman, G. Unal, *Infect. Drug Resist.*, **2014**, 6, 99.
[2] A.M. Caminade, R. Laurent, A. Ouali, J.P. Majoral, *Inorg. Chim. Acta,* **2014***,* 409, 68.
[3] I. Heredero-Bermejo, J.L. Copa-Patiño, J. Soliveri, S. García-Gallego, B. Rasines, R. Gómez, F.J. de la Mata, J. Pérez-Serrano, *Parasitol. Res.*, **2013,** 112(3), 961.

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Obtención de hidrógeno a partir de aductos aminoborano catalizada por comejos de rutenio

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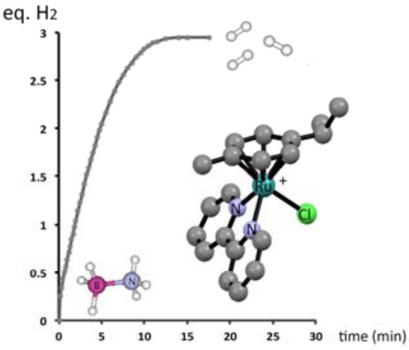
Hipótesis de trabajo y objetivo:

El uso del hidrógeno como vector energético es una prometedora alternativa a los combustibles fósiles pero su transporte y almacenamiento seguros suponen aún uno de sus hándicap para su implementación. Una posible solución a dichos problemas es el uso de hidruros metálicos, siendo el amoniaco borano (AB) uno de los ejemplos más prometedores por su elevado contenido gravimétrico en hidrógeno.

La liberación química de este hidrógeno del AB puede llevarse a cabo mediante deshidrogenación o hidrólisis. La hidrólisis es la opción más atractiva, ya que lleva a la liberación de 3 equivalentes de hidrógeno, la mitad del cual proveniente del agua. Sorprendentemente, existen contados ejemplos de catalizadores homogéneos para esta reacción.[1,2]

Resultados:



Se ha demostrado que el [Ru(p-cym)(bipy)Cl]Cl es capaz de liberar 2,8 equivalentes de H_2 en menos de 10 minutos a 40ºC operando en disolventes no desoxigenados y mezclas acuosas; además, el sistema permanece activo 6 ciclos catalíticos consecutivos.

Por otro lado, el mismo sistema cataliza en ausencia de disolvente la deshidrogenación del dimetil amino borano. El producto es una especie cíclica $[(Me_2NBH_2)_2]$ que sublima y cristaliza sobre las paredes del recipiente, en un proceso del que no existen precedentes.

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[2] D. J. Nelson, B. J. Truscott, J. D. Egbert and S. P. Nolan, *Organometallics*, **2013**, *32,* 3769-3772.

Organocatalytic synthesis of aminoalcohols through β- boration of α-β unsaturated imines generated “in situ”

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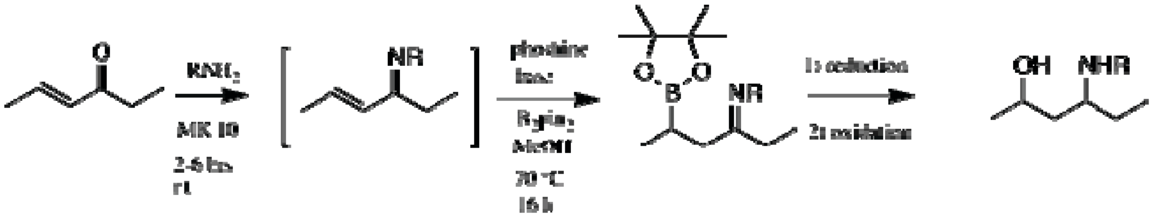
Work hypothesis and objective:

Enantioenriched aminoalcohols are stalwart linchpins in organic synthesis. In fact, these compounds are involved in, amongst others, drug synthesis[1] and as chiral auxiliaries[2] justifying in large part the considerable interest in them.

For this reason we started to think about new strategies to obtain aminoalcohols wherein the crucial step is the β-boration of α,β-unsaturated imines formed in situ, i.e. in the reaction medium. To achieve the desired β-borated product, a metal catalyst, such as Cu(I) is generally required.[3]

Results:

We were pleased to see that this reaction could also be performed in an organocatalytic fashion through the addition of a catalytic amount of a suitable phosphine. Additionally, when a chiral phosphine is used, moderate to high asymmetric induction with high conversion was also observed. In this presentation, we present our recent results in this area.



[1] a) S. Shibahara, S. Kondo, K. Maeda, H. Umezawa, M. Ohno*, J. Am. Chem. Soc*. 1972, 94,4353; b) Y.-F. Wang, T. Izawa, S. Kobayashi, M. Ohno, *J. Am. Chem. Soc*. 1982, 104, 6456. [2] a) B. M. Trost, V. Yeh, *Angew. Chem*. 2002, 114, 889; *Angew. Chem. Int. Ed*. 2002, 41, 861; b) Y. Ukaji, K. Yamamoto, T. Fukui, T. Fujisawa, *Tetrahedron Lett*. 1991, 32, 2919; c) S. E. Denmark, C. T. Chen, *J. Am. Chem. Soc*. 1992, 114, 10674 [3] a) C. Solé, E. Fernández, *Chem., Asian J,* 2009, 4, 1790; b) C. Solé, A. Whiting, H. Gulyás, E. Fernández. *Adv. Synth. Catalysis* 2011, 353, 376-384; c) C. Solé, A. Whiting, H. Gulyás, E. Fernández, *Chem. Eur J.,* 2011, 17, 14248; d) A. D. J. Calow, Andrei S. Batsanov, E. Fernández, C. Solé, A. Whiting. *Chem. Commun.* 2012, 48, 11401- 11403; e) A. D. J. Calow, Andrei S. Batsanov, A. Pujol, C. Solé, E. Fernández, *Org. Lett* 2013, 15, 4810-4813; f) A.D.J. Calow, C. Solé, A. Whiting, E. Fernández, *Chem Cat Chem.,* 2013, 8, 2233.

Exploring the anticancer properties of Ru(II) arene complexes

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Natalia Busto,[a] **Félix A. Jalón,**[b] **Blanca R. Manzano,**[b]
Ana M. Rodríguez.[b]

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b) Dpt. of Inorganic, Organic Chemistry and Biochemistry,
Universidad de Castilla-La Mancha, Ciudad Real, España.

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Work hypothesis and objective:

Ruthenium complexes are a good alternative to platinum anticancer drugs and some of them have even entered clinical trials. In particular, Ru(II) arene complexes such as RAPTA-C and their derivatives have shown promising anticancer properties [1]. In addition, DNA is thought to be one of the most sensitive targets for this kind of complexes, which are able to bind N7 of guanine after an activation by aquation step [2]. Our working hypothesis is that it is possible to fine-tune the anticancer properties of these specimens by mean of a subtle modification of their structural elements. Thus, the aim of this work is to design, synthesize and characterize different Ru(II) arene complexes, as well as to study their antitumor activity in several cancer cells. Moreover, we intend to establish possible correlations between the antiproliferative activity and other properties such as hydrophobicity and aqueous solubility and reactivity.

Results:

We have synthesized six new complexes with two different bidentate ligands (N-N = L1, L2) and different leaving groups (X = Cl, I and H_2O). All of them have been completely characterized by spectroscopic and analytic techniques. The aquation-anation equilibria have been studied under pseudo-pharmacological conditions. Moreover, the cytotoxic activity of the new derivatives will be presented and compared with that of similar compounds previously synthesized in our group.

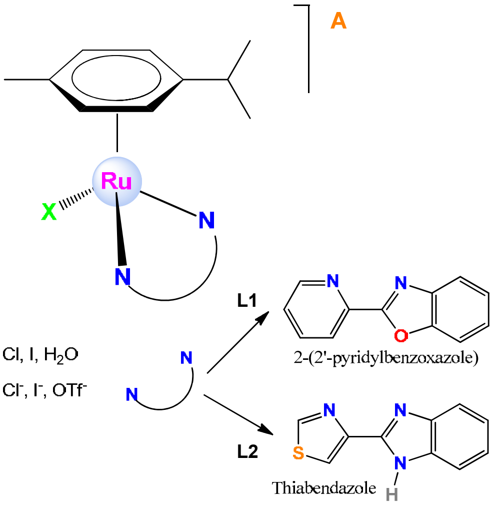

Figure 1. Synthesized complexes

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Second-Generation Amino Acid Furanoside Based Ligands from D-Glucose for the Asymmetric Transfer Hydrogenation of Ketones.

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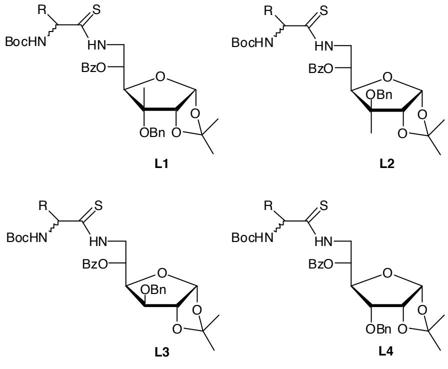
Work hypothesis and objective:

Enantiopure alcohols have important uses in the pharmaceutical, agrochemical, fragance, and flavor industries.[1] Asymmetric transfer hydrogenation (ATH) of prochiral ketones has proven to be a sustainable, efficient, mild, and versatile method for their synthesis.[2]

In this communication we present the use of a novel series of modular carbohydrate-based amino acid thioamide ligands (Figure 1) in the Rh-catalyzed ATH of aryl / alkyl ketones, including the less-studied heteroaromatic ketones.



R= (*S*)-*i*Pr, (*S*)-Ph, (*S*)-Bn, (*S*)-Me, H, (*R*)-*i*Pr

Figure 1

Results:

Excellent enantioselectivities comparables with the best one reported (up to 99% *ee*) were achieved for a wide range of aryl alkyl ketones, including less-studied heteroaromatic ketones. Interestingly, both enantiomers of the alcohol product could be obtained changing the absolute configuration of the thioamide substituent.[3]

[1] a) *Modern Reduction Methods* (Eds.: P.G. Andersson, I.J. Munslow), Wiley-VCH, Weinheim, **2008**; b) V. Farina, J. T. Reeves, C. H. Senanayake, J. J. Song, *Chem. Rev.* **2006**, *106*, 2734-2793.

[2] a) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300-1308; b) S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226-236; c) T. Ohkuma, R. Noyori in *Comprehensive asymmetric Catalysis I-III*, *Vol. 1* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, p. 199-246.

[3] M. Coll, O. Pàmies, H. Adolfsson, M. Diéguez*,* *ChemCatChem* **2013**, *5*, 3821-3828.

Reduction of Carbon Dioxide to Methane by a Nickel Boryl Pincer Catalyst

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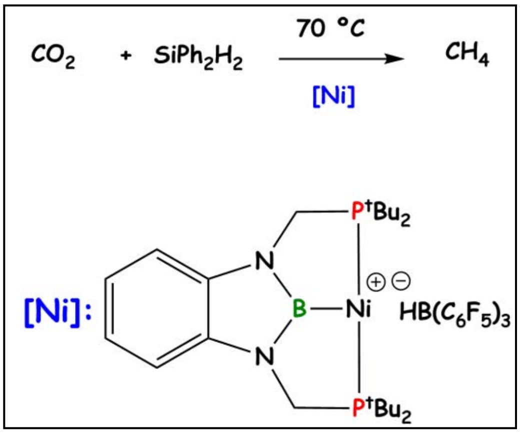
Carbon dioxide is a non-toxic, abundant, renewable and inexpensive C1 source and can potentially be transformed into hydrocarbon fuels that constitute alternatives to the use of fossil fuels in our current energy infrastructure. [1] In the last years, there has been an increasing interest in developing homogenous catalyst for the reduction of carbon dioxide to methanol or methane. Important advances have been achieved both employing transition-metal catalyst and metal-free systems.[2] However, carbon dioxide conversion is challenging due to its high thermodynamic stability and to date, only five catalysts can effectively accomplish the total reduction of carbon dioxide to methane. [3]



Here we describe the synthesis and characterization of the first nickel pincer complexes supported by a bis-phosphino-boryl (PBP) ligand and their use for the homogenously reduction of carbon dioxide to methane. The PBP-pincer nickel hydride derivative in combination with $B(C_6F_5)_3$ was found to be an excellent catalyst for this transformation employing diphenylsilane as the hydrogen source. Details on the mechanism based on the observed intermediates and DFT calculations will be given.

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One-pot synthesis of γ-ketoamides from γ-alkynoic acids and primary amines under solvent-free conditions: A cycloisomerization/amidation process catalyzed by $PdCl_2$.

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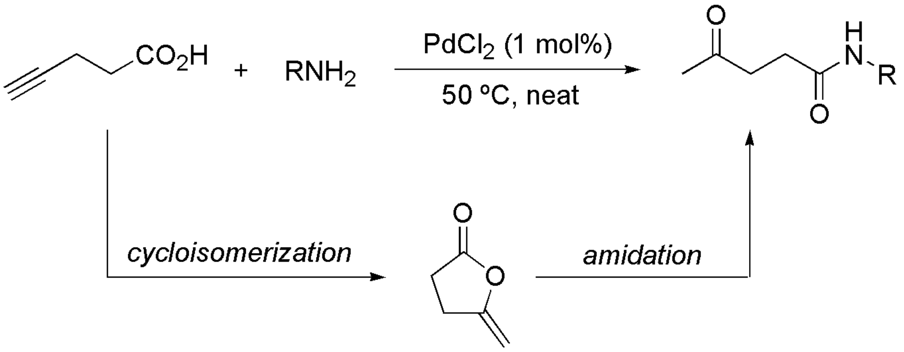
The replacement of multistep transformations by more straightforward "one-pot" processes has attracted considerable research efforts in the last decades due to the obvious advantages of the latter, *i.e.* they minimize the overall reaction time, the generation of chemical waste and the energy consumption, therefore limiting the global cost of the synthetic pathway.

Following with the recent interest of our group in the catalytic cycloisomerization of γ-alkynoic acids into enol-lactones [1], in this contribution we will present a simple and fully atom-economic protocol for synthesis of γ-ketoamides starting from γ-alkynoic acids and primary amides. The process involves a "one-pot" cycloisomerization/amidation cascade reaction catalyzed by inexpensive $PdCl_2$ under solvent-free conditions (Scheme 1).



Scheme 1: One-pot cycloisomerization/amidation cascade reaction for the synthesis of γ-ketoamides promoted by $PdCl_2$ under mild and neat conditions.

[1] (a) Tomás-Mendivil, E., Toullec, P. Y., Díez, J., Conejero, S., Michelet, V., Cadierno, V., *Org. Lett.* **2012**, *14*, 2520-2523; (b) García-Álvarez, J., Díez, J., Vidal, C., *Green Chem.* **2012**, *14*, 3190-3196; (c) Tomás-Mendivil, E., Toullec, P. Y., Borge, J., Conejero, S., Michelet, V., Cadierno, V., *ACS Catal.* **2013**, *3*, 3086-3098.

Synthesis and catalytic activity of Ruthenium based-P-stereogenic PNP complexes in Asymmetric Hydrogenation

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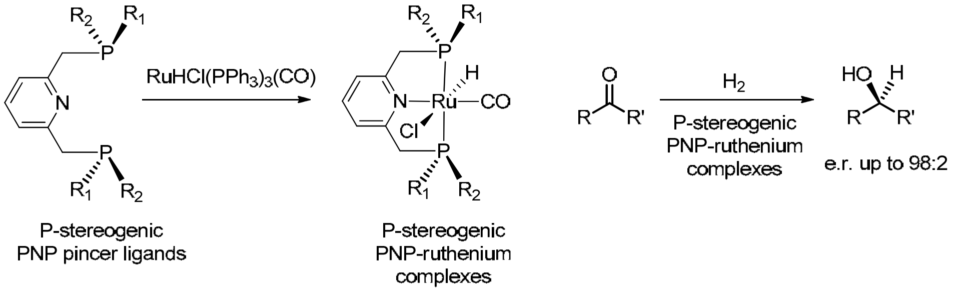
Work hypothesis and objective:

Pincer type ligands and their metallic complexes have received considerable attention since the late 1970s, as a result of their high activity, variability and stability. The pincer ligand platform has enabled the synthesis of multifunctional building blocks that are used in a wide variety of metal complexes applied in a great number of organic transformations, such as C-C and C-N forming bonds, hydrogenation reactions, dehydrogenation reactions, C-H or N-H activation, aldol reactions, hydroamination reactions, allylation of aldehydes or imines, supramolecular chemistry and photochemistry.[1] Among all possibilities of chirality in pincer ligands,[2] coordination of P-stereogenic phosphines to the metal center is an appealing strategy since an efficient and proximate chiral environment around the metal is created and thus, effective transfer of chirality might be expected.

Results:

A novel family of P-stereogenic PNP ligands has been synthesized as well as the corresponding PNP-ruthenium complexes. Their catalytic properties in asymmetric reduction of ketones have been investigated. Excellent conversions and enantiomeric ratios have been observed in a wide range of ketones.



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Efficient Ullmann-type synthesis of aryl sulfides using ligand –free nickel catalytic system.

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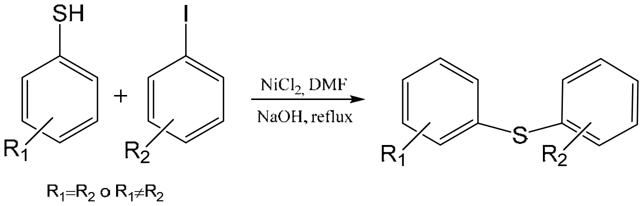
Work hypothesis and objective:

Transition metal-catalyzed cross-coupling reactions of aryl halides and aryl thiols provides a simples and efficient route for the synthesis of diaryl sulfides,[1] which are of significant importance to the pharmaceutical industry.[2] Copper,[3] palladium,[4] nickel[5] catalytic system have since been studied for this purpose. It is known that palladium compounds are found to be more effective than those of copper and nickel, but palladium has a high economic cost, in this case the nickel may provide alternative solutions to catalytic C-S cross-coupling to be an economical metal and similarity of its compounds with the palladium. Note that these nickel catalyst systems have certain limitations, usually require high temperatures,[5a] long reaction times,[5e] increased amount of catalyst,[5c] and low yields.[6] Our goal is to develop a nickel catalytic system with improved reaction conditions have been reported so far.

Results:

Herein we report that ligand-free nickel $NiCl_2{\cdot}6H_2O$ shows catalytic activity in C-S cross-coupling of thiols with aryl iodides. The optimal catalytic conditions involve 2.5% of $NiCl_2{\cdot}6H_2O$, NaOH in DMF at reflux. In these conditions corresponding aryl sulfides are obtained in excellent yields.



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Hiyama coupling reaction of aryl chlorides in water based on sulfonated N-heterocyclic carbene palladium (II) complexes

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The palladium-catalyzed Hiyama coupling reaction of organic halides with organosilanes in water has become an interesting alternative to the Suzuki and Stille reactions because organosilanes are agents in transmetallation with low toxicity, easy handling and high stability. In addition, the use of water as solvent has gained increasing attention for safety, inexpensive and environmental reasons. Recently, we have reported successful processes of synthesis of biphenyls and styrenes in water, using haloarenes (X = I, Br), organosilanes and [Pd(OAc)$_2$] as catalyst. However, this process is not effective with chloroarenes[1].

The new sulfonated N-heterocyclic carbene palladium (II) complexes prepared in our group showed excellent catalytic behavior in organic reactions carried out in aqueous media [2]. For this reason, we decide to study these complexes in the Hiyama coupling using aryl chlorides.

In this communication, we will show the results obtained in the reactions of arylsilanes and chloroarenes carried out in water. Notably, most of the tested subtrates afforded biphenyls at high temperatures with 2 mol % of [(IPr-SO$_3$)Pd(acac)Cl], TBAB and NaOH as promoter (eq. 1). The combination of the silanolate (previously isolated), basic aqueous, anaerobic media, TBAB and low Pd loadings allows reactions with good yields.

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P-S Ligands for the highly enantioselective Ir-catalyzed hydrogenation of unfunctionalized olefins.

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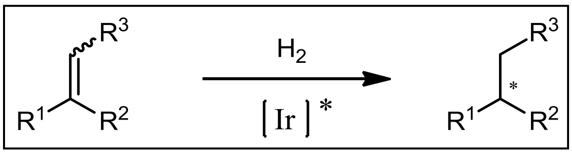
Work hypothesis and objective:

The asymmetric hydrogenation of olefins is one of the most powerful and sustainable transformations for preparing chiral compounds. Whereas the reduction of olefins containing an adjacent polar group has a long history, the hydrogenation of unfunctionalized olefins is less developed because these substrates have not adjacent polar group to direct the reaction.[1] Iridium complexes with chiral P-N ligands have become established as one of the most efficient catalyst types for this reaction. However, the possibility of changing the nature of the N-donor atom in these heterodonor ligands has only been contemplated very recently.[2] Here, we show a successful application of non-N donor heterodonor ligands, thioether-phosphite ligands, in the reduction of unfunctionalized olefins (Scheme 1).



Scheme 1. Ir-catalyzed asymmetric hydrogenation of unfunctionalized olefins

Results:

Excellent enantioselectivities (ee's up to 99%) have been obtained for a range of substrates, including challenging terminal disubstituted substrates, under standard conditions.

[1] See, for example: (a) X. Cui, K. Burgess, *Chem. Rev.* **2005**, *105*, 3272; b) S. J. Roseblade, A. Pfaltz, *Acc. Chem. Res.* **2007**, *40*, 1402; c) T. L. Church, P. G. Andersson, *Coord. Chem. Rev.* **2008**, *252*, 513; d) O. Pàmies, P. G. Andersson, M. Diéguez, *Chem. Eur. J.* **2010**, *16*, 14232; e) D. H. Woodmansee, A. Pfaltz, *Chem. Commun.* **2011**, *47*, 7912; f) Y. Zhu, K. Burgess, *Acc. Chem. Res.* **2012**, *45*, 1623.

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Highly nucleophilic dimolybdenum phosphinidene complexes: Unusual reactions with C-based electrophiles.

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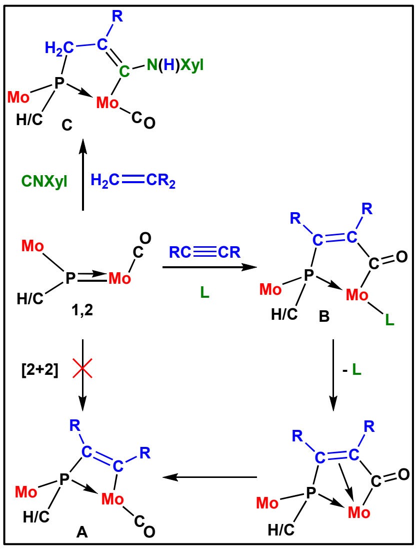
Work hypothesis and objective:

During the last years our group has developed selective synthetic routes for the preparation of dinuclear complexes having bridging phosphinidene ligands, which has allowed us to start a systematic study of the reactivity of these molecules. We have reported recently the synthesis of complexes $[Mo_2Cp\{\mu\text{-}\kappa^1:\kappa^1,\eta^5\text{-}P(C_5H_4)\}(HMes^*)(CO)_2]$ (**1**)[1] and $[Mo_2Cp_2(\mu\text{-}PH)(HMes^*)(CO)_2]$ (**2**)[2] (Mes* = 2,4,6-$C_6H_2{}^tBu_3$), both having asymmetric bridging phosphinidene ligands linking 17– and 15–electron metal fragments. This coordination mode has limited precedents in the literature, and the bonding in these compounds can be represented by several canonical forms,[3] some stressing the idea that its reactivity might be related to that of double or even triple M–C bonds. This has prompted us to develop a systematic study of the reactivity of these compounds, in particular when confronted with alkynes and alkenes.

Results:

Complexes **1** and **2** react with alkynes to give products having either 4-membered (in the absence of added ligands, **A**) or 5-membered phosphametallacyclic rings (in the presence of added ligands, **B**). However, according to our results both products follow from analogous multicomponent reaction pathways involving intermediate species with a pyramidal phosphinidene of increased nucleophilicity. Similarly, **1** reacts rapidly with electron poor alkenes in the presence of CO or CNR to give exclusively products having 5-membered phosphametallacycles (**C**). All these processes are highly regioselective, with the terminal carbon of the electrophile being bound to the P atom, and chemoselective, the ring is preferentially formed with the CNR (if added) rather than the CO ligands.



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P81

Rhodium-catalyzed hydration of nitriles: key role of the ligands.

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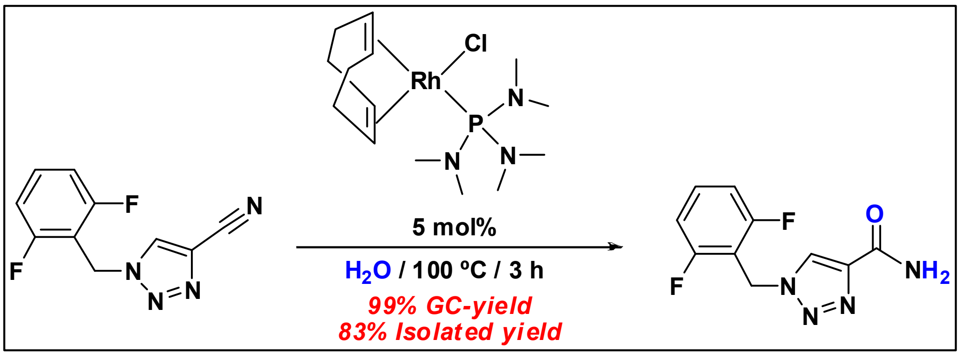
The hydration of organonitriles is a relevant transformation in both academia and industry because the products of the reaction, *i.e.* primary amides, are versatile synthetic intermediates, as well as useful building blocks for the manufacture of pharmaceutical molecules and engineering polymers. Recent works by us and others have demonstrated that ruthenium complexes containing cooperative phosphine ligands are particularly effective catalysts for this transformation [1]. Following with our interest in this chemistry, several rhodium(I) complexes [RhCl(COD)(PR$_3$)] have been now synthesized and evaluated as potential catalysts for the selective hydration of nitriles into amides in water [2]. Among the different phosphines screened, those of general composition P(NR$_2$)$_3$, capable to establish H-bonding with water, led to the best results. In particular, complex [RhCl(COD){P(NR$_2$)$_3$}] was able to promote the selective hydration of a large range of nitriles in water without the assistance of any additive, showing a particularly high activity with heteroaromatic and heteroaliphatic substrates. As an example, through this methodology, the antiepilectic drug rufinamide was synthesized in high yield from the appropriate nitrile (see Scheme).



[1] R. García-Álvarez, P. Crochet, V. Cadierno, *Green Chem.*, **2013**, *15*, 46 and references therein.

[2] Full details of this work can be found in: E. Tomás-Mendivil, R. García-Álvarez, C. Vidal, P. Crochet, V. Cadierno, *ACS Catal.*, **2014**, *4*, 1901.

Synthesis of N- and S-Containing Heterocycles by Insertion of Internal Alkynes in Primary Amines and Thiols Catalysed by Ru(II).

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Work hypothesis and objective:

The functionalization and modification of organic molecules through C-H bond activation is one of the most active areas of the chemistry nowadays. The use of organometallic complexes as synthetic tools constitutes a well-established alternative to the classical organic methods, mainly due to the relative easiness with which the C-H bond is activated. More specifically, the use of orthometallated derivatives affords fully regio- and chemoselective processes, due to the selectivity provided by the directing group.[1]

Results:

This contribution reports the synthesis of isoquinolines,[2] benzoisoquinolines, thieno[3,2-c]pyridines,[2] thieno[2,3-c]pyridines,[2] pyridines, thiols and thiopyranes (Figure 1) which can be catalytically synthesized from thienomethylamines, benzyl- and naphthylmethylamines, allylamines and thiols and internal alkynes using Ru(II) catalyst and Cu(OAc)2 as oxidant. These and other results will be described in this communication.

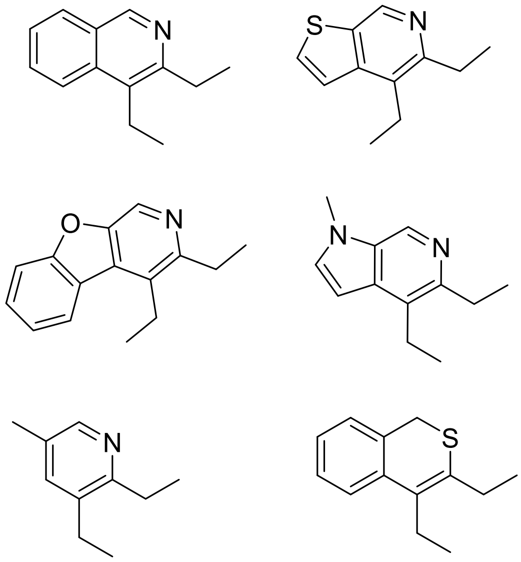

Figure1

[1] C-H and C-X Functionalization, X. Ribas, **2013**, RSC publishing.

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Mechanistic Study on the reaction of esters with ethyl diazoacetate catalyzed by silver complexes.

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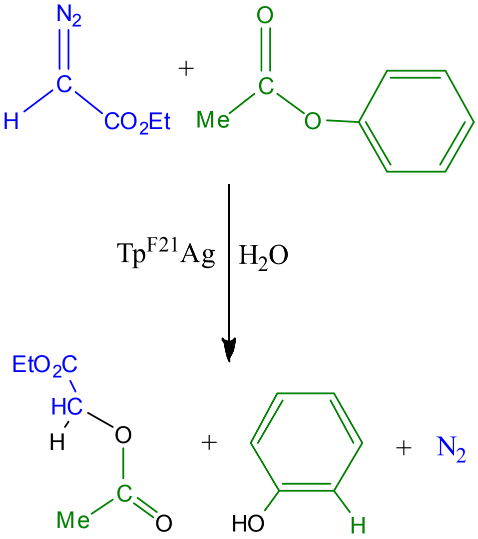
Work hypothesis and objective:

We have studied the reaction of esters with ethyl diazoacetate (EDA) which produces α–(acyloxy)acetates and alcohols, see Scheme 1. The reaction is catalyzed by silver complexes with a Tp based ligand, being [F_{27}-$Tp^{4Bo,3CF2CF3}$Ag(acetone)] the one that achieves better results. We have computationally investigated by DFT means the details of the reaction with the aim of postulating a mechanism.

Results:

We computationally studied the reaction between the esters, ethyl and phenyl acetate, EDA and a model of the silver catalyst. According to our postulated mechanism, the reaction takes place in 4 main steps: i) formation of the metallocarbene from the EDA, ii) reaction of the ester with the metallocarbene, that gives access to a zwitterionic species iii) reaction of this zwitterion with water and finally iv) elimination of the alcohol takes place. According to our calculations the silver catalyst participates not only in the formation of the metallocarbene but in all the steps of the reaction. The mechanistic proposal is confirmed by experiments with deuterium-labelled substrates.



Scheme 1

[1] R. Gava, M.A. Fuentes, M. Besora, T.R. Belderrain, K. Jacob, F. Maseras, A. Caballero, P.J. Pérez. *ChemCatChem* **2014**, DOI:10.1002/cctc.201402241 in press.

Detection and characterization of a new heterometallic bisalkynyl gold(I) allyl palladium complex

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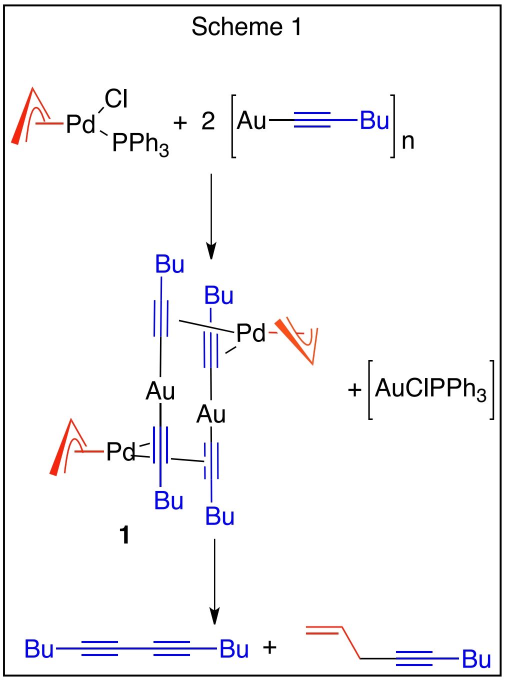
Work hypothesis and objective:

The transmetallation of alkynyl groups from copper to palladium is a common way to form palladium alkynyls, and it is an important step in the classical Sonogashira reaction. We have reported the reaction of palladium allylic complexes with $[M(alkynyl)]_n$ (M = Cu, Ag), where we observed some interesting heterometallic derivatives as a result of the alkynyl transmetallation from Cu or Ag to Pd, but with the Cu or Ag still bound to the alkynyl fragment [1]. The present study focuses on the different behavior found in the reaction of palladium allylic complexes with gold(I) alkynyls.

Results:

When $[Au(C{\equiv}C^nBu)]_n$ is reacted with the allylic palladium complex $[Pd(\eta^3\text{-allyl})ClPPh_3]$ a ligand rearrangement occurs that leads to $[AuClPPh_3]$ and the dimeric complex **1**. Complex **1** was completely characterized in solution, and its molecular structure was confirmed by X-ray crystal diffraction. The decomposition of **1** gives the dialkyne and the enyne formed by cross-coupling between allyl and alkyne. This suggests that after the formation of complex **1**, alkynyl transmetallation from Au to Pd takes place, leading to a palladium alkynyl, which can decompose: i) by reductive elimination to give the enyne; ii) by additional alkynyl transmetallation and reductive elimination to give the dialkyne. The latter reaction has been observed in the decomposition of M-Pd heterometallic complexes (M = Cu, Ag) where the transmetallation intermediate has been observed [1].

Scheme 1



[1] I. Meana, P. Espinet, A.C. Albéniz, *Organometallics*, **2014**, *vol 33*, page, 1-7

Discovery of New Gold(I)-Catalyzed Intermolecular Reactions of Alkynes with Alkenes through Computational Catalysis

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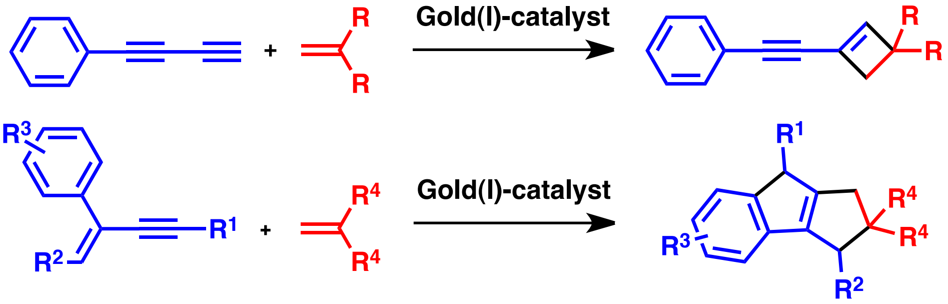
Despite significant advances in homogeneous gold catalysis [1], intermolecular reactions between alkynes and alkenes leading to functionalized alkenes are still challenging due to the competition of the final products with the initial alkenes leading to the generation of oligomers or polymers [2]. Based on the precedents in gold(I)-catalyzed cycloisomerizations and cycloadditions [1,3], we decided to study the reaction of 1,3-enynes or 1,3-diynes with alkenes followed by subsequent rearrangements using sterically hindered cationic gold(I) catalysts.

Gold(I) selectively activates alkynes in the presence of other functional groups. The electrophilic addition to an alkene generates a highly distorted cyclopropyl gold(I) carbene which can undergo ring expansion to give a cyclobutene. In addition, the gold(I) carbene can be intramolecularly trapped with unsaturated moieties leading to more complex polycyclic structures.



Acknowledgments. We thank the European Research Council (Advanced Grant No. 321066), MINECO (project CTQ2010-16088/BQU), and the ICIQ Foundation for financial support.

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Theoretical study on the metal mediated migration and deamination of cytosine: the role of the dien ligand

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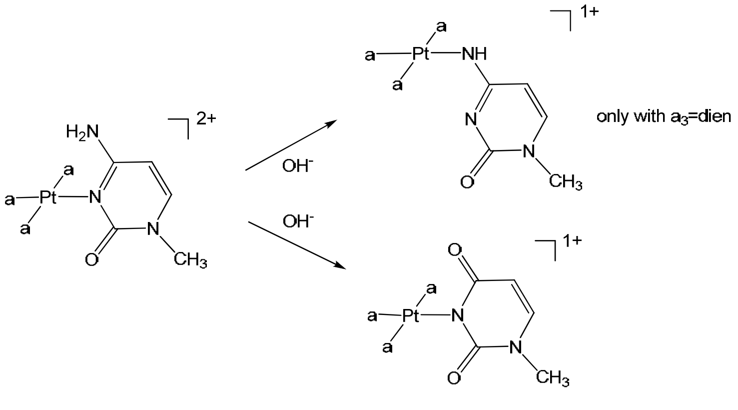
Work hypothesis and objective:

In this work we investigate the molecular mechanism and reaction pathways of metal mediated migration and deamination of 1-methylcitosine (1-MeC) with two different metallic ligands: (dien)Pt^{II} and $(NH_3)Pt^{II}$. A systematic study using DFT methodology and including discrete and continuum solvent effects will be carried out in order to understand the observed different behaviour.

Results:

DFT calculations show that migration of (dien)Pt^{II} from the *N4* to the *N3* sites of 1-MeC occurs through a ring-opened intermediate. This finding agrees with the fact that metal migration of $(NH_3)_3Pt^{II}$ under the reaction conditions was not observed experimentally, giving only the deamination product. We can therefore exclude a migration pathway involving a previous deprotonation of the exocyclic amino group, and conclude that our DFT study clarifies this unexpected behaviour.



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Fluorescent pyrene-based azole compounds: synthesis and photophysical analysis

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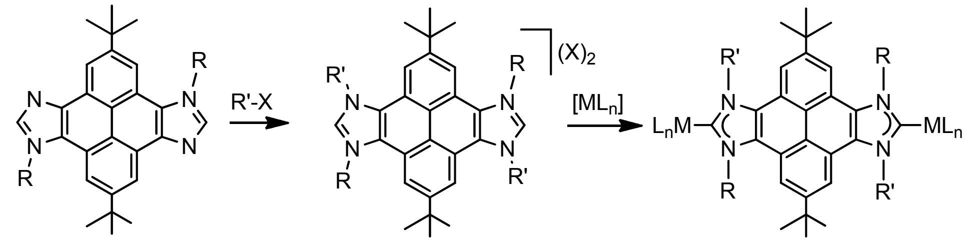
We have recently demonstrated that mono-[1] and bis-imidazolium[2] salts decorated with a polyaromatic ring such as pyrene present interesting fluorescence properties. Keen to further explore the photophysics and applications of these pyrene-based azole compounds, a systematic series of these materials has been prepared and studied.

The neutral compounds **1**, isolated as a 1:1 mixture of the *syn* and *anti* isomers (only the *anti* isomers are depicted in Scheme 1), emit near-ultraviolet and violet fluorescence peaking at 379, 399 and 421 nm. The emission quantum yields (Φ_f) vary from 0.75 to 0.50, with **1**-Me being the most efficient fluorophore among all the neutral compounds studied.

Subsequent alkylation of compounds **1** with different alkylating agents afforded symmetrical and unsymmetrical bis-imidazolium salts **2**. All bis-azolium salts show fluorescence properties, with emissions in the range of 370-420 nm and high Φ_f values, which should facilitate applications as solution-based fluorophores.

Since a number of emissive transition metal complexes containing N-heterocyclic carbene ligands have been described in the literature,[3] we believe that the coordination of the NHC ligands derived from salts **2** to gold and platinum fragments will provide complexes with interesting photophysical properties.



1*anti*, R = Me, Et, *n*Pr, *n*Bu, Bn
λ_{em} = 379, 399, 421 nm
ϕ_f = 0.75-0.50 (MeCN)

2*anti*, R = Me, Et, *n*Pr, *n*Bu, Bn
λ_{em} = 371, 391, 412, 416 nm
ϕ_f = 0.40-0.30 (MeCN)

Scheme 1

[1] Gonell, S.; Poyatos M.; Peris E. *Chem. Eur. J.* **2014**, DOI: 10.1002/chem.201304952. [2] H. Valdes, M. Poyatos, E. Peris, *Organometallics* **2014**, *33*, 394. [3] Visbal, R.; Gimeno, M.C. *Chem. Soc. Rev.*, **2014**, 43, 3551.

Hydride Ligands in Orbit around Low-Coordinate Metal Centres

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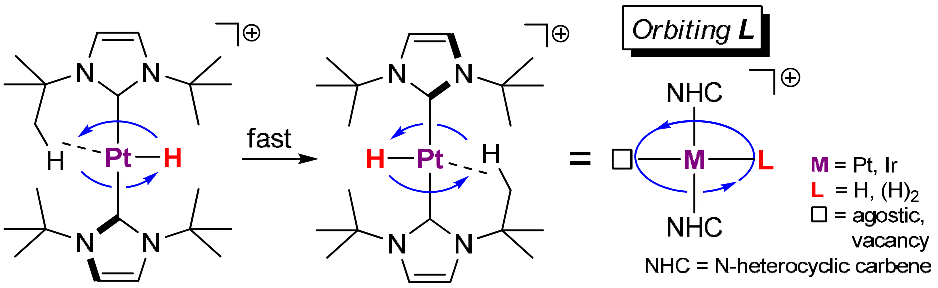
Hydrogen atoms in the coordination sphere of transition metal complexes are highly mobile particles, displaying an extensive dynamics.[1] In this communication we describe a new type of fluxional process involving hydride ligands, which can be described as an orbiting movement around low-coordinate T-shaped Pt(II) centres.

Recently, we have characterised a family of hydride species $[PtH(NHC)_2]^+$ (NHC = N-heterocyclic carbene).[2] In the case of the I*t*Bu ligand (1,3-di-*tert*-butyl-imidazol-2-ylidene), no agostic interactions were detected according to NMR spectroscopy. Contrary to this finding, Density Functional Theory (DFT) clearly predicts an agostic contact between Pt and one methyl group. On the basis of DFT calculations, we explain the discrepancy in terms of a fast orbiting movement of the hydride around Pt, which averages the agostic NMR signal and hampers the characterisation in solution. This fluxional event shows up in related systems, e.g. $[Ir(H)_2(NHC)_2]^+$ complexes,[3] and thus appears as an important feature to take into account for the interpretation of NMR spectra.



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Synthesis and Applications of Water-Soluble Dimethyl NHC Platinum(II) Complexes

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N-heterocyclic carbenes (NHC) have shown to be an interesting class of ligands in organometallic chemistry due to their exceptional electronic and steric properties, and the stability of their bonding to transition metals.[1] The important contributions of NHC complexes in catalysis have been recently extended to aqueous media thanks to the synthesis of water-soluble NHC complexes.[2] However, these efforts in synthesis and catalysis have been scarcely accompanied by fundamental studies on the chemical reactivity of such complexes in water.

We have recently reported the synthesis of Pt(0) and Pt(II) complexes with sulfonated NHC ligands that showed a notable hydrolytic stability.[3] Herein, we present the synthesis of dimethyl NHC Pt(II) complexes (**1**, Figure 1) and the most relevant results gathered in the reactivity of such species in aqueous-phase. Intramolecular C(*sp*^{3})–H bond activations in complexes **1** have been studied using a Triple Cuadrupole in line with high resolution FT-ICR (Fourier Transform Ion Cyclotron Resonance) mass spectrometer. Energetic profiles experimentally obtained are in good agreement with those theoretically calculated. On the other hand, thermal decomposition of complexes **1** in water generates Pt(0) nanoparticles which are very soluble and indefinitely stable in this medium. Surface characterization of such nanoparticles has shown the robust coordination of the NHC ligand to the NP surface ($^1J(^{13}C\text{-}^{195}Pt)$ = 940 Hz).

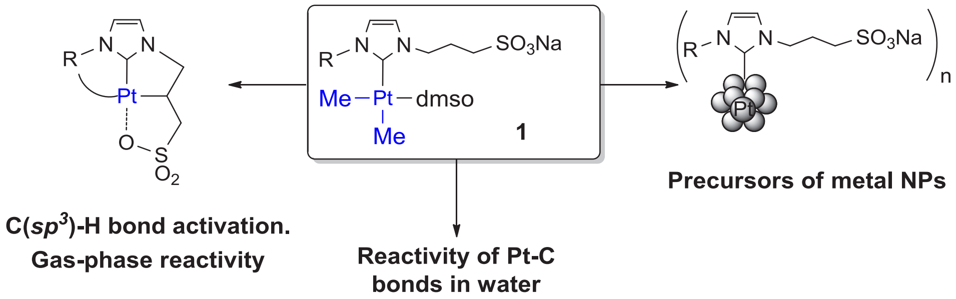

Figure 1. General scheme of the chemistry explored for sulfonated-NHC Pt complexes **1**

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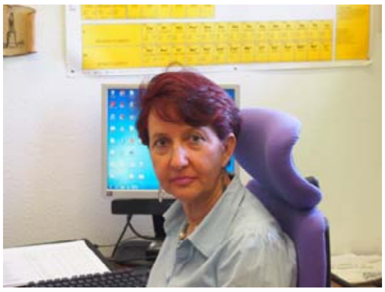
Self-Assembly of Silver(I) and Ditopic Heteroscorpionate Ligands. Spontaneous Chiral Resolution in Helices and Sequence Isomerism in Coordination Polymers



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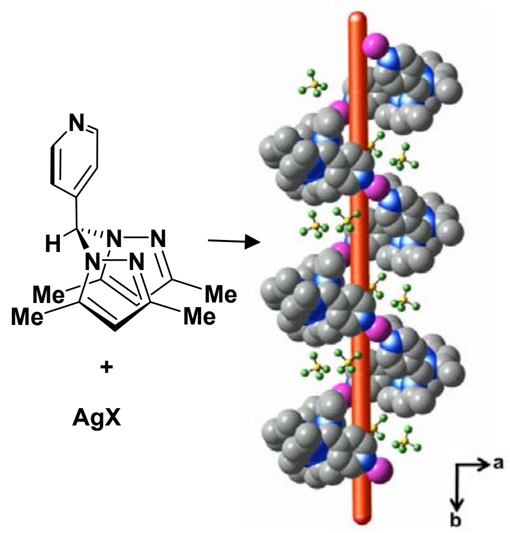
Work hypothesis and objective:

The coordination-driven self-assembly of metal-organic supramolecular architectures, including coordination polymers is an area of intense current interest in inorganic crystal engineering. This interest arises not only because of their fascinating structures but also due to their multiple applications such as gas storage and separation, ion exchange, catalysis, etc. The helices are especially interesting because they may be chiral and, although not frequent, spontaneous resolution could be observed.

Results:

The self-assembly of the ligand bis(3,5-dimethylpyrazol-1-yl)(pyridine-4-yl)methane with silver salts leads to three types of species: box-like cyclic dimers, helical or zig-zag polymers, with the polymers being sequence isomers [1]. The formation of a specific structure depends on the coordination ability of the anions or the crystallization solvents. Spontaneous resolution is observed in the crystals of the helical polymers. Solid-state circular dichroism (CD) spectroscopy applied to bunches of crystals revealed that locally one enantiomer is formed in excess, possible even exclusively.



Helical polymers obtained from the ligand and silver salts

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Bulky (terphenyl)phosphanes: synthesis and copper(I) complexes

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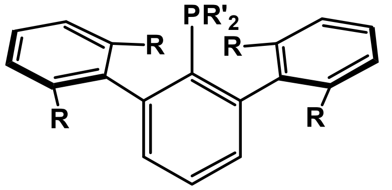
Work hypothesis and objective:

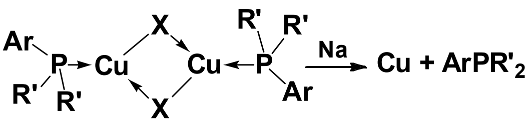
Dialkylbiaryl phosphine ligands have found widespread applications in catalytic organic synthesis. Palladium-catalyzed Buchwald amination of arenes is one of the most spectacular results in this field.[1] In spite of the great variety of biaryl-type phosphanes described to date, only a few terphenyl substituted phosphanes have been prepared and used in coordination chemistry and catalysis.[2] In this context, we have developed new synthetic strategies leading to a variety of bulky (terphenyl)phosphines and -phosphonites and prepared coordination compounds of copper(I) with some of these ligands.

Results:

Ligands **1a-d** and **2a-c** have been synthesized by reaction of the parent dihalophoshines with the appropriate Grignard reagent. The increased steric demand of the isopropyl and cyclopentyl groups impedes this straightforward procedure for the preparation of ligands **1e-f**, which requires the stoichiometric formation of a Cu(I) complex that is finally reduced with sodium to give copper and the free phosphine. Terphenyl phosphonites (**1g-h**) have been obtained from the corresponding phosphites. A variety of copper(I) complexes derived from Cu(I) halides and Cu(I) triflate have also been prepared and fully characterized.



1: R = Me: R' = Me (**1a**), Et (**1b**), $CH_2CH{=}CH_2$ (**1c**), $(CH_2)_2CH{=}CH_2$ (**1d**), ^{i}Pr (**1e**), Cyclopentyl (**1f**), OMe (**1g**), OPh(**1h**)
2: R = ^{i}Pr: R' = Me (**2a**), R' = Et (**2b**), $CH_2CH{=}CH_2$ (**2c**)



R' = ^{i}Pr, Cyclopentyl

[1] D. S. Surry, S. L. Buchwald, *Chem. Sci.,* **2011***, 2,* 27 and references therein.

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Highly selective synthesis of cyclic carbonates from CO_2/epoxides catalysed by Zn(II) and Fe(III) Schiff base complexes at mild conditions.

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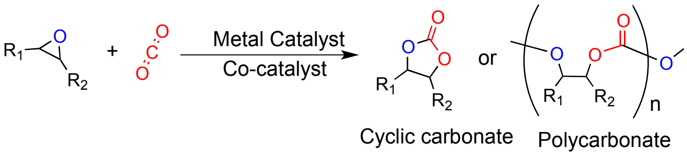
Work hypothesis and objective:

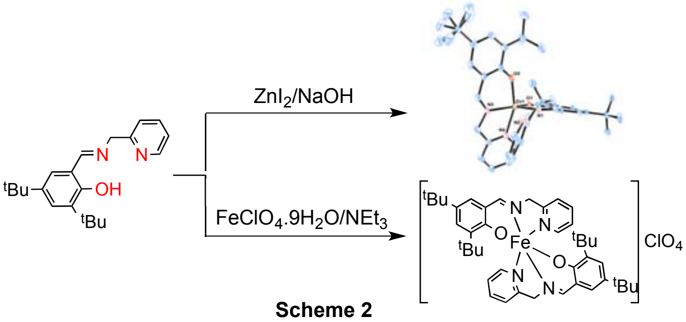
Chemical fixation of CO_2 to produce valuable chemicals is attracting significant interest as a result of growing concerns of the environmental impact of this greenhouse gas but also because CO_2 is inexpensive, widely available, non-toxic and renewable carbon source [1]. The main drawback for the utilization of this source is its high thermodynamic stability and kinetic inertness that implies the use of catalysts or compounds with a relatively high free energy to activate it [2]. The addition of carbon dioxide to epoxides to produce either cyclic carbonates or polycarbonates is an alternative to the classical method involving highly toxic phosgene (Scheme 1) and those products are valuable compounds with a wide range of applications [3].

Results:

In this work we prepared Zn(II) and Fe(III) complexes with tridentate NN'O-donor ligands (Scheme 2) to be used as catalysts. DFT calculations were also performed. These complexes together with a co-catalyst were found to be active in the coupling of CO_2 with different epoxides also at mild conditions providing high selectivity to cyclic carbonates (TOF up to 580 h^{-1}). The epoxidation of the corresponding alkenes has been also undertaken.



Scheme 1



Scheme 2

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Asymmetric 1,3-Dipolar Cycloaddition Reaction between α,β-Unsaturated Aldehydes and Nitrones Catalyzed by Complexes Based on the Chiral Fragment (η^5-C_5Me_5)M(chiral diphosphane) (M =Rh, Ir).

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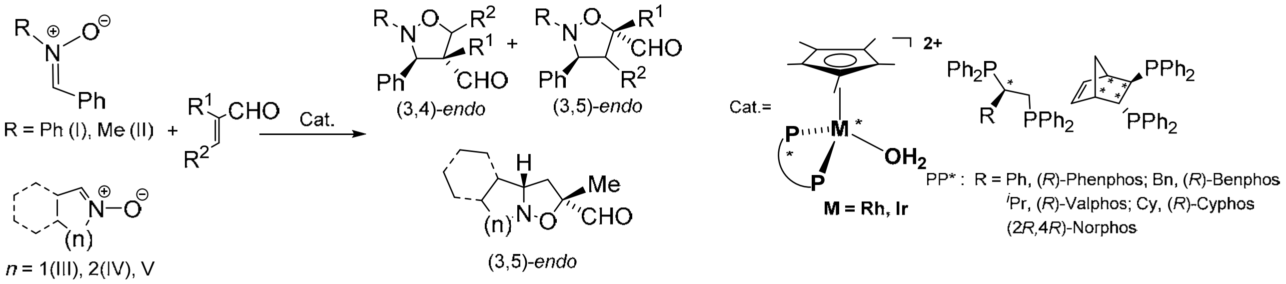
Work hypothesis and objective: The 1,3-dipolar cycloaddition reaction (DCR) is one of the most important method for the preparation of five-membered heterocyclic rings. It has been recently shown that the (η^5-C_5Me_5)M{(*R*)-Prophos} fragment (M = Rh, Ir) is well suited for this type of transformation.[1] We plan to apply related chiral half-sandwich complexes of the formula [(η^5-C_5Me_5)M(PP*)(H_2O)](SbF_6)$_2$ containing the chiral diphosphanes (*R*)-Phenphos, (*R*)-Benphos, (*R*)-Valphos, (*R*)-Cyphos or (2*R*,4*R*)-Norphos], to DCR reactions between nitrones and α,β-unsaturated aldehydes.

Results: The well defined chiral diphosphane complexes efficiently catalyze the above mentioned reaction (Scheme). Good conversions, perfect *endo* diastereoselectivity high or perfect regioselectivity and enantioselectivities up to 98% e.e. were obtained. The influence of the geometry of the intermediate enal complex on the stereochemical outcome is clearly established.



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Novel Rhodium and Iridium Complexes Coordinated to a *C*$_3$-symmetry-tris-NHC ligands based on a 1,3,5-Triphenyl-benzene Core.

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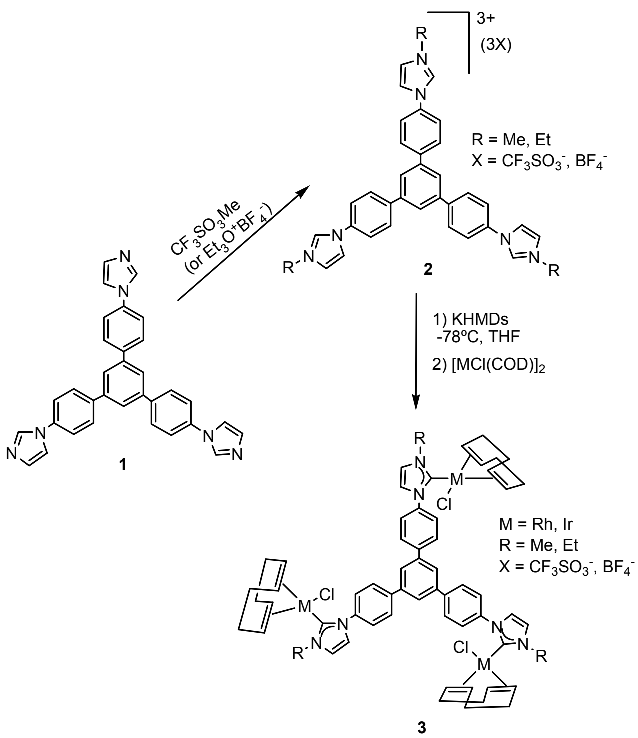
The increasing interest towards poly-NHCs stems from their multiple applications, [1] in particular as useful tools for preparing homogeneous catalysts and multifunctional materials. We aimed to prepare new trisazolium salts based on triphenyl-benzene cores, and to obtain the related tris-NHC rhodium and iridium complexes.

As shown in the scheme, we prepared the novel trisazolium salts precursors **2** (Scheme) based on 1,3,5-triphenyl-benzene. These salts exhibit fluorescence emission in the 320-370 nm region. The coordination of **2** to $[MCl(COD)]_2$ (M = Rh, Ir) was carried out in the presence of KHMDS, and allowed the formation of the related tris-NHC complexes of Rh and Ir in high yield. The electronic properties of the new complexes were analysed by means of cyclic voltammetry and IR spectroscopy of the related carbonylated species. The catalytic activity of the tri-rhodium complex **3** toward the addition of arylboronic acids to cyclohexe-2-one has been evaluated, and compared to the activity shown by a related monometallic complex.



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[1] a) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677; b) Mata, J. A.; Poyatos, M.; Peris, E. *Coord. Chem. Rev.* **2007**, *251*, 841; c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122.

New Ruthenium homoleptic carbenes as solar antennas for green catalytic proceses.

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Work hypothesis and objective:

$[Ru(bpy)_3]Cl_2$ like complexes are widely known to have interesting photochemical properties when irradiated with visible light, to the point of being called “solar antennas”. This family of compounds have excellent fluorescent properties, and their triplet state after light-driven excitation is able to transfer the exceeding energy to other molecules in the medium that may act as catalysts in many kinds of reactions.[1] This allows to produce some reactions in softer conditions and with less energetic cost than the traditional way.

One of the fields when the solar antennas are more interesting is in the water splitting reaction to produce hydrogen.[2] If a renewable and ecologic source of energy as sunlight is used to produce the reaction, hydrogen could be obtained as a cheap and environmental green fuel, usable a substitute of the more contaminating petroleum.

Results:

New solar antennas have been developed in our group, employing N-heterociclyc carbene based ligands (Fig. 1) with the aim of tuning the photochemical properties of the ruthenium complexes. Homoleptic ruthenium compounds have been obtained and are being tested in the hydrogen generation by water splitting reaction. A full characterization of their optical properties (fluorescence, lifetimes, quantum yields…) is being carried out in order to correlate them to their activity and stability in the reaction conditions.

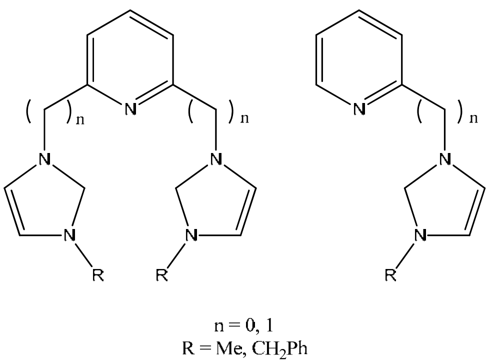

Fig.1: Structure of the pre-carbene ligands.

[1] Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. *J. Inorg. Chem.*, **2005**, *44*, 6802-6827.

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P96

Functionalisable alkoxy-tethered NHC ligands: synthesis and application in Pd-mediated C-C and C-N bond formation processes.

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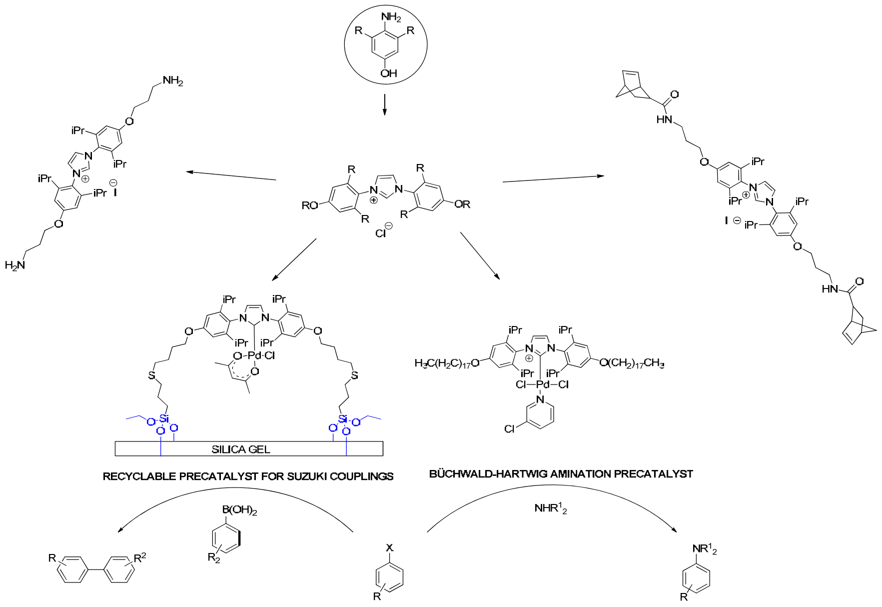
Work hypothesis and objective:

Para-alcoxy substitution of N,N'diaryl N-Heterocyclic Carbenes is taken up in this work for the preparation of pro-immobilisable functionalised NHCs. The recyclability and catalytic activity of these heterogenised NHC-Pd complexes will be studied in different cross-coupling reactions.

Results:

In this work, we describe the preparation of NHCs bearing various functionalities such as triethoxysilyl, primary amino, norbornenyl and long chain alkyl groups.

Preformed Pd complexes bearing triethoxysilyl functionalised NHC's were immobilised onto silica and applied as recyclable precatalysts in the Suzuki-Miyaura coupling in batch and in continuous flow mode. A long alkyl chain-decorated NHC ligand furnished a Pd catalyst which provided excellent activity and selectivity in challenging Buchwald-Hartwig aminations.



P97

Cylinder-shaped Bis(benzene-hexaNHC) Coinage Metal Complexes

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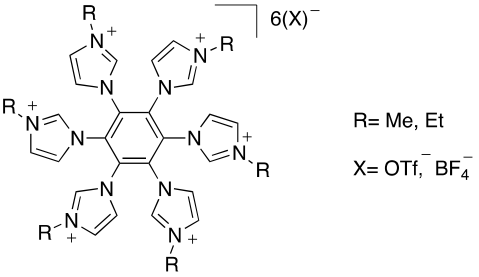
The interest in the design of macromolecular self-assembled structures with nanocavities has increased very recently.[1] The reason is not only because of their fascinating architectures that these supramolecules possess, but their unusual sensing, magnetic, optical, gas storage and catalytic properties. While a large number of poly-NHC ligands are known, those featuring the topologic requirements to serve as convenient bridging ligands for the construction of metallo-organic frameworks are still limited to a few well-defined examples.[2]



Scheme 1.

Inspired by these unique NHC-based polyhedral coordination cages with hollow central cavities, a new disk-shaped hexa-azolium benzene salt precursor has been prepared, Scheme 1. The synthesis of the related Ag(I) and Au(I) coordination cages will also be presented, along with the X-ray structure of a [Ag(I)] complex featuring six metals sandwiched between two six-fold symmetry hexa-NHC ligands.

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Synthesis and reactivity of terminal azolate complexes of Nickel stabilized with PCP pincer ligand.

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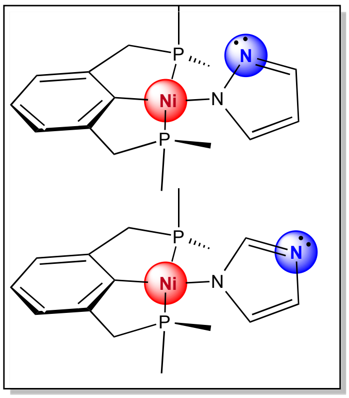
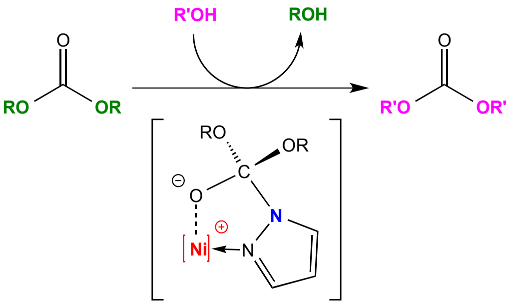
In our research group, we are interested in the reactivity of metal complexes that contain strongly basic and nucleophilic ligands, such as alkoxides, amides or fluorides. These complexes exhibit two adjacent reactivity sites, one in in the metal and the other in the ligand. In this contribution we discuss Nickel (II) complexes containing azolate (pyrazolate, imidazolate or 1,2,4-triazolate) and tridentate pincer ligands. Azole and azolate ligands play an important role in enzymatic catalysis[1] and have often been applied in the design of biomimetic catalysts.[2]
In our compounds, the pincer ligand saturates three of the four coordination positions of the square-planar metal center, enforcing the terminal coordination of the azolate. This leaves a nitrogen atom with significant nuecleophilic character in the vicinity of the 16e nickel atom, which retains a residual Lewis acidic character.
Azole heterocycles are known to act as organocatalysts in acyl transfer reactions.[3] Therefore, in order to validate our hypotheses and evaluate the cooperative metal/ligand effect, we have studied the catalytic activity of our complexes as tranesterification catalysts.





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Palladium(II) complexes containing enantiopure bis(diamidophosphite) ligands as catalytic precursors in asymmetric allylic amination

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Work hypothesis and objective:

Chiral P-donor ligands containing P-O and/or P-N bonds are efficient and versatile ligands in asymmetric homogeneous catalysis. Among them bis(diamidophosphite) ligands have proved to be very active and enantioselective in the asymmetric hydrogenation catalysed by Rh(I) complexes [1]. With the aim to test this type of ligands in Pd-catalysed asymmetric allylic amination, allylpalladium(II) complexes with different bidentate diamidophosphites were prepared and characterised. The cooperative effects of the different elements of chirality were evaluated.

Results:

Allylpalladium complexes with bis(diamidophosphite) ligands **a**, **b** and **c** (Figure 1) were synthesised and characterised by NMR spectroscopy and X-ray diffraction. It was found that the complex with ligand **b** was present as a mixture of two isomers in the solid state and showed a fluxional behaviour in solution.

All complexes showed good activity (100% conversion at 24 h) in the allylic amination of 1-acetoxy-1,3-diphenylprop-2-ene with benzylamine as nucleophile. Moderate enantioselectivities were observed for complexes with ligands **a** and **b**. A match-mismatch effect was observed with ligand **c**: good enantiomeric excess (83% ee) was obtained with (*R;R_{al};R*)-**c** while a racemic amination product was obtained with the diastereoisomer (*S;R_{al};S*)-**c**.

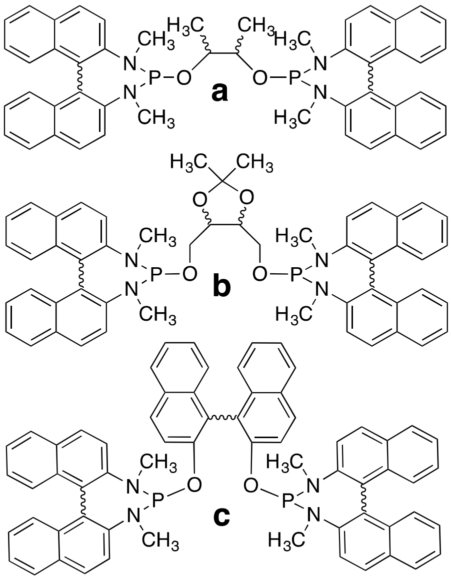

Figure 1

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Synthesis of Homo- and Heterobimetallic Porphyrin-Acetylide Complexes: Potential Precursors for *Tandem* Catalysis

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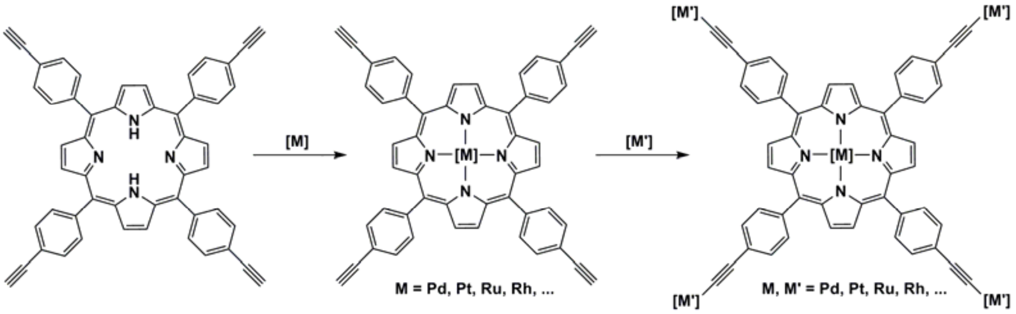
The substitution of multistep, salt-generating chemical synthetic processes by productive catalyzed reactions that commit for atom economy is having denoting impact on the manufacture of pharmaceutical intermediates and fine chemicals, among others. In this sense, Concurrent Tandem Catalysis (CTC) is a technique in chemistry which combines multiple catalytic centers on a single molecule in order to synthesize a product.[1] This has been reported extensively in the synthetic chemistry literature and, in a practical sense, it allows for reactions to be carried out in a single reaction vessel without purification between steps. On the other hand, porphyrin derivatives shown a number of interesting characteristics, such as their high aromaticity, symmetry and planarity.[2] Due to the influence of this unique structure on their properties, many research groups focused on the synthesis of new porphyrin based systems. However, there are only few examples of functionalized porphyrins with more than one potential catalytic centre in its structure.

With these precedents in mind, we decided to accost the synthesis of new homo- and heterobimetallic porphyrinic systems which could be potentially employed as precursors in different *tandem* catalytic processes. The initial metallation of the porphyrin core, followed by the transformation of the terminal alkyne groups into different acetylide complexes employing some classical organometallic fragments, allow us to obtain new homo- and heterobimetallic porphyrinic structures which could be potentially active in *tandem* catalytic processes (see Scheme).



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Supramolecular structures based on Au(I) luminescent hydrogels

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[1] *Departament de Química Inorgànica, Universitat de Barcelona, Barcelona, Spain.*
[2] *REQUIMTE, Departamento de Química, CQFB, Universidade Nova de Lisboa, Monte de Caparica, Portugal*

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Molecular (supramolecular) gels have attracted much attention in the last decade both in terms of fundamentals as well as applications in a wide variety of fields such as Materials Science, Catalysis, Regenerative Medicine, Drug Delivery and Environmental Science.[1]

We recently reported on the formation of luminescent Au(I) hydrogels with organometallic alkynyl complexes where aurophilic intermolecular interactions should to be involved on the gelation process (Fig. 1).[2,3] We have studied the effect of introducing slight modifications on the chemical structure of these gold(I) supramolecular assemblies. Positively charged species have been synthesized by the introduction of methyl uni (Fig. 2).The results show that positive charged spe structure or vesicles instead of hydrogels.

As well, introduction of positive charge is observed to modulate their luminescence. Thus, they have been explored in molecular recognition processes. Moreover, we have recently developed different Au(I) organometallic systems containing terpyridine and bipyridine units (Fig. 3). These new complexes give also rise to the formation of hydrogels with different luminescent properties.

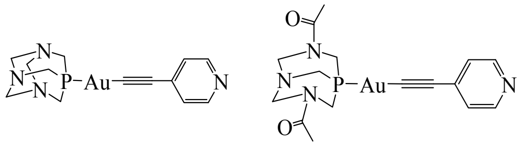

Fig. 1. General structures of phosphine-gold-alkynyl.

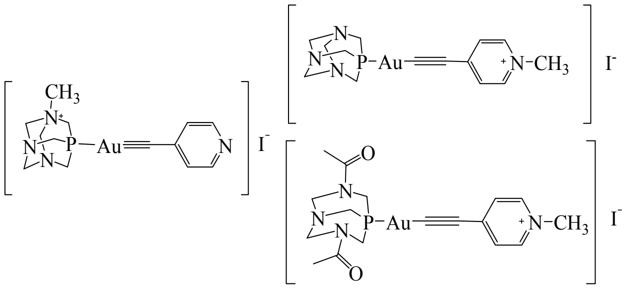

Fig. 2. General structures of positive charged derivatives.

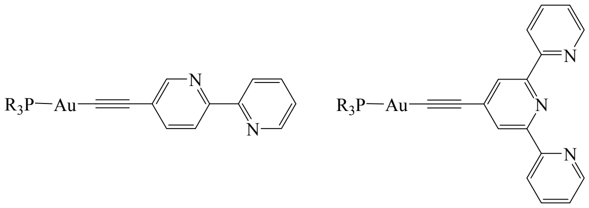

Fig. 3. General structures of phosphine-gold-pyridines derivatives.

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Sequential β-boration / α-chlorination of α,β-unsaturated carbonyl compounds

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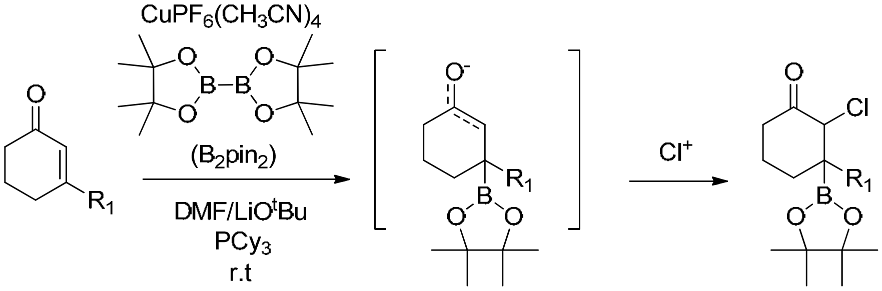
Work hypothesis and objective:

Current emphasis on the development of multiple chemical transformations sequentially performed in a single reaction vessel has deserved special attention to generate molecular complexity in a concise fashion[1,2]. Towards this end, we have recently developed a protocol that allows sequential C-B and C-F bond formation of activated alkenes through a one pot regio-, diaestereo- and enentioselective strategy[3]

Results:

Along with the above mentioned methodology, we now explore compatibility between borylation and chlorination protocols[4] and taking into consideration the already mentioned importance of introducing two vicinal groups in a selective way, we have reported a sequential β-boration of a wide range of β-substituted enones and further chlorination in a selective α-position.



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Scope and DFT mechanistic study of the synthesis of benzoisoquinolines from primary amines and internal alkynes catalyzed by ruthenium.

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E. P. Urriolabeitia[a]

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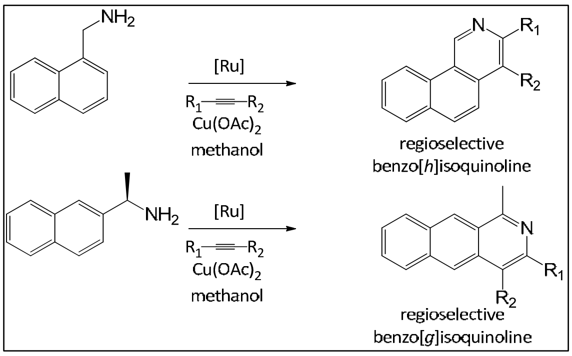
Work hypothesis and objective:

The activation of C-H bonds in aryl derivatives catalyzed by transition metals is a very active field in organometallic chemistry, due to the innumerable synthetic possibilities that it provides.[1] The presence of a directing group in the substrate makes it possible for the reactions to take place regioselectively. Primary amines can act as efficient directing groups, enabling the regioselective synthesis of N-heterocycles. In spite of the availability of primary amines as versatile and accesible raw materials, their use as building blocks in metal-catalyzed organic synthesis is still scarce. We have recently shown the potential of these materials in the Ru-catalyzed synthesis of isoquinolines and fused pyridines.[2] Our objective is to expand the scope of this reaction and to gain an insight into its mechanism by means of DFT calculations.

Results:

In this communication we describe how some Ru(II) complexes can catalyze the coupling between primary naphthylmethylamines and internal alkynes, to afford benzo[*g*]isoquinolines and benzo[*h*]isoquinolines. We have also elucidated the mechanism of this reaction by DFT methods. We have studied all the catalytic steps involved in the formation of the products (CH activation, migratory insertion and formation on the C-N bond), determining also their activation barriers.



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C-H Bond Activation Reactions Promoted by POP-Osmium and Ruthenium Complexes

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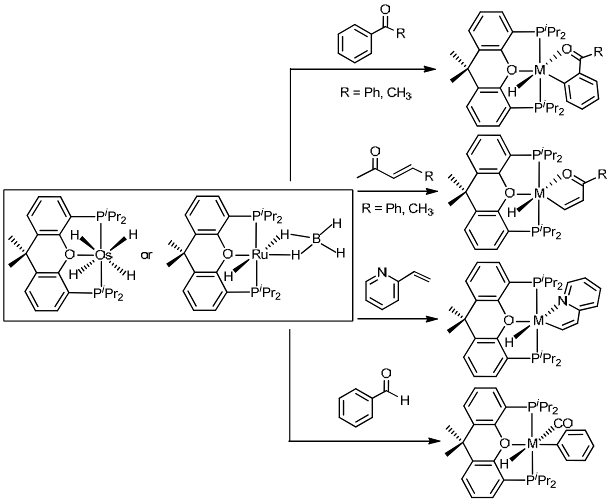
Work hypothesis and objective:

C-H bond activation and subsequent formation of C-C and C-heteroatom bonds mediated by transition metal complexes have been an important topic in chemistry for many years, and are still relevant fields of study.[1] In this context, we present here the study of the reactivity of the osmium-tetrahydride $OsH_4\{xant(P^iPr_2)_2\}$ and the ruthenium-hydride-tetrahydroborate $RuH(\eta^2\text{-}H_2BH_2)\{xant(P^iPr_2)_2\}$ towards a wide range of unsaturated substrates containing a coordinating functionality.[1]

Results:

It was found that these complexes efficiently activate CH bonds of a representative series of aromatic and olefinic ketones, as well as 2-vinylpyridine. For benzaldehyde, the activation of the more reactive C(O)-H bond is preferred, and the substrate is decarboxylated to give $MH(Ph)(CO)\{xant(P^iPr_2)_2\}$ (M = Os, Ru). For the reaction of 1-cyclohexene-1-carboxaldehyde and cyclohexanecarboxaldehyde with the osmium-tetrahydride complex, a β-hydrogen elimination on the $OsH(R)(CO)\{xant(P^iPr_2)_2\}$ (R = cyclohexenyl and cyclohexyl) intermediates takes place to form a *trans*-dihydride species.



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Highly Reactive Osmium (II) Hydrides and their Reactivity versus Unsaturated Organic Molecules

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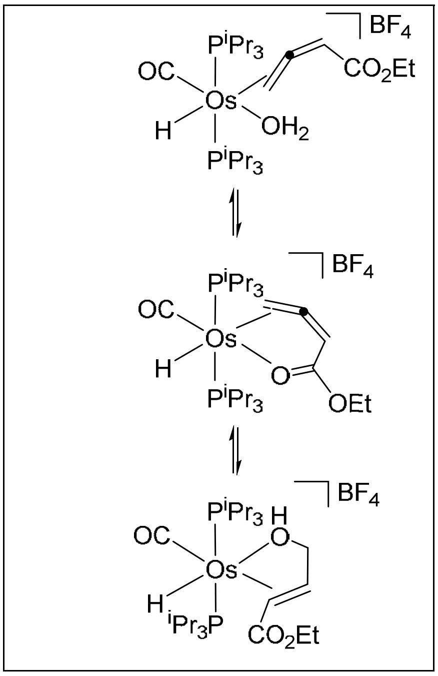
Work hypothesis and objective:

Our research group works on the design of new transition-metal complexes for the functionalization of organic molecules. Bis-solvate osmium hydride complexes have shown a rich chemistry promoting new reaction patterns including carbene-carbyne transformations, formation of osmacyclopentapyrrol derivatives or Nazarov cyclizations among others.[1]

Results:

We have recently synthesized two new bis-solvate complexes $[OsH(CO)(S)_2(PiPr_3)_2]^+$ (S = H_2O, acetone), which are easily obtained by reaction of $OsHCl(CO)(PiPr_3)_2$ with $AgBF_4$ in presence or absence of water. In solution, these complexes afford the highly reactive 14-electron fragment $[OsH(CO)(PiPr_3)_2]^+$ and react with unsaturated organic molecules such as olefins, ketones or allylamines. The same reaction with allenes affords the corresponding -coordinated complexes and catalyzes the hydration of ethyl buta-2,3-dienoate to give the corresponding allyl alcohol



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[1] See for example: (a) T. Bolaño, R. Castarlenas, M. A. Esteruelas, F. J. Modrego, E. Oñate *J. Am. Chem. Soc.* **2005**, *127*, 11184. (b) T. Bolaño, R. Castarlenas, M. A. Esteruelas, and E. Oñate *J. Am. Chem. Soc.* **2006**, *128*, 3965. (c) T. Bolaño, R. Castarlenas, M.I A. Esteruelas, E. Oñate *J. Am. Chem. Soc.* **2009**, *131*, 2064.

Competition Between Hiyama and Heck Pd-Catalyzed Cross-Coupling Reactions in Water: Computational Explanation

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A. Gordillo,[2] **C. López-Mardomingo**,[2] **E. de Jesús**[2]

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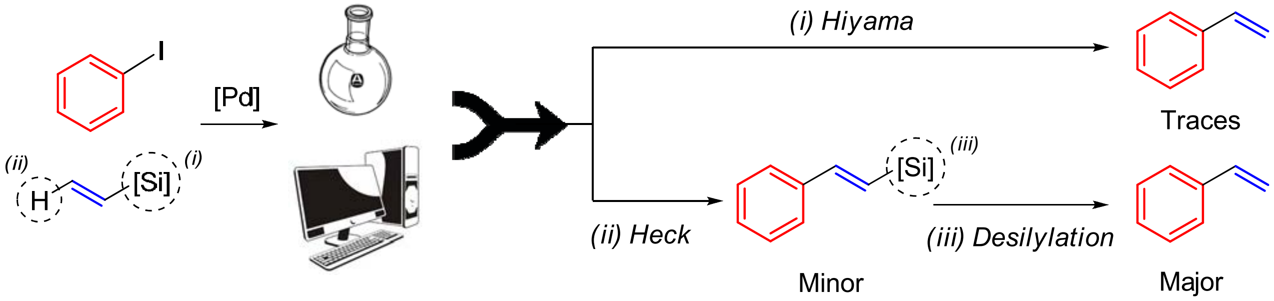
Work hypothesis and objective:

The Pd-catalysed cross-coupling reaction of arylhalides with vinylsilanes in water is herein discussed.[1] Several reaction mechanisms are analyzed by means of DFT calculations to account for the major product coupling product (Scheme 1). The Hiyama process (i) implies C–Si bond activation and transmetalation steps. The Heck route (ii) involves a C-H bond breaking process and the subsequent desilylation (iii) eliminates the silicon moiety. Labelling studies using deuterated vinylsilanes indicated that the Hiyama-type mechanism is unlikely operative, favouring the Heck–desilylation process instead. Density functional theory calculations are then performed to evaluate the reaction mechanisms as well as to evaluate the most feasible pathways for the desilylation step.



Results:

Will be explained at the poster.

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Reacción de hidruroirida-β-dicetonas con aminoalquilpiridinas

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Hipótesis y objetivo:

Es conocido que ligandos del tipo 2-aminopiridina reaccionan con el complejo $[IrHCl\{(PPh_2(o\text{-}(C_6H_4CO))_2H\}]$ (**1**) formando complejos de tipo *trans*-$[IrCl\{(PPh_2(o\text{-}C_6H_4CO))(PPh_2(o\text{-}C_6H_4CHNRC_5H_3R'N))\}]$ (R y R' = H o CH_3) que contienen un ligando PCN terdentado en una disposición facial y con los fósforos en *trans*.[1] El objetivo de este trabajo ha sido estudiar la reactividad de los complejos irida-β-dicetona **1** y $[IrH_2\{(PPh_2(o\text{-}(C_6H_4CO))_2H\}]$ (**2**) frente a ligandos aminoalquilpiridinas con posibilidades quelatantes.

Resultados:

Cuando se hace reaccionar **1** o **2** con los ligandos 2-(aminometil)piridina (AMPy), 2-(2-aminoetil)piridina (AEPy) o 2-[(metilamino)metil]piridina (MAMPy) se obtienen complejos diferentes. En la reacción del complejo **1** con los ligandos AMPy y AEPy, en disolventes apróticos, se produce una reacción de condensación que conduce a los complejos de tipo hidruroirida-β-cetoimina $[IrHCl\{(PPh_2(o\text{-}C_6H_4CO))(PPh_2(o\text{-}C_6H_4CN(CH_2)_XC_5H_4N))H\}]$ (X = 1 (**3**); 2 (**4**)) también estabilizados por enlace de hidrógeno N···H···O y con el fragmento piridínico no coordinado. Cuando se trabaja en medios próticos el ligando AMPy conduce al complejo con ligando terdentado PCN $[IrH(PPh_2(o\text{-}C_6H_4CO))(PPh_2(o\text{-}C_6H_4C{=}NCH_2C_5H_3N))]$ (**5**), mientras que AEPy conduce al complejo $[IrH(PPh_2(o\text{-}C_6H_4CO))_2NH_2(CH_2)_2C_5H_4N]$ (**6**). Cuando se hace reaccionar el complejo **1** con el ligando MAMPy se da la condensación completa obteniéndose un complejo catiónico de iminio $[IrH(PPh_2(o\text{-}C_6H_4CO))(PPh_2(o\text{-}C_6H_4C{=}NCH_2C_5H_3NCH_3))]ClO_4$ (**7**).

En la reacción del complejo **2** con los ligandos AMPy y AEPy se obtienen complejos hidrurodiacilamino neutros $[IrH(PPh_2(o\text{-}C_6H_4CO))_2R]$ (R = AMPy (**8**); AEPy (**6**)) con los fósforos en *cis* y coordinados por la amina.

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Terminal-Phosphanide Iridium Complexes: Synthesis and Reactivity

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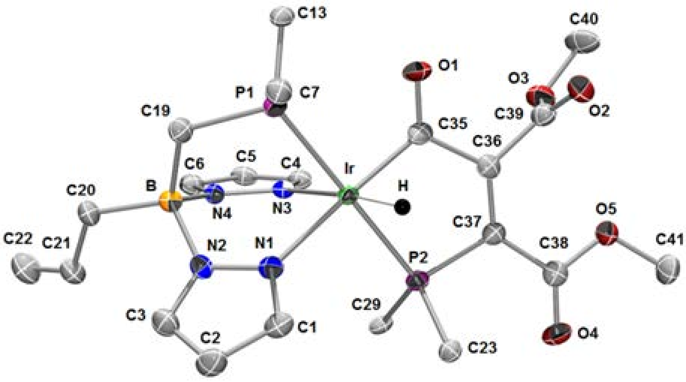
Work hypothesis and objective:

Transition metal–phosphanide complexes [M–PR_2] are valuable species proposed to be actively involved in catalytic transformations, such as the dehydrocoupling of phosphanes,[1] and concerned in the formation of new P–E bonds (E = B, C, P) present in added value phosphorus-containing products.[2] While terminal-phosphanide early transition metal complexes are well-known and easily prepared through P–H bond activation pathways,[3] few examples of terminal-phosphanide complexes of the late transition metals, and more specifically even less with iridium, have been reported.[4]

Results:

We will showcase the synthesis of a terminal-phosphanide iridium complex resulting from the oxidative-addition of the H–P bond of a secondary phosphane to iridium. Mechanistic insights (from DFT-calculations) into this unusual process in which the hydride and phosphanide ligands remain bound to the metal in the product will be discussed. Moreover, the reactivity of this unusual type of complex towards protic acids, activated olefins and alkynes (see Figure) and metallic fragments, will also be considered.



[1] R. Waterman, *Chem. Soc. Rev.* **2013**, *42*, 5629.

[2] S. Greenberg, D. W. Stephan, *Chem. Soc. Rev.* **2008**, *37*, 1482.

[3] D. W. Stephan, *Angew. Chem. Int. Ed.* **2000**, *39*, 314.

[4] Y. Gloaguen, W. Jacobs, B. de Bruin, M. Lutz, J. I. van de Vlugt, *Inorg. Chem.* **2013**, *52*, 1682; M. D. Fryzuk, K. Bhangu, *J. Am. Chem. Soc.* **1988**, *110*, 961.

Synthesis of polinuclear copper(I) and silver(I) complexes containing the enantiopure [(S,S)-^{i}Pr-phebox]H ligand.

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Work hypothesis and objective:

In the last decade, the use of 2,6-bis[4´-R-oxazolin-2´-yl]phenyl (phebox) transition metal complexes has experienced a significant increase[1]. Up to now, most of the research in this area has been limited to rhodium(III) complexes[2] and some iridium(III) complexes[3]. In all cases, the phebox ligand is bonded as a *N,C,N* anionic tridentate ligand. However, no quiral silver-phebox-H (phebox-H = 1,3-bis(oxazolini-2’-yl)benzene) examples have been reported wherein the phebox-H ligand is coordinated to the metal centre through the nitrogen atoms[4].

Results:

In this scenario, we now report the first examples of polinuclear copper(I) and silver(I) complexes bearing the [(S,S)-iPr-phebox]H neutral ligand. We have also studied the catalytic activity of some of these complexes in the asymmetric necleophilic addition of alkynes to imines.

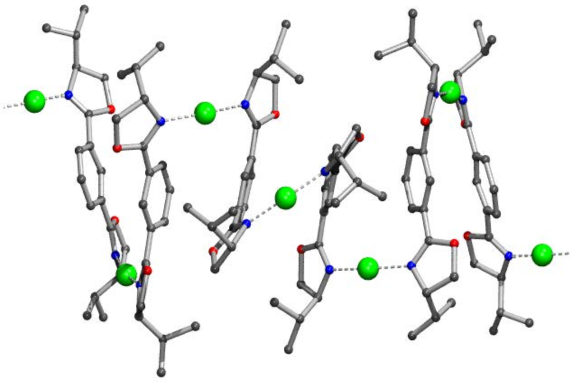

Figure 1. POV-Ray view of a portion of the polymeric cationic complex [Ag(κ^2-*N,N*-^{i}Pr-phebox)]^+_n

[1](a)J. Ito, H. Nishiyama, *Synlett*, **2012**, *23*, 509. (b)H. Nishiyama, J. Ito, *Chem. Commun.* **2010**, *46*, 203.

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Carboxylated triarylphosphines containing trifluoromethyl groups: synthesis and applications in catalysis

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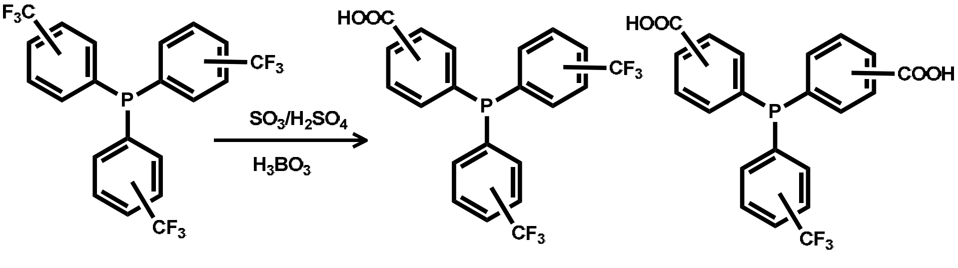
Work hypothesis and objective:

Despite the great versatility of carboxylated triarylphosphines, the synthesis of these compounds shows some difficulties [1]. The most common procedure to synthesize triarylphosphines, the reaction between Ar_xPCl_{3-x} (x=0-3) and a MAr' compound (M=Li or MgBr), cannot be applied in this case because of the incompatibility between carboxylic acids and organolithium or Grignard reagents. On the other hand, the hydrolysis of the trifluoromethyl group in aryl derivatives has been known for more than 60 years [2]. However, no applications of this reaction to the synthesis of phosphines have been previously reported. Recently, we have found that trifluoromethyl substituents in triarylphosphines can be converted into carboxylic groups, by using fuming sulfuric acid, in the presence of boric acid:



MIRANPHOS MIRAN2PHOS

Results:

We will report a method to synthesize triarylphosphines containing both carboxylic and trifluoromethyl groups [3,4]. It has been observed that the rate of the reaction depends on the relative position of the trifluoromethyl group, being easier to hydrolyze when it is located at *meta* position to P atom than when it is at *para* or *ortho* positions. The mixture of products obtained from the hydrolysis of the trifluoromethyl groups has been successfully separated and purified. The new phosphines have been essayed as ligands in the phase switchable Rh-catalyzed hydroformylation of styrene. This strategy allows the recovery of the catalyst by changing the pH [5].

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(b) Ravindar, V; Hemling, H; Schumann, H; Blum, J. *Synth.Comm*. **1992**, *22*, 841.
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[3] Herrera, D; Peral, D; Bayón, J.C. ES 2 459 790 A1, **2012**, for UAB.
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Reactivity of half-sandwich iridium complexes bearing hemilabile alkenylphosphines

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Work hypothesis and objective:

We have recently synthesized rhodium(III) and rhodium(I) complexes [Rh(η^5-C_5Me_5)Cl_2(κ^1-*P*-$R_2PCH_2CH{=}CH_2$)], [Rh(η^5-C_5Me_5)Cl{κ^3-*P*,*C*,*C*-$R_2PCH_2CH{=}CH_2$)][BPh_4], [Rh(η^5-C_9H_7){κ^3-*P*,*C*,*C*-$Ph_2PCH_2CH_2CH{=}CH_2$)] [1], which feature different coordination mode of the allylphosphine ligands. Moreover, these complexes have been demonstrated to be useful as substrates in stereoselective nucleophilic addition and oxidative addition reactions.

Results:

With these precedents in mind, we have focused on the synthesis and reactivity of the analogous pentamethylcyclopentadienyl and indenyl iridium(III) complexes containing allyldiphenylphosphine (ADPP) and allyldiisopropylphosphine (ADIP) ligands.

Herein, it is presented the synthesis of the neutral complexes [Ir(η^5-C_5Me_5)Cl_2(κ^1-*P*-$R_2PCH_2CH{=}CH_2$)] (R = ^{i}Pr, Ph) and [Ir(η^5-C_9H_7)Cl_2(κ^1-*P*-$R_2PCH_2CH{=}CH_2$)] (R = ^{i}Pr, Ph) as well as preliminary studies on their reactivity towards different nucleophiles. We have observed that the nucleophilic attack occurs selectively at either the metallic center or the alkenylphosphine ligand depending on the nature of the nucleophile employed [2].

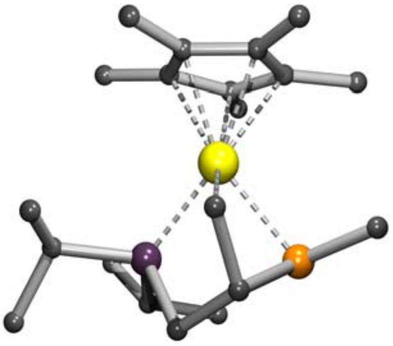

Figure 1. POV-Ray view of the molecular structure of the cationic complex [Ir(η^5-C_5Me_5){κ^3-*P,C,S*-$^i Pr_2PCH_2CH(SMe)CH_2$}]$^+$

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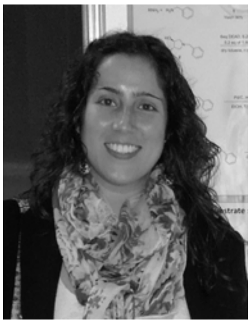
P112

Synthesis of chiral PNNP ligands bearing a pyrrolidine backbone. Application in ATH of ketones.



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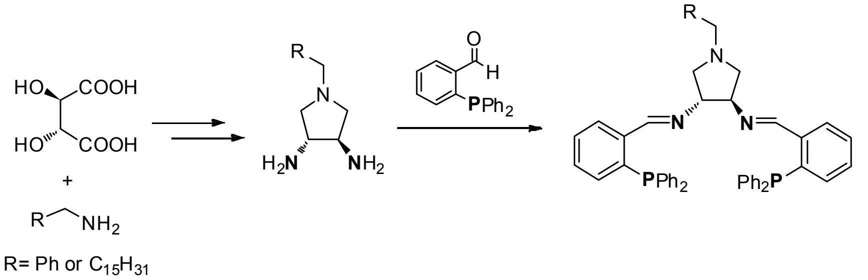
Work hypothesis and objective:

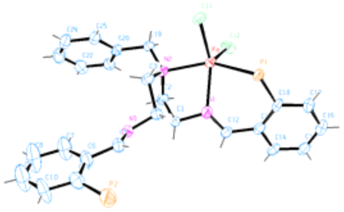
Homogeneous catalysis with iron complexes offers a highly attractive alternative to late transition metals such as rhodium, iridium or ruthenium which have proven to be efficient for large number of transformations[1,2].

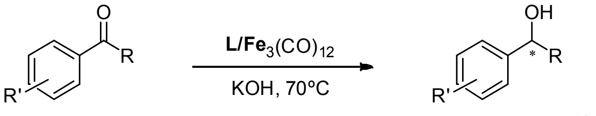
Based on the excellent results obtained with iron catalysts incorporating chelating bis(phosphino)diimine (PNNP) ligands for the asymmetric transfer hydrogenation of ketones[3] and imines[4], the design of new systems with a modular backbone for further progress in this area will be investigated. Currently, the synthesis of a pyrrolidine backbone is explored in our laboratory.

Results:

The PNNP ligands containing a chiral pyrrolidine backbone have been synthesized and fully characterized. Results obtained in the asymmetric transfer hydrogenation of ketones will also be described.







ee's up to 97%

[1] S. Enthaler, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317.

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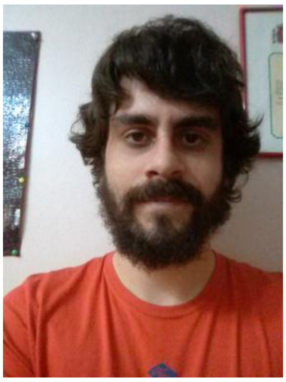
[4] M. Beller et al, *Angew. Chem. Int. Ed.* **2010**, *49*, 8121.

2-Pyridonate- and 8-quinolinate-acylrhodium complexes. Synthesis and catalytic activity



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A. Rodriguez[b], M.A. Garralda[a *]

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Work hypothesis and objective:

2-Hydroxypiridine (PyOH) and 8-hydroxyquinoline (QOH) can easily coordinate to late transition metals as anionic ligands, pyridonate (PyO) [1] or 8-quinolinate (QO) [2]. The objective of this work is to synthesize and characterize new acylrhodium complexes derived from *o*-(diphenylphosphane)benzaldehyde ($P(C_6H_5)_2(o\text{-}C_6H_4CHO)$) and PyOH or QOH with the target of studying their potential catalytic properties.

Results:

Three different complexes, acyl, diacyl and acylhydride species were obtained.

The acylcomplex $[Rh\{\kappa^2\text{-}P(C_6H_5)_2(o\text{-}C_6H_4CO)\}(PyO)Cl]_n$ **(1)** (n=1 or 2), was synthesized by performing the chelate-assisted oxidative addition of $P(C_6H_5)_2(o\text{-}C_6H_4CHO)$ on $[Rh(COD)Cl]_2$ (COD:1,5-cyclooctadiene) in the presence of PyOH (Rh:PyOH:P=1:2:1). The reaction occurs with COD displacement giving a mixture of two isomers. This complex fails to promote the hydrolysis of ammonia-borane to release hydrogen under air at room temperature.

The diacylcomplex $[Rh\{\kappa^2\text{-}P(C_6H_5)_2(o\text{-}C_6H_4CO)\}_2(PyO)]$ **(2)**, was synthesized by reacting $[Rh(COD)(PyO)]_2$ with $P(C_6H_5)_2(o\text{-}C_6H_4CHO)$ (Rh:P=1:2) with hydrogen evolution, giving a mixture of two isomers (**2a**:**2b**=7:1). The major isomer, **2a**, contains a P-Rh-P *trans* conformation with *cis* acyl groups, while **2b** shows a P-Rh-P *cis* distribution with phosphorus atoms *trans* to acyl and to oxygen. This complex effectively catalyses the hydrolysis of ammonia-borane to produce hydrogen, under air at room temperature, giving a yield of 81% in 240 seconds.

Finally, the acylhydridecomplex $[RhH\{\kappa^2\text{-}P(C_6H_5)_2(o\text{-}C_6H_4CO)\}\{\kappa^1\text{-}P(C_6H_5)_2(o\text{-}C_6H_4CHO)\}(QO)]$ **(3)**, was synthesized by reacting $[Rh(COD)(QO)]$ with $P(C_6H_5)_2(o\text{-}C_6H_4CHO)$ (Rh:P=1:2). The chelate-assisted oxidative addition of only one $P(C_6H_5)_2(o\text{-}C_6H_4CHO)$ occurs and the second aldehyde-phosphine ligand coordinates as monodentate.

[1] M. Ciriano, B. Villarroya, L. Oro, *Journal of Organometallic Chemistry*, **1989**, *366*, 377-388

[2] J.G. Leipoldt, E.C. Grobler, *Inorganica Chemica Acta*, **1983**, *72*, 17-20

Compuestos semi-sandwich con cisteínas y cisteínas modificadas

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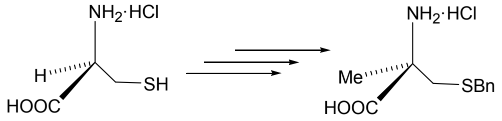
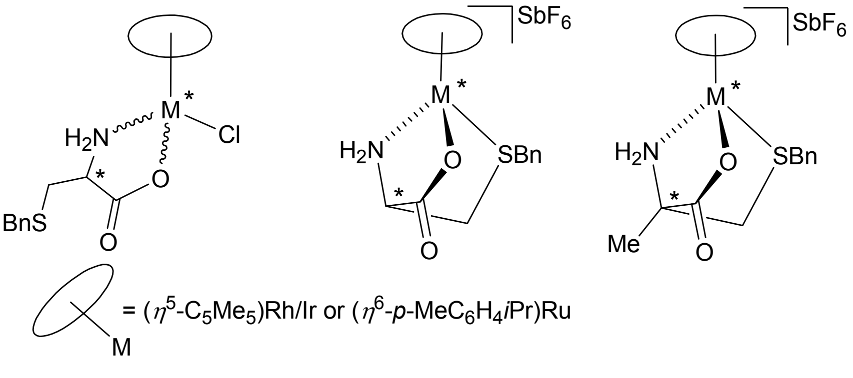
Work hypothesis and objective: La mayoría de los péptidos naturales carecen de la estabilidad metabólica y especificidad suficientes para ser utilizados con fines terapéuticos, debido a la gran libertad conformacional que poseen. Una de las estrategias más habituales para mejorar estas propiedades consiste en la introducción de aminoácidos modificados que confieran rigidez a su estructura secundaria y dentro del amplio abanico de aminoácidos modificados cobran gran interés los aminoácidos cuaternarios.

La cisteína es un α-aminoácido natural con importantes propiedades antioxidantes. Modificaciones de su estructura deben implicar un cambio importante en sus propiedades macroscópicas. Se pretende combinar dos opciones de gran interés: la síntesis de cisteínas modificadas y la preparación de compuestos organometálicos derivados de cisteína que permitan “modular” la liberación de cisteína de una manera controlada.



Results: Se ha preparado α-metil cisteína *S*-bencilada a partir de cisteína. Este aminoácido y cisteína *S*-bencilada se han empleado como presursores para la preparación de compuestos semi-sandwich de rodio (III), iridio (III) y rutenio (II) en los que el metal es un centro estereogénico (Esquema).



De particular interés, es la preparación de compuestos con cisteínas coordinadas trihapto que por hidrólisis podrían liberar el aminoácido de manera controlada.

P115

Estudio teórico y experimental de la transferencia del grupo oxo en oxo-imiduro complejos de molibdeno(VI).

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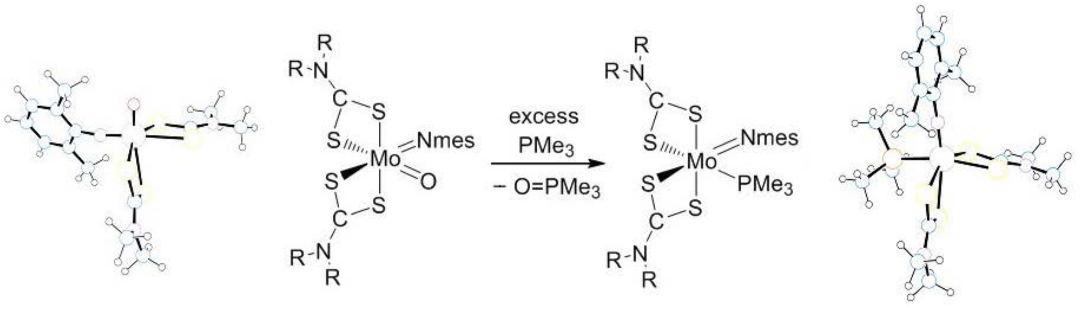
Objetivos:

La reacción de transferencia de un átomo de oxígeno (OAT) es un paso clave en un buen número de procesos de interés [1]. Esta transferencia ha sido ampliamente investigada en complejos modelo de molibdeno [2], sin embargo, esta situación contrasta con la poca atención que ha recibido la reacción análoga de transferencia de grupos imiduro.

Resultados:

La síntesis de los complejos $[Mo(O)(NAr)(Rdtc)_2]$ (Rdtc = dialquilditiocarbamato, Ar = 2,4,6-$Me_3C_6H_2$) [3] ha permitido llevar a cabo un estudio comparativo de los dos posibles procesos de transferencia de los grupos oxo e imiduro a sustratos de tipo PR_3. En el tratamiento de $[Mo(O)(NAr)(Rdtc)_2]$ con un exceso de PMe_3 se observó exclusivamente la formación de $[Mo(NAr)(Rdtc)_2(PMe_3)]$ y $OPMe_3$, de acuerdo con un proceso OAT y sin ninguna evidencia de la transferencia de grupos imiduro. Para obtener más información acerca de los procesos de transferencia de los grupos oxo e imiduro y de la transferencia selectiva del grupo oxo en nuestro sistema, se realizaron cálculos de DFT (B3LYP) con los complejos modelo $[Mo(O)(NAr)(Medtc)_2]$ (Ar = Ph, 2,6-$Me_2C_6H_3$) y el substrato PMe_3. Se investigaron los mecanismos de ambas reacciones de transferencia y, en esta comunicación, se presentarán los resultados de este estudio.



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[2] Por ejemplo: (a) J.H. Enemark, J. J. A. Cooney, J. J. Wang, R. Holm, *Chem. Rev.* **2004**, *104*, 1175. (b) R. Holm, *Coord. Chem. Rev.* **1990**, *100*, 183.

[3] F. Montilla, A. Pastor, A. Galindo, *J. Organomet. Chem.* **1999**, *590*, 202.

New palladium(II) catalysts for the dehydration and rearrangement of aldoximes.

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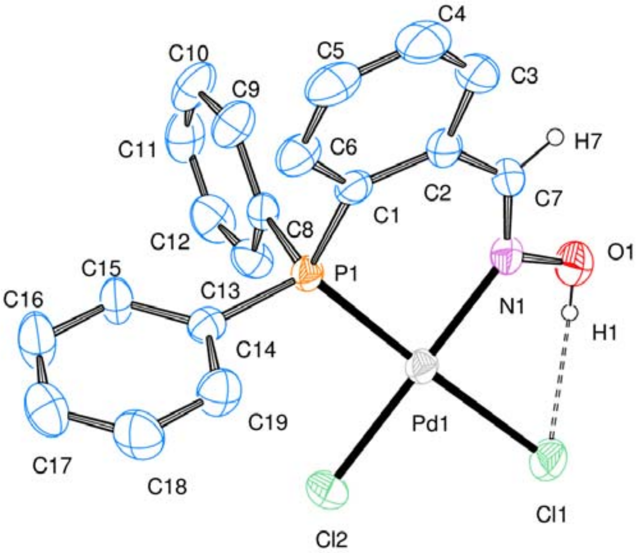
Among the heteroditopic bidentate ligands presently known, those featuring mixed *P,N*-donor sets are the most common examples. The ability of these ligands to liberate a coordination site for substrate binding, owing to the different steric and electronic properties of the donor groups, has been widely exploited in the chemistry of transition-metal complexes providing unique examples of chemical reactivity, including a large number of applications in homogeneous catalysis.

Despite its great potential and commercial availability, the coordination chemistry and catalytic applications of the potentially *P,N*-donor ligand 2-(diphenylphosphino)benzaldoxime remain to date virtually unexplored.[1] In this communication we will present the preparation and structural characterization of the first palladium(II) complexes containing this ligand (an example is given in the Figure), as well as their application in the catalytic rearrangement and dehydration of aldoximes to form primary amides and nitriles, respectively.



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[1] (a) Xu, L.; Zhu, D.; Wu, F.; Wang, R.; Wan, B. *J. Mol. Catal. A: Chem.* **2005**, *237*, 210-214. (b) Xu, L.; Zhu, D.; Wu, F.; Wang, R.; Wan, B. *Tetrahedron* **2005**, *61*, 6553-6560. (c) Zhu, D.; Xu, L.; Wu, F.; Wan, B. *Tetrahedron Lett.* **2006**, *47*, 5781-5784.

P117

The search for new anticancer drugs: Ir^{III} derivatives with arylazole ligands

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Natalia Busto,[a] **Félix A. Jalón**,[b] **Blanca R. Manzano**,[b]
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Universidad de Castilla-La Mancha, Ciudad Real, España.

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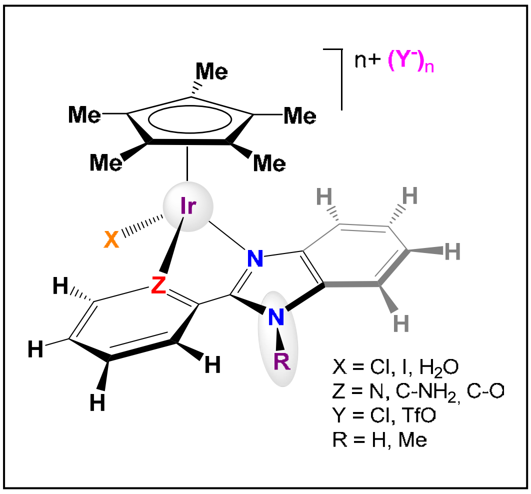
Work hypothesis and objective:

The search for new anticancer drugs with a wider action spectrum and reduced side-effects is leading the scientific community into the almost unexplored territories of transition metals (Os, Ir, Rh and Pd). The combination of organic compounds together with metallic fragments in a single chemical molecule can improve some properties of the formers, such as the aqueous solubility and can also enhance their therapeutic effects due to the synergistic action of both elements [1]. Bearing this in mind, we have decided to extrapolate our previous experience in the synthesis of Ru(II) arene complexes with arylazole ligands and the study of their anticancer properties to the field of the Cp*Ir(III) derivatives. Thus the main objective will be to screen for the most active specimens in different cancer cells, through in vitro assays.

Results:

In this communication we intend to present the synthesis and characterization of several new Ir(III) compounds with different arylazole ligands, as well as to study their aqueous solubility, their reactivity against different biomolecules and their cytotoxic potency. Structure-activity relationships will be establish in order to identify the most prominent elements in the antiproliferative activity of the above-mentioned compounds.



$X = Cl, I, H_2O$
$Z = N, C\text{-}NH_2, C\text{-}O$
$Y = Cl, TfO$
$R = H, Me$

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Rh- NPs stabilised by P- based ligands. Synthesis, characterisation and application in selective hydrogenations.

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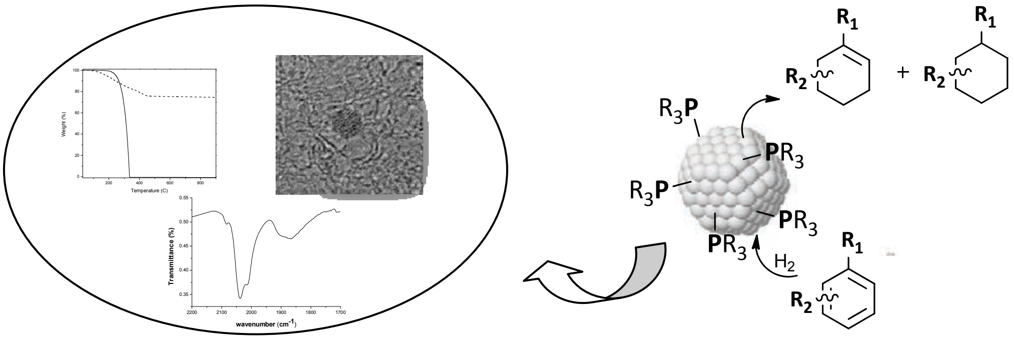
Work hypothesis and objective:

Phosphorus based ligands such as phosphines and phosphites are extensively used in homogeneous catalysis due to their broad coordination chemistry with transition metals and the possibility to fine-tune the electronic and steric properties of the catalysts through structural modifications of the ligands to obtain high activity and selectivity in catalytic processes.[1] In the last decade, these ligands were also shown to efficiently stabilize metal nanoparticles that are catalysts in several catalytic reactions.[2] [3] However, to date, the fine tuning of the properties of this type of catalysts to achieve specific selectivities remains a challenge.

Results:

Here, we describe the synthesis and characterization of rhodium nanoparticles stabilized by common phosphorus compounds molecules and their application in chemoselective hydrogenation. Part of these results were recently reported.[4] The effect of these ligands on the structure and catalytical behavior of the NPs are included. Variations of several parameters such as the concentration of ligand, the nature (phosphite vs. phosphines, mono vs. bidentates) and their electronic and steric properties, were also studied and the catalytic results are correlated with spectroscopic results using techniques such as TEM, Infra-red, CO adsorption, TGA…) with the results.



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Monodentate thiolphosphine-functionalized metal nanoparticles: synthesis and catalytic activity

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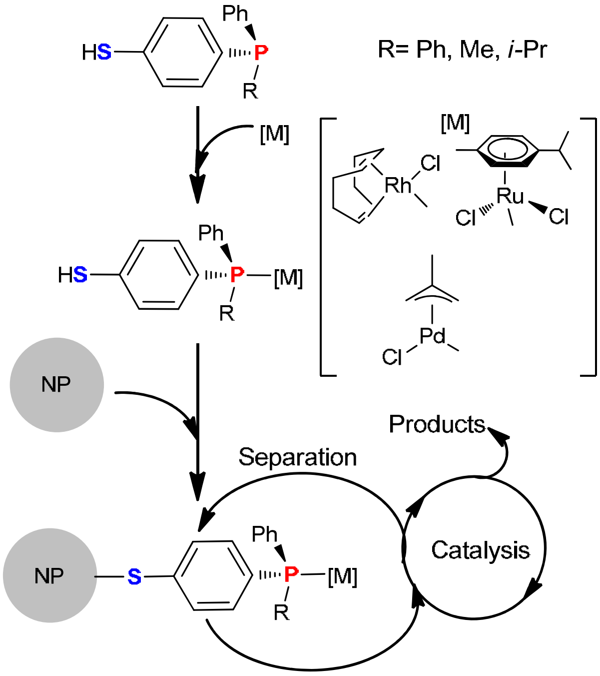
Work hypothesis and objective:

Besides the nanoscale properties, metal nanoparticles (NPs) exhibit an outstanding behaviour that combines high dispersion grade and easy separation. In addition, their properties can be extended towards catalytic activity by immobilization of organometallic compounds [1]. For this purpose, several (chiral and non-chiral) monodentate thiolphosphines were synthesized as organic linkers between NP's surface and organometallic compounds in order to explore their potential catalytic activity.

Results:

The synthesis of monodentate P-sterogenic thiolphosphines was carried out by the Jugé method [2]. The obtaining of the thiolphosphine requires deprotection with Na/NH_3(l), and phosphine deprotection with morpholine. Next, metal complexes of each phosphine were prepared and their structures were established by ^{1}H, ^{13}C, and ^{31}P NMR.

NPs (Pd and Fe_3O_4) were prepared according to literature procedures [3] and then functionalized with the desired thiolphosphine. The new NPs were characterized by HRTEM and XPS. The metal content was obtained by ICP analyses, and the organic fraction by TGA. The catalytic activity has been explored.



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Oxidative Cleavage *vs* Wacker-Type Profiles in Oxygenation Reactions

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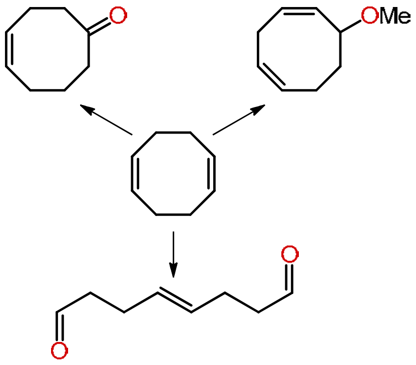
Work hypothesis and objective:

The catalytic oxidation of olefins to give oxygenated compounds such as aldehydes, ketones or ethers are some of the most important transformations in the industry due to the high impact that these products have in our daily life.[1] Despite the enormous efforts of the chemists, some of these processes are still dangerous or contaminant. For example, ozonolysis is a good method for the synthesis of aldehydes; however ozone can be explosive under the drastic reaction conditions used. Other oxidizing agents such as permanganates, iodates or dichromates are toxic. Therefore, the search of alternative systems able to cleanly and safely oxidize C=C bonds is a priority goal in current chemistry. In this sense, the use of oxygen from the air as a friendly oxidant in the oxygenation of organic compounds is a challenge that remains unsolved nowadays.[2]

Results:



In this communication we will show that rhodium complexes bearing robust bidentate N,O-ligands are able to activate oxygen and transfer it to olefins to give a variety of oxygenated species Thus, ketones, ethers or aldehydes (see figure) can be isolated from a fine tuning of the reaction conditions. Mechanistic features directing the selectivity to one or other type of products will be discussed. In addition, one complex derived from the regioselective hydroxylation of one of the C=C bonds of cod (1,5-cyclooctadiene) has also been isolated and its formation will be discussed in the overall scheme.

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Molecular complexes anchored on graphene: Catalyst activity and reciclability studies

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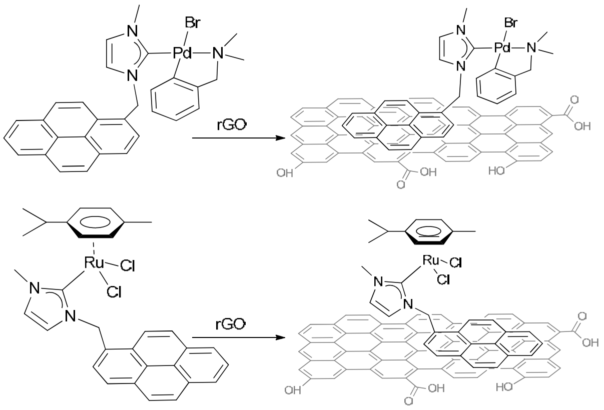
Despite the attractive properties of many homogeneous catalysts in terms of activity and selectivity, they suffer from difficulties associated with separating the products from the catalyst and catalyst recycling, for which an enormous effort in the immobilization of known catalysts onto solid supports is currently being carried out.[1]

The immobilization of a homogeneous catalyst onto a solid surface is one of the major challenges in catalysis, because it may facilitate the separation of the catalyst and the reaction products, and may also give rise to the reutilization of the catalyst in multiple subsequent cycles.



Graphene and derivatives have attracted increasing attention because of their unique physical and chemical properties, which make them particularly interesting in the fields of nanochemistry and catalysis.[2] Together with their inherent properties, graphene and derivatives offer a unique opportunity to non-covalent modifications by π-stacking interactions with molecules containing polycyclic aromatic hydrocarbons.[3]

In this work, we study the preparation and catalytic properties of two hybrid catalysts based on N-heterocyclic carbene ligand with a pyrene-tag and reduced graphene-oxide (rGO). The molecular complexes could be immobilized onto the surface of rGO by π-stacking.

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Enones activate ArS-Bpin to synthesize 4-sulphanyl ketones

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and Elena Fernández[a]

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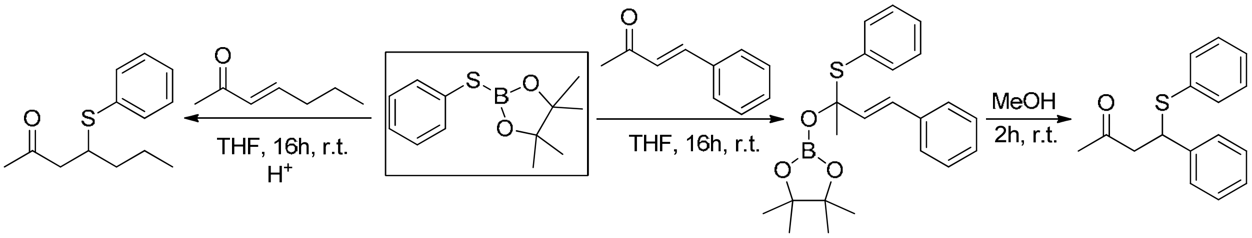
[b]Department of Chemistry and Biochemistry, Mount Allison University, Sackville, NB (Canada).
Email: marc.garciac@estudiants.urv.cat

Work hypothesis and objective:

1,4- addition of thiols to α,β-unsaturated carbonyl compounds constitutes a key reaction in biosynthetic and organic processes. Following this strategy, the C-S bond formed requires the use of strong bases or Lewis acids [1],[2] which promote the formation of undesirable side products owing to side reactions, such as self-condensation of enones, rearrangements or polymerization.

Results:

We report here a direct α-sulfido carbonyl compound synthesis by the easy activation of ArS-Bpin reagents with the enone used as substrate. This convenient methodology can be performed at room temperature with no other additives. The key point of this reactivity is based on the acidic properties of the boryl unit of the ArS-Bpin reagent, which in the presence of the α,β-unsaturated carbonyl compound, an interaction occurs between the C=O and the Bpin. Consequently, the SAr unit becomes more nucleophilic and promote the 1,4- versus the 1,2 addition, as a function of the substrate involved.



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Synthesis of water-soluble NHC-Pt(0) complexes and their application in the hydrosilylation reaction of phenylacetylene

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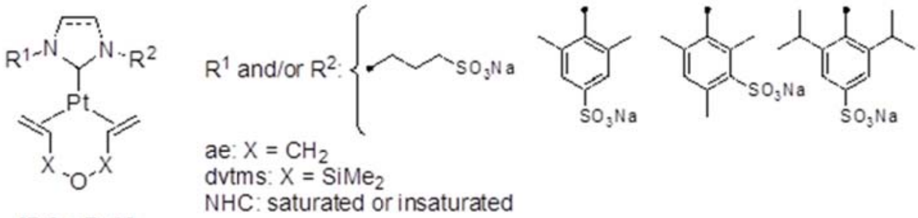
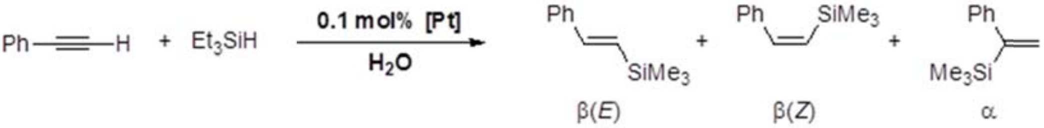
N-Heterocyclic carbene (NHC) ligands tend to bind strongly to metal centers, usually imposing them steric protection, resulting in robust organometallic complexes [1]. Furthermore, those NHCs derived from imidazole can be easily functionalized with hydrophilic groups, such as sulfonates, which render water-soluble complexes [2]. Platinum complexes containing hydrophilic NHC ligands were unknown until 2012, when our group reported the synthesis of water-soluble (NHC)Pt(0) [3], complexes, and of Pt(II) later on [4]. Here we present the synthesis of new Pt(0) mono(NHC) complexes of this type, and their behaviour in the hydrosilylation of phenylacetylene in water.



[Pt] = 7–13



Complexes **7-13** can be prepared by NHC/labile ligand substitution in suitable Pt(0) sources (*e.g.*, Karstedt's complex). Complexes containing sulfonated mesityl substituents are obtained as pairs of rotamers in solution. And all complexes catalyze the model hydrosilylation reaction of phenylacetylene with triethylsilane in water and can be easily recovered and reutilized.

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Alkyl Effect on Organylmagnesium 2,6-bis(imino)pyridine systems. Synthesis of Square Planar Alkylmagnesium(II) Dihydropyridinates.

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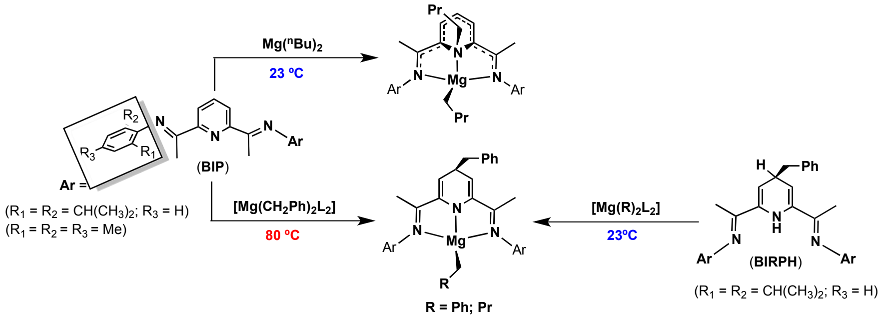
The synthesis and catalysis associated bis(imino)pyridine alkyl complexes has been widely investigated over the last fifteen years.[1,2] However, most of the studies suggest the inherent instability of such derivatives so, their isolation is restricted to just few examples.[2a,b,d] On the other hand, there are several well-defined products related to the evolution of these species. One of the commonest leads to monoalkyl derivatives, in which the ancillary ligand shows one of the alkyl groups, previously attached to the metal centre, on the remotest position of the pyridine ring, but the majority of these species are un-stable too. Thus, other subsequent transformations follow,[2d,e,3] which are the origin of novel structures. We discovered that zinc monoalkyl dihydropyridinates are exceptionally stable compounds.[2f] This inspired us for new investigations whose results will be presented in here, including a synthetic study centred on combinations of unexplored alkyl metals, for what we chose magnesium (MgR_2), as shown in the Scheme below.

Mg^nBu_2 reacts with {2,6-[2,6-($^iPr_2C_6H_3$)NCMe]$_2C_5H_3N$} yielding pyridine N-butyl systems such as [Mg^nBu{2,6-[2,6-($^iPr_2C_6H_3$)NCMe]$_2C_5H_3N(^nBu)$}](Scheme, top). [$Mg(Bz)_2THF_2$] gives rise to a kinetically controlled product consisting of a mixture of iminopyridine-enaminate(-1) and bis-imino-dihydropyridinate(-1) magnesium monobenzyls in a 1:1.5 ratio. At 80 ºC, this rearranges affording the most thermally stable isomer, the dihydropyridinate (Scheme, bottom). Conversely, 4-benzyl-dihydropyridinate(-1)MgR were prepared by deprotonation of bis(imino)-4-benzyl-dihydropyridine. All these are remarkably stable and promising catalysts for ring opening polymerization (ROP) of lactones and lactides, among other catalytic reactions. These applications are now under development in our laboratories and preliminary results will be presented in this contribution as well.



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Understanding the aggregation behaviour and spectral properties of alkynyl gold(I) compounds

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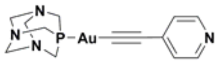
Work hypothesis and objective:

Alkynyl gold(I) complexes are attractive building blocks for the development of supramolecular architectures, that can find applications in molecular electronics and materials science.[1,2] This is mainly due to the linearity imposed by gold(I) and the acetylide unit, together with the occurrence of aurophilic interactions. Moreover, gold(I) compounds usually exhibit interesting luminescent properties that can be tuned by the presence of Au···Au interactions.

Our objective is to analyze the aggregation mechanisms and spectral properties of the aggregates recently reported for compounds **1** and **2** in water.[3,4]

Results:

Microscopy studies reveal that the compounds can generate several kinds of aggregates, showing different morphologies and luminescent properties. Absorption and emission measurements indicate that aurophilic and π- π interactions should play a key role in the aggregation process. The thermal stability of the aggregates has been also studied in order to gain insight into the energetic parameters of the interactions. Moreover, the growth of the aggregates as a function of time has been monitored by means of DLS analysis.



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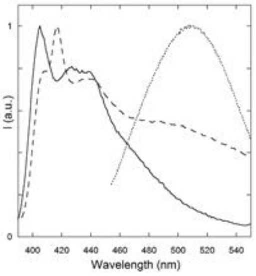

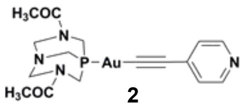

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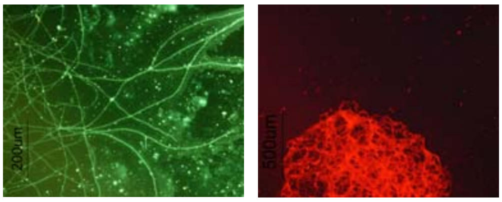

Figure 1. Up: Luminescent hydrogel and emission spectra corresponding to compound **1**. Bottom: Fibrillar luminescent aggregates from compound **2.**

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Selective Iridium-Catalyzed Reduction of CO_2 with Hydrosilanes: Current State and Future Outlook

Francisco J. Fernández-Alvarez,[*a] **E. A. Jaseer,**[b]
Muhammad N. Akhtar,[b] **Mogahid Osman,**[b] **A. Al-Shammari,**[b]
Karin Garcés,[a] **Victor Polo,**[c] **Sulaiman Al-Khattaf**[*b]
and Luis A. Oro[*a,b]

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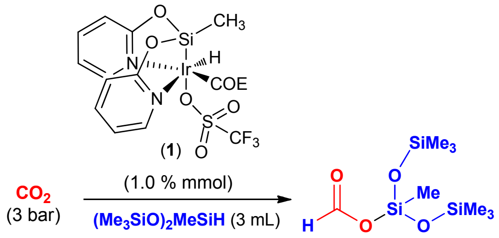
Work hypothesis and objective:

CO_2 hydrosilylation is an important and feasible challenge for large-scale transformations of this greenhouse gas. In any case the initial reaction product, silyl formate, is interesting in its own or as intermediate towards others interesting compounds including formic acid, CH_4, CH_3OH or formamides.[1]

Results:

The iridium(III) complex[Ir(H)(CF_3SO_3)(NSiN)(coe)] (**1**) has demonstrate to be an active catalyst for the solvent-free hydrosilylation of CO_2 with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) (Scheme 1).[2] We have found that the catalytic activity depends strongly on the temperature. The best catalytic performance has been achieved at 75 °C (Figure 1). An outer sphere mechanism based on kinetic and theoretical calculations at the DFT level has been proposed.



Scheme 1

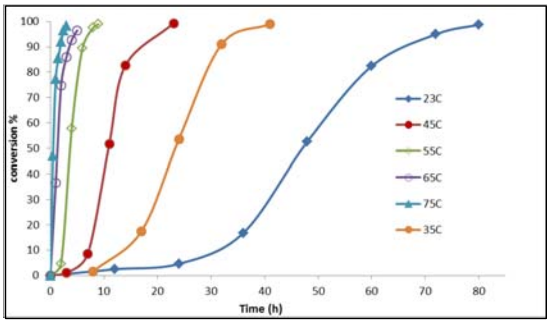


Figure 1

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Reactivity of $[Pt(pq)(\mu{-}C{\equiv}C^{t}Bu)]_2$ with N-donor ligands and mercaptopyridines. Study of the photophysical properties.

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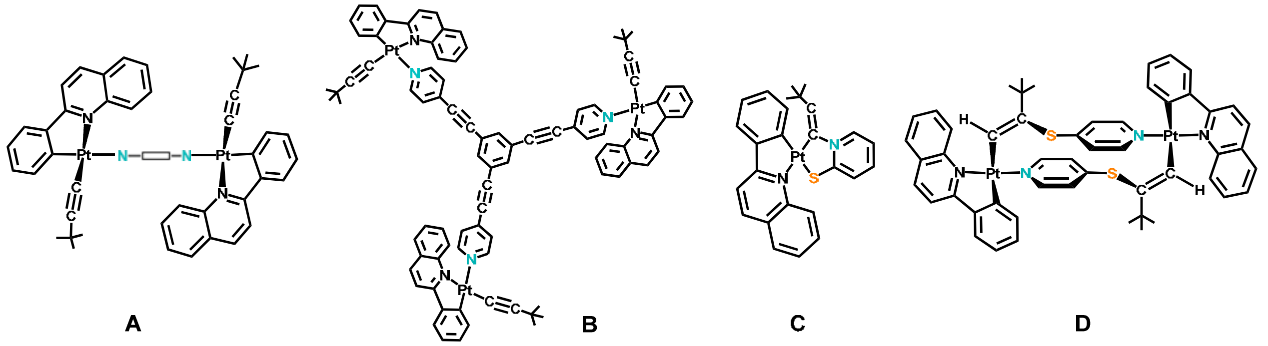
Work hypothesis and objective:

A good number of di- and triplatinum complexes in which the Pt(II) centers are stabilized by double bridging alkynyl systems with different conformations have been reported.[1] Some of these derivatives suffer bridge-splitting reactions with neutral ligands (PPh_3, PPh_2H, CO, py, tht) to give mononuclear σ-alkynyl Pt(II) complexes.[1] Particularly interesting is the reaction of [*trans*-$Pt(\mu{-}\kappa C^{\alpha}{:}\eta^{2}\text{-}C{\equiv}C(OH)EtMe)(C_6F_5)(PPh_3)]_2$ with HSPh, which afford a diplatinum complex bridged by a mixed thiolate/cyclobutenedylidine bridging system.[2] We have recently reported the series of luminescent cyclometalated complexes $[Pt(pq)(\mu{-}\kappa C^{\alpha}{:}\eta^{2}\text{-}C{\equiv}CR)]_2$ (pq = phenylquinoline), stabilized by a double alkynyl bridging system.[3]

Results:

Herein, we report the reactivity of the *ter*butylderivative $[Pt(pq)(\mu{-}\kappa C^{\alpha}{:}\eta^{2}\text{-}C{\equiv}C^{t}Bu)]_2$ toward dinucleating or trinucleating nitrogen ligands and mercaptopyridines. This study has allowed us to synthesize a series of diplatinum(II) derivatives $[\{Pt(pq)(C{\equiv}C^{t}Bu)\}_2(\mu\text{-}L)]$ (L = pyz, bpy, bpa, bpe and bpac) (**A**) and the trinuclear derivative $[\{Pt(pq)(C{\equiv}C^{t}Bu)\}_3(\mu\text{-}L)]$ (**B**), containing a rigid conjugated pyridyl alkynyl ligand. Furthermore, the reactions with 2- and 4-mercaptopyridine give rise to mononuclear $[(SP\text{-}4\text{-}2)Pt\{\kappa C{:}\kappa S\text{-}2\text{-}SC_5H_4N\text{-}(Z)\text{-}C{=}CH^{t}Bu\}(pq)]$ (**C**) and $[(SP\text{-}4\text{-}2)Pt\{\mu\text{-}Z{-}\kappa C{:}\kappa N{-}C{=}CH^{t}Bu\text{-}4\text{-}SC_5H_4N\}(pq)]$ (**D**), respectively. A detailed examination was performed on the photophysical properties of these complexes.



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[3] E. Lalinde, M. T. Moreno, S. Ruiz, S. Sánchez. (Submitted to *Organometallics*).

18-VE Iridium Complexes for Asymmetric Transfer Hydrogenation - Catalytic Activities and Mechanism

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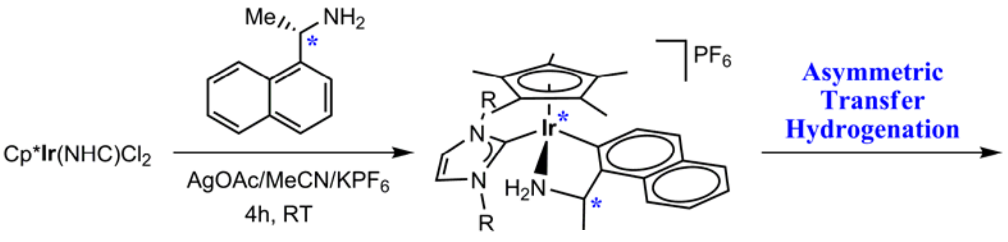
Inert, octahedral, chiral-at-metal complexes are more than mere lab curiosities. They have proven to be very promising species for the design of asymmetric catalysts. Due to the inertness of these complexes, successful catalytic processes must occur through the ligand set rather than through the metal center.

Asymmetric transfer hydrogenation (ATH) reactions are attracting growing interest as an efficient method to prepare enantioenriched organic substrates.[1] The design of highly active catalysts capable of inducing enantiomeric excess in the hydrogenation products is the main goal to be achieved in this research field. Thus, mechanistic studies of ATH processes are crucial in order to understand both the activity of the catalyst and the origin of the enantioselectivity.

In this communication we report the diastereoselective synthesis of novel half sandwich Iridium(III) complexes bearing *N*-heterocyclic carbene ligands and a chelated primary benzylamine. Despite the inertness of these pseudo-octahedral Iridium(III) derivatives towards ligand substitution, complexes **1** and **2** are highly active catalysts under mild conditions for the ATH of prochiral ketones in the presence of catalytic amounts of base, inducing low to moderate ee's. DFT modelization has shed light on the reaction mechanism and the experimental observations have been reproduced accurately. Both the catalytic results and the discussion on the reaction mechanism will also be provided.



1, R = Me (**R_{Ir}**, **S_c**)
2, R = ^{n}Bu (**R_{Ir}**, **S_c**)

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Rhodium Complexes with Redox-Active Tetrazene Ligands

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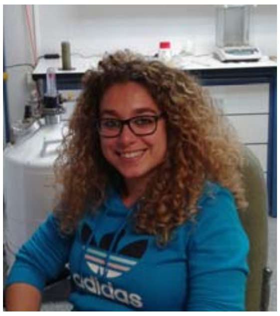
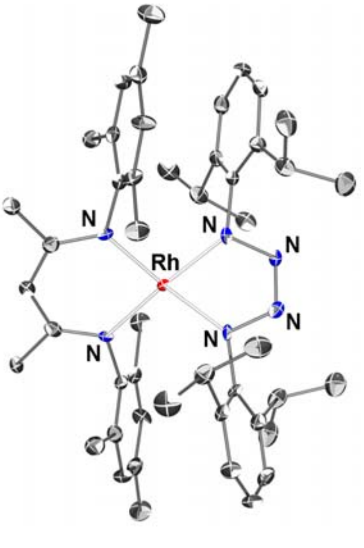


Work hypothesis and objective:

The availability of empty d orbitals to accept π-electron density is a prerequisite for stabilization of M=NR species through multiple bonding between transition metals and imido (RN_2^-) ligands. For this reason, group 9–11 transition-metal ions with high d-electron counts and imido ligands are usually considered to be "incompatible". However, the use of low-coordinate architectures has enabled various groups to uncover the synthesis and reactions of a number of terminal imido complexes of cobalt and nickel.[1] Accordingly, we selected rhodium complexes with bis(N-aryl)-β-diiminato (L^{Me}) ligands that are effective in stabilizing low-coordination numbers[2] with the aim of generate imidorhodium complexes by reaction with organic azides (RN_3).

Results:

Reactions of $[Rh(L^{Me})(C_2H_4)_2]$ with a a variety of aliphatic and aromatic azides gave the tetrazene complexes $[Rh(L^{Me})(R\text{-}N_4\text{-}R)]$, as the result of a dipolar 1,3-addition of the azide to a transient imido complex. The structure of one of them is shown in the Figure.



Tetrazadienes (R-N=N-N=N-R) are unknown in the free state, but they can be found coordinated to transition metals. In these complexes the oxidation state of the metal and tetrazene ligand is not immediately clear since the RNNNNR fragment can be described at least as a neutral or a dianionic ligand and thus, they are non-innocent ligands. Attempts to isolate the transient imido complexes, studies on the redox properties and bonding of the isolated tetrazenes, and further reactions will be described.

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Theoretical study on the C–NH_2 Bond Formation Mediated by Iridium Complexes: migratory insertion versus nucleophilic attack.

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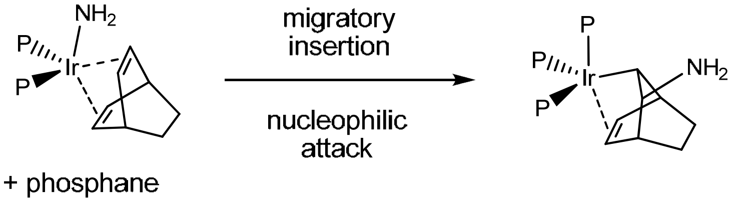
Work hypothesis and objective:

Catalytic hydroamination of unactivated olefins with ammonia to yield added-value chemicals is a rare but highly interesting process. It is required the N–H bond activation of NH_3 to form metal-amido complexes followed by the C–N bond formation. Despite of sound advances in this direction with primary and secondary amines, transfer of the parent amido group from late transition metals to organic substrates through C–NH_2 bond formation still remains a challenge. Recently, we showed that methoxo-bridged d^8 complexes smoothly interact with ammonia to yield amido-bridged species, a strategy that has allowed to prepare the first [Rh–NH_2] complexes.[1] Furthermore, the –NH_2 group can be transferred to a coordinated olefin.[2] However, it is still not clear the mechanism involved in the C–N bond forming process in this catalytic intermolecular hydroamination. Using theoretical calculations at the DFT level, the possible molecular mechanisms for these reactions will be analyzed and new insights into the hydroamination of olefins catalyzed by iridium complexes will be obtained.

Results:

In excess of methyldiphenylphosphane, the trinuclear bridging-parent amido complex $[\{Ir(\mu\text{-}NH_2)(tfbb)\}_3]$ (1) yields $[Ir(1,2\text{-}\eta^2\text{-}4\text{-}\kappa\text{-}C_{12}H_8F_4N)(PMePh_2)_3]$. This complex bears the amino group in *exo* position. A migratory insertion of the olefin into the metal-amido bond can explain the formation of the C-N and the C-Ir bonds. However, DFT calculations discard this mechanism due to the large activation energy. A stepwise intermolecular nucleophilic attack of the –NH_2 group to the more accessible carbon atom has been found to be energetically preferred.



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Luminescent Polypyridine Gold(I) Metallaligands and their use in the Self-Assembly of Heterometallic Macrocycles.

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Laura Rodriguez,[a] **Oriol Rossell**,[a] **Rakesh Puttreddy**,[b]
Kari Rissanen,[b] **Adelino Vieira de Godoy Netto**[c]

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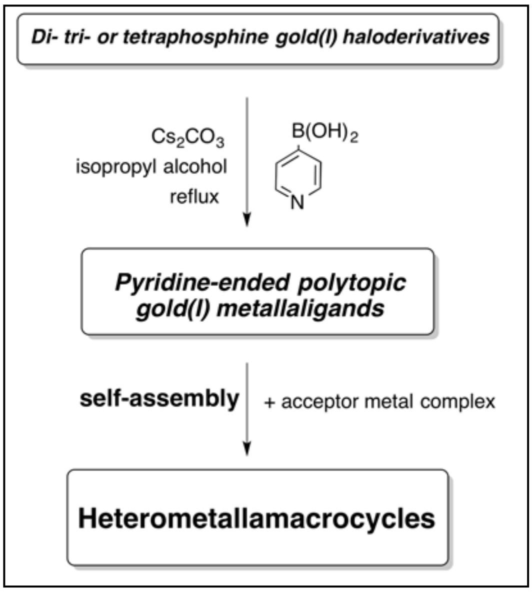
Work hypothesis and objective:

There has been a remarkable interest in the synthesis and properties of metallamacrocycles constructed through coordination self-assembly of metal centers and multidentate ligands.[1] In particular, heterometallic cyclic assemblies can display interesting properties due to the characteristics of the different metal centers. Due to the interesting photophysical properties exhibited by a number of polynuclear gold(I) complexes,[2] our objective involved the synthesis of luminescent heterometallacycles containing gold(I) polyphosphine fragments and the study of their potential use in molecular recognition processes.

Results:

A series of polypyridine Au(I) organometallic metallaligands of the type [$Au_2(\mu_2$-diphos)(py)$_2$], [$Au_3(\mu_3$-triphos)(py)$_3$] and [$Au_4(\mu_4$-tetraphos)(py)$_4$] (py=pyridine) have been prepared in good yield by reaction of the suitable phosphine gold(I) haloderivative with 4-pyridylboronic acid in the presence of Cs_2CO_3.[3] Their self-assembly reactions with selected transition metals have been assayed. Multinuclear NMR spectroscopy in combination with ESI mass spectrometry has showed the formation of heterometallamacrocycles of different charges and sizes. The photophysical properties of both the metallaligands and macrocycles have been investigated.



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Substrate control of the regioselectivity in Palladium-Catalyzed Allylic Substitution Reaction

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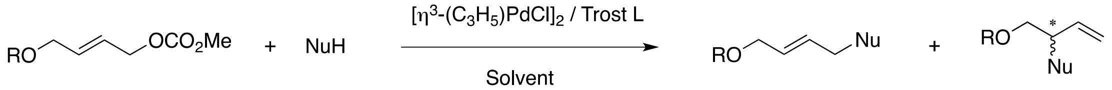
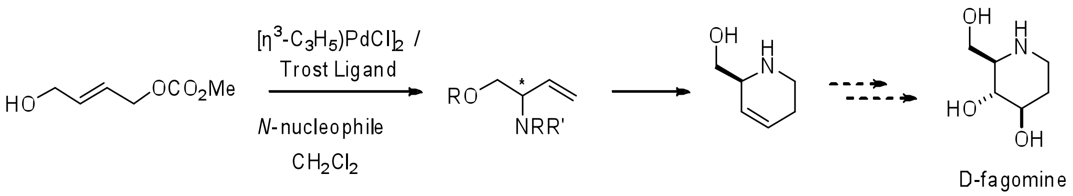
Metal-catalyzed allylic substitution is one of the most powerful methods for the construction of carbon-heteroatom and carbon-carbon bonds and, in this regard, palladium has far proven to be the most versatile metal catalyst for its easy manipulation, high catalytic activity and high enantioselectivity.[1] Despite the importance of this transformation and the enormous amount of work in this field, the control of regioselectivity is still an unresolved problem, limiting the chances for the development of asymmetric versions. Indeed, with the exception of a few examples, the easily accessible linear monosubstituted allylic electrophiles are not suitable substrates for asymmetric palladium-catalyzed substitution, because they typically yield achiral, linear substituted products.[2]



In this communication, we describe our investigations on Pd-catalyzed allylic amination reactions of linear allylic carbonates with different *N*-nucleophiles, showing that regioselectivity can be tuned by an interplay of steric and hydrogen bonding interactions due to the presence or absence of protecting groups at the OR group. This method can be used to give access to enantioenriched branched allylic amines using the DPPBA catalysts developed by Trost, as exemplified by our enantioselective formal synthesis of the iminosugar fagomine.



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Activation of C-H and C-X Bonds by Chiral Phosphano-oxazoline Iridium Complexes

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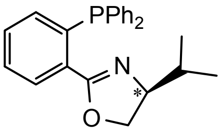
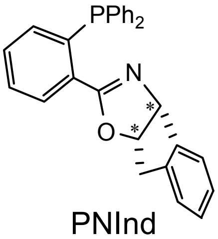
Work hypothesis and objective: Chiral phosphano-oxazoline ligands (PN*) with a soft phosphorus donor atom and a hard nitrogen have been successfully applied to an increasing number of organic transformations.[1] Here, we report the preparation of a series of octahedral iridium(III)/PN* complexes and the preliminary results on their catalytic activity in the 1,3-dipolar cycloaddition reaction of the nitrone *N*-benzylidenphenylamine *N*-oxide to methacrolein.

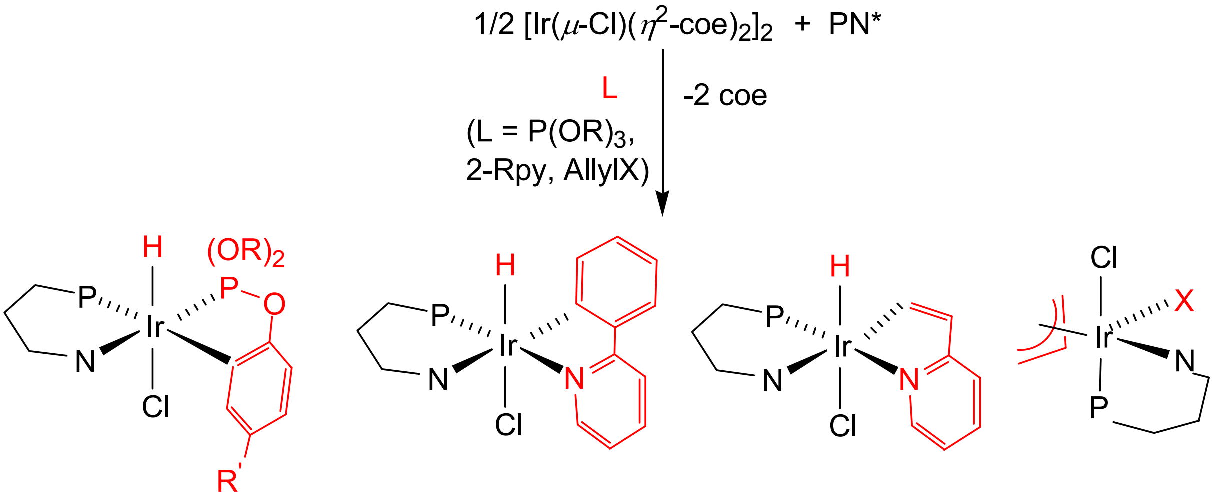


PN*i*Pr



PNInd

Results: Neutral iridium(III) complexes of the stiochiometries shown in the Scheme have been prepared by oxidative addition of a carbon-hydrogen or carbon-halogen bond arising from tertiary arylphosphites, 2-substituted-pyridines, or allyl halides to adequate iridium(I)/PN* precursors. The new compounds have been completely characterized, including the assignment of the absolute configuration at the metal.



Scheme

[1] See for example: D. Carmona, J. Ferrer, N. García, P. Ramírez, F. J. Lahoz, P. García-Orduña, L. A. Oro, *Organometallics*, **2013**, *32*, 1609-1619, and refs. therein.

Simple phosphite-amine ligands for palladium catalyzed allylic substitution reactions

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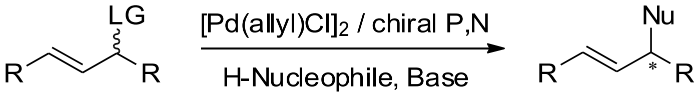
Work hypothesis and objective:

The formation of chiral carbon-carbon bonds is the most fundamental process in the synthesis of complex molecules from simple ones. Of all the C-C bond forming strategies, asymmetric Pd-catalyzed allylic substitution is the one that has received most attention for decades. Most of the successful catalysts reported to date make use of either ligands with large bite-angles to create a chiral cavity in which the allyl system is embedded or ligands containing different donor atoms, which can electronically discriminate the two allylic terminal carbon atoms.[1] Our group has demonstrated that the presence of biaryl-phosphite moieties in ligand design is highly advantageous by overcoming the most common limitations of this process, such as low reaction rates and high substrate specificity.[2] In this poster, we therefore present the synthesis and application of a simple new phosphite-amine ligand library derived from the chiral pool in allylic substitution of a wide range of substrates using several carbon nucleophiles.

Results:

The results a comparable to the best one reported. In addition, the potential application of allylic substitution using functionalized malonates will be also demonstrated by the synthesis of important building blocks.



Scheme 1. Asymmetric Pd-catalyzed allylic substitution reaction

References:

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Calixarene-type Complexes of Rhodium and Iridium with Nucleobases

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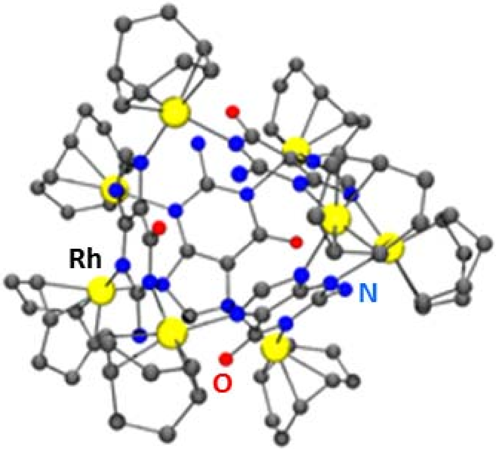
Work hypothesis and objective:

Metal ion complexes containing nucleobases as ligands are interesting because of their involvement and their significance in nucleic acid processes.[1] Moreover, because of the different binding sites and their relative disposition they have allowed the access to macromolecular structures as building blocks in coordination chemistry, including “organometallic-boxes” suitable for trapping cations, anions or neutral molecules.[2] Representative examples are metallacalixarene-type complexes of platinum[3] and copper[4] derived from uracile and citidine, respectively.

Results:

In this communication we will show some calixarene-type complexes of rhodium and iridium based on double deprotonated uracile and guanine anions. In particular, hexa and octanuclear metallamacrocycles (see figure) will be described. Analysis of the wideness of the hole in these compounds to host molecules inside derived from the different disposition of the N- and O- donor atoms in the two mentioned nucleobases will also be discussed.



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Cobalt Particle Size Effects in the Fischer-Tropsch synthesis: comparison between colloidal and TiO_2 supported nanocatalysts

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[c] *Total Research and Technology Feluy, Zone Industrielle Feluy C, B-7181 Seneffe, Belgium*
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Work hypothesis and objective:

The Fischer-Tropsch Synthesis (FTS) has been considered a key process of the biomass-to-liquid (BTL), gas-to-liquid (GTL) and solid-to-liquid technologies (STL)[1] since through this catalytic reaction, syngas can be transformed into high quality synthetic fuels.[2] The study of the particle size effect in FTS has for many years attracted the attention of the scientific community, with the goal to improve the catalytic performance of the catalysts in terms of activity and selectivity. Our approach to aboard this issue was the synthesis of well-defined particle size cobalt nanoparticles (CoNPs) and their testing in FTS using two set-ups: STR (using water as solvent) and fixed bed reactors.

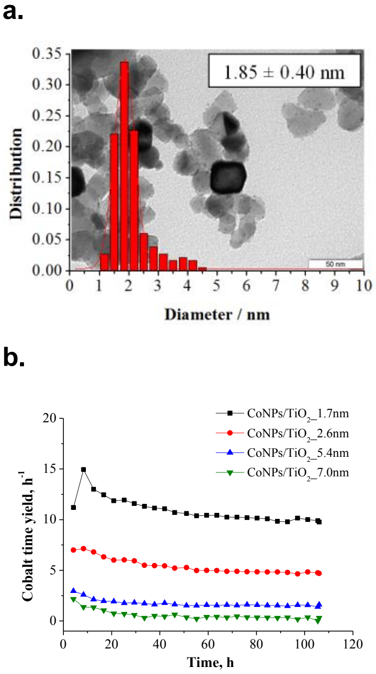

Figure 1. (a) Size histogram and TEM micrographs of CoNPs/TiO_2; **(b)** Evolution of cobalt-time yield during time in FT experiments.

Results:

Well dispersed CoNPs in the range of 1.7-7.0 nm were synthesized in water by a chemical reduction methodology, using $NaBH_4$ as reducing agent and PVP as stabilizer. The series of CoNPs were immobilized on TiO_2 (Figure 1b), and both, the colloidal and the supported catalysts were tested in the aqueous FTS (AFTS) and the gas phase FTS using STR and fixed bed reactors respectively. The catalytic performance of colloidal and supported catalysts resulted to be size dependent with an increase of activity when the particle size decreases (Figure 1b). The observed behavior will be discussed in terms differences of the catalysts according to characterization techniques such as TEM, HR-TEM, XRD, TGA, XPS, TPR among others.

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Pt(II) and Pt(0) complexes with terphenylphosphine Ligands

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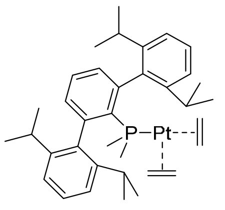
Work hypothesis and objective:

Bulky phosphine ligands find widespread applications in organometallic chemistry and catalysis.[1] The main objective of this work is to synthetize new Pt(0) and Pt(II) complexes using the sterically encumbered dialkyl(aryl)phosphine, PMe2Ar', where Ar' is a terphenyl group, namely C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$.

Results:



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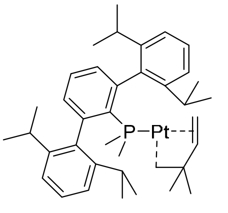

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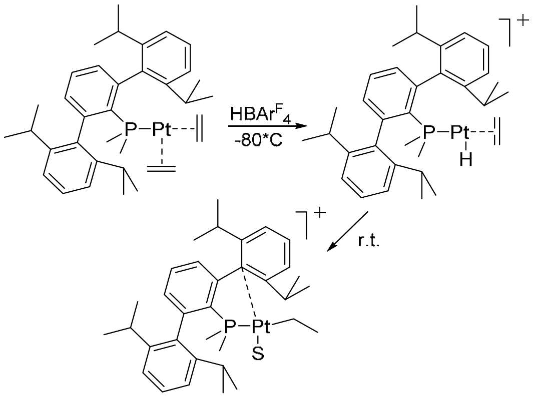

The Pt(II) precursor $PtCl_2(PMe_2Ar')$ can be readily made from commercially available $PtCl_2$ and the phosphine. Other Pt(II) compounds such as $PtMe(Cl)(PMe_2Ar')$, $PtMe_2(PMe_2Ar')$ and $PtH(SiEt_3)(PMe_2Ar')$, where the phosphine acts as a bidentate, κ^2-*P*,*C* ligand, by means of a Pt-C_{arene} interaction with the *ipso* carbon atom of a flanking aryl ring (as demonstrated by X-ray studies for some of the above complexes), have also been investigated.

Corresponding Pt(0)-PMe_2Ar' complexes with olefin ligands can be obtained from $PtH(SiEt_3)(PMe_2Ar')$ by alkene-induced reductive elimination, or by reduction of $PtCl_2(PMe_2Ar')$ in the presence of the olefin. Reactivity studies on some of these Pt(0) complexes (protonation, oxidative addition, catalytic alkene hydrosilylation and other reactions) will also be described.

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Access to Novel Dinuclear Osmium Complexes Enclosing a Bis(arylimino)isoindoline ligand: Electrochemical & Theoretical Study.

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Enrique Oñate,[a] Alicia Santiago[b] and Miguel A. Sierra[b]

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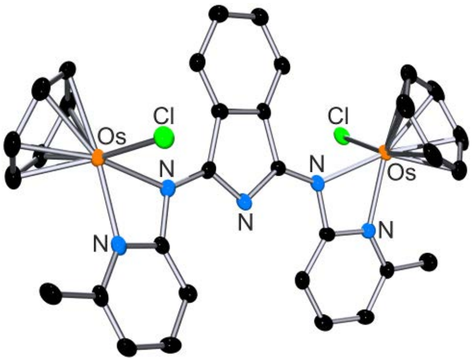
Work hypothesis and objective:

With the aim of preparing new late transition metal complexes with easily tuneable electronics for reactivity studies (including water splitting catalysis), we started looking for a robust osmium(II) system supported by *N*-based ligands. Bis(arylimino)isoindolines (HBAII) are typically classified as tridentate, monoanionic nitrogen ligands possessing high oxidative and thermal stability.[1] We present here the access to a series of dinuclear osmium complexes enclosing the 1,3-bis(6'-methyl-2'-pyridylimino)-isoindoline ligand (exhibiting a non-conventional coordination mode), together with their electrochemical and theoretical studies.

Results:

The dimer $[OsCl_2(\eta^6\text{-}C_6H_6)_2]_2$ reacts with the afore mentioned HBAII ligand to afford the cationic dinuclear osmium complex $[(\eta^6\text{-}C_6H_6)ClOs(BAII)OsCl(\eta^6\text{-}C_6H_6)]Cl$ (See Figure). Besides, the unsaturated complex $OsH(OH)(CO)(P^iPr_3)_2$ acts as the precursor for the preparation of $[(\eta^6\text{-aryl})ClOs(BAII)OsH(CO)(P^iPr_3)_2]Cl$ and $[(P^iPr_3)_2(CO)HOs(BAII)OsH(CO)(P^iPr_3)_2]$. The homoleptic dimer $[(\eta^6\text{-}C_6H_6)ClOs(BAII)OsCl(\eta^6\text{-}C_6H_6)]Cl$ suffers a photochemically catalyzed isomerization process that will be also detailed.



View of $[(\eta^6\text{-}C_6H_6)ClOs(BAII)OsCl(\eta^6\text{-}C_6H_6)]^+$

References:

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Pyrene-based bisazolium salts: from luminescence Properties to *Janus*-type bis-N-heterocyclic carbenes

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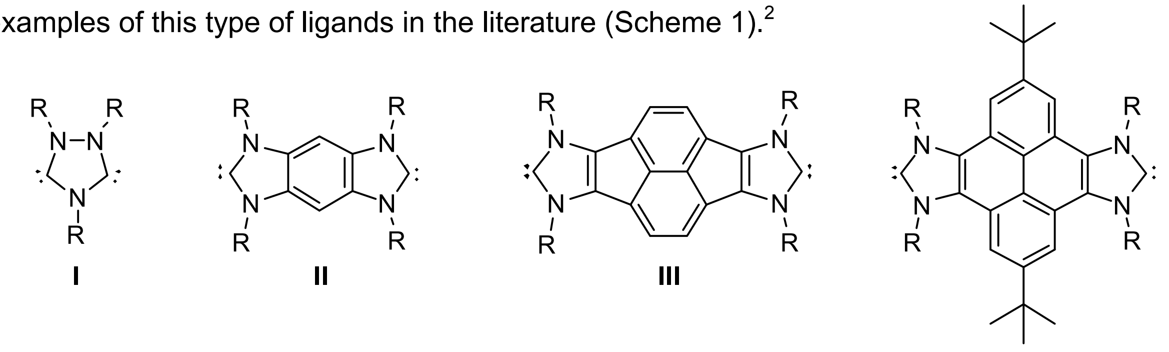
During the last years, N-heterocyclic carbenes (NHCs) have emerged as a very important kind of ligands for the design of polimetallic complexes, which usually show better catalytic properties than their monometallic counterparts.[1] In this sense, *Janus*-type bis-NHCs are a really attractive kind of ligands since they can bear two metals in a facially opposed disposition. However, there are just a few examples of this type of ligands in the literature (Scheme 1).[2]



IV (this work)

Scheme 1. Examples of *Janus*-type bis-NHCs described in the literature

In order to expand this family of ligands, we have synthesized a series of pyrene-based bisazolium salts, precursors of NHC ligand **IV** depicted in Scheme 1.[3] These compounds show fluorescence properties with emissions ranging from 370 to 420 nm, and quantum efficiencies in the range of 0.29-0.41. The bisazoliums were used as precursors for *Janus*-type bis-NHCs. These ligands were coordinated to rhodium and iridium fragments and their donor properties as well as the electronic communication between the metal centres were investigated.

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Steric and Electronic Properties of Bulky yet Flexible *N*-Heterocyclic Carbenes.

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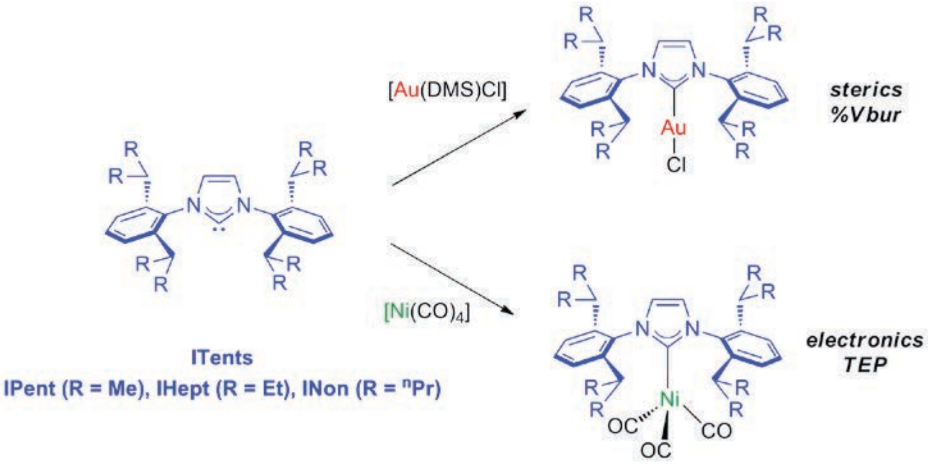
N-Heterocyclic carbenes (NHC) have become a well-established tool in organometallic chemistry.[1] NHCs have been successfully employed as ancillary ligands in various transition-metal catalysed processes. Their steric and electronic properties have proven to have a dramatic effect on the catalytic performance. Therefore, much effort has been devoted to the design of new NHCs and the characterization of their properties. Inspired by the concept of 'flexible bulk', e.g. ligands capable of adjusting their steric bulk as a function of incoming substrates, first proposed by Glorious[2] and applied to palladium catalysis by Organ,[3] our group has developed a simple procedure to obtain the 'ITent' (Tent for tentacular) family of bulky yet flexible NHCs.[4] The steric properties of the ITent family, comprised of IPent, IHept, and INon, have been evaluated using the established AuCl(L) model. [AuCl(ITent)] complexes were synthesized and their %Vbur and steric maps were calculated. The electronic properties were determined by means of the synthesis of [Ni(ITent)$(CO)_3$] complexes. IR measurements of solutions of these complexes allowed us to calculate the Tolman Electronic Parameter (TEP) of the ITent ligands.



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Synthesis and Characterisation of Thiolate Bridged Gold(I)-NHC Complexes and their Application in Catalysis

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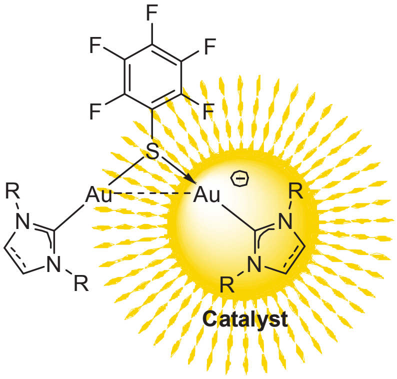
Work hypothesis and objective:

In recent years, the development of gold catalysis has attracted great interest and gold complexes, especially gold species bearing an N-heterocyclic carbene (NHC) ligand, have become very important in synthetic chemistry and have allowed the design of numerous gold(I) complexes, which are precursors to active species in different catalysed reactions.[1] Recently, the formation of chloride bridged phosphine complexes of the form $[(AuL)_2Cl]^+$ has been reported, resulting from the incomplete removal of the chloride ligand of the corresponding gold(I) phosphine complex with different silver salts.[2] These results could have significant implications in catalytic processes that involve *in situ* activation of the gold catalyst. In this work we aim to synthesise and characterise new thiolate bridged gold(I)-NHC complexes which are very stable under ambient conditions. Furthermore, the possibility to release the active gold species without further addition of any silver salt is highly desirable.

Results:

Thiolate bridged gold(I)-NHC complexes were successfully prepared by the addition of 0.5 equivalents of AgOTf to the corresponding thiolate derivative. Both the neutral and cationic complexes were fully characterised by conventional spectroscopic techniques and X-Ray diffraction analysis. As expected, all complexes are catalytically active in several reactions such as cycloisomerisation, endocyclisation of enynes and N-propargylcarboxamides, and hydroarylation–aromatisation reactions.



NHC = IPr, SIPr, IMes, SIMes

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P142

Rhodium-Catalyzed Anti-Markovnikov hydroamination of olefins.

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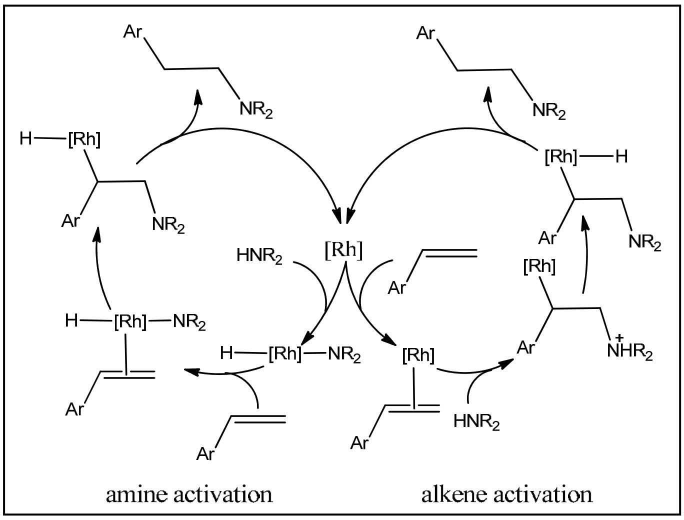
Work hypothesis and objective:

Hydroamination of olefins is one of the most economical pathways for synthesis of nitrogen containing compounds (amines, imines and enamines). This reaction is particularly interesting because of the atom efficiency of the process and the availability of feedstocks but has associated very high activation energies which make necessary use of catalysts. Anti-Markovnikov hydroamination of olefins catalyzed by transition metals, in turn, was named as one of 10 challenges for homogeneous catalysis [1].

We studied by means of DFT calculations the reaction mechanism of anti-Markovnikov hydroamination catalyzed by cationic rhodium complexes using DPEPhos as ligand [2].

Results:

The complete cycle of the two main proposed mechanisms of hydroamination reaction (amine activation mechanism and alkene activation mechanism) [3] of styrene are evaluated. The β-elimination reaction from the hydrido complex as competing side reaction to yield enamine product is also analyzed. Results of this study will be presented the poster.



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P143

Aerobic alcohol oxidations catalyzed by copper complexes containing β-ketiminate ligands derived from keto-enhydrazines.

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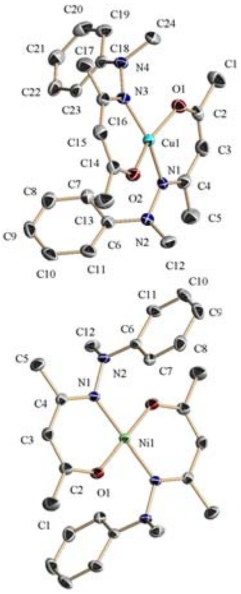
Work hypothesis and objective:

The oxidation of alcohols to aldehydes and ketones is an essential transformation in organic chemistry at both laboratorial and industrial level [1]. There are many known means of achieving this conversion but due to environmental concerns more sustainable processes are continually sought. Oxidation by molecular oxygen represents the cleanest, most sustainable option and catalytic facilitation of this reaction by copper compounds is well established. Herein, we describe the synthesis and characterization of several M(II) complexes of the deprotonated version of 4-(N,N-methyphenylhydrazino)-3-penten-2-one ($HL^{Me,Ph}$), and 4-(N,N-diphenylhydrazino)-3-penten-2-one ($HL^{Ph,Ph}$), and the use of Cu(II) complexes as catalysts in the selective aerobic oxidation of alcohols.

Results:



β-Ketiminate ligand precursors, $HL^{Me,Ph}$ and $HL^{Ph,Ph}$, were synthesized by condensation of acetylacetone and the corresponding N,N-substituted hydrazine. The further reaction of these ligands with $M(OAc)_2$ (M = Cu, Ni, Mn) in refluxing EtOH afforded the corresponding bis(β-ketiminate) metal(II) complexes, $M(L)_2$, in moderate yields. The structures of $M(L^{Me,Ph})_2$ (M = Cu, Ni), determined by X-ray crystallography, showed that ligand $L^{Me,Ph}$ chelate metal(II) ion to form a centrosymmetric complex (see figure) where the N2O2 environment around metal center is, for copper complex, half way between SP and Td. $Cu(L)_2$ complexes were successfully used as catalyst in the selective aerobic oxidation of alcohols in combination with TEMPO as co-catalyst.

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[Ir(IMes”)] complexes with bipy ligands.

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Work hypothesis and objective:

The development of effective water oxidation (WO) catalysts is a critical issue to achieve future energy scenarios.[1] Several organometallic iridium complexes have been recognized as excellent catalysts precursors for this reaction,[2] and their study might provide the keys to access more affordable catalysts. Yet, basic features of their behaviour, such as their homogeneous or heterogeneous nature, are still controversial.[3] The controversy feeds mainly on the exigent reaction conditions required by the routine catalytic tests that use cerium(IV) salts as sacrificial oxidants, which may favour decomposition of the organometallic precursors. In addition, IrO_2 surfaces and nanoparticles are known to make outstanding WO catalysts. Not surprisingly, recent studies point to the ancillary ligands as ultimately responsible for the outcome of the catalyst precursor during the reaction. Oxidatively stable κ-*N,N* and κ-*C,N* chelating ligands such as 2,2’-bipyridine or 2-phenylpyridine have been found effective in preventing nanoparticle formation, and their iridium complexes are thus believed to be truly homogeneous catalysts.[4]

Results:

We have recently reported iridium(III) complexes containing the doubly-cyclometalated NHC ligand IMes”,[5] which are stable under the conditions of the cerium(IV) catalytic tests and have three available coordination positions to prepare almost any other conceivable Ir(III) derivative, either neutral, cationic or zwitterionic. The progress of this chemistry towards WO catalysts and photocatalysts using bipyridine ligands is presented.

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Boron Functionalization of Hydridotris(pyrazolyl)borate Ligand on Osmium Complexes.

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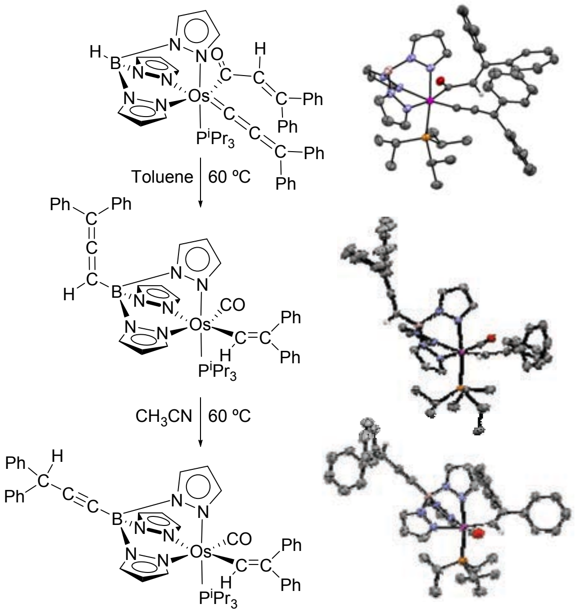
Work hypothesis and objective:

In most Tp-complexes (Tp = hydridotris(pyrazolyl)borate), the Tp ligand acts as an spectator that rarely undergoes transformations. As a part of our ongoing chemistry on Os-Tp complexes we report here the unexpected role of the B-H unit of the ligand, which acts as a claw-tail of the scorpionate to abstract an unsaturated group from the saturated metal center, allowing a subsequent reaction in another ligand.

Results:



The ethylene-pyridyl derivative OsTp{κ^1-C[NC$_5$H$_3$Me]}(η^2-CH$_2$=CH$_2$)(P^{i}Pr$_3$) [1] reacts with two equivalents of phenylacetylene or 1,1-diphenyl-2-propyn-1-ol to give the corresponding alkynyl-vinylidene derivatives. Treatment of the hydroxyalkynyl-hydroxyvinylidene derivative with aluminium oxide promotes the dehydration of the hydroxyvinylidene to allenylidene and the subsequent isomerization of the hydroxyalkynyl ligand into an α,β-unsaturated acyl group. The B–H bond of the Tp ligand abstracts the allenylidene ligand from the metal center providing an allenyltris(pyrazolyl)borate ligand. As a result of the migration, the decarbonylation of the acyl group takes place to form the alkenyl-carbonyl derivative OsTp$^{CH=C=CPh2}$(CH=CPh$_2$)(CO)(P^{i}Pr$_3$). The isomerization of the allenyl substituent of the borate ligand to alkynyl is promoted by a weak base as acetonitrile. These transformations represent very rare examples of boron functionalization of a Tp ligand.

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