BOOK OF ABSTRACTS

XXXIV GEQO CONGRESS ORGANOMETALLIC CHEMISTRY GROUP

Girona (Spain)
September 7-9, 2016

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XXXIV GEQO CONGRESS
ORGANOMETALLIC CHEMISTRY GROUP

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WELCOME

On behalf of the organizing committee it is our pleasure to welcome you to Girona, to the XXXIV Congress of the Organometallic Chemistry Specialized Group of the Spanish Royal Society of Chemistry (XXXIV GEQO meeting) that will take place at the Girona Auditorium and Conference Center between 7th and 9th September 2016.

The biennial GEQO has an outstanding reputation for excellence and highly engaged discussion, and has long been a focal point for scientists at the forefront of organometallic and homogeneous catalysis to present and discuss their latest developments. This edition of the GEQO meeting is a follow-up of the previous ones, with special emphasis on increasing the international dimension of the event by inviting renowned scientists working in the field of organometallic chemistry.

This edition is organized by the Bioinspired, Supramolecular Chemistry and Catalysis Group (QBIS-CAT) of the Department of Chemistry at the University of Girona (Catalonia, Spain). As organizers, we are very proud of the speakers that have accepted our invitations to participate in the event to give either plenary or session lectures. Moreover, we are confident that the 16 oral communications (selected among more than 50 applications) will also contribute to the scientific excellence of this conference. Overall, the latests advances in the field of organometallic chemistry will be presented in more than 230 contributions either as oral presentations or posters.

We hope that you take the opportunity to discuss and exchange ideas with other participants. Estimulating the participation of younger PhD students and scientists is one of the main objectives of the organizing committee. With this aim, two poster sessions have been scheduled in which we hope that students and professors can interact in an informal environment.

Finally, for those who have not visited Girona yet, remember that it is one of the cities with most personality in Catalonia, with a very rich heritage from the past and an impossing series of historial monuments. We hope you will have time to walk through the city and get lost in the small historical streets of the Girona’s old quarter.

Have a nice time in Girona and enjoy the XXXIV GEQO Congress.

Miquel Costas, Chair of the Organizing Committe of XXXIV GEQO Congress.

PROGRAMME

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Wednesday, September 7

11:00	Registration	
14:30	Opening Ceremony	
15:00	PL1	Synthetic single-site iron nitrogenases. *Jonas Peters (Caltech)*
16:00	SL1	Converging strategies in homogeneous and heterogeneous catalysis. *Núria López (ICIQ, Tarragona)*
16:30	SL2	Applications of N-Heterocyclic Carbenes and N-Heterocyclic Imines in Main Group Chemistry. *Shigeyoshi Inoue (Technische Universität München)*
17:00		Coffee Break
17:30 19:00		Poster Session (P1 to P79)

Thursday, September 8

09:00	PL2	From Alkylidynes via Alkynes to Carbenes: Mechanistic Studies and Synthetic Implications. *Alois Fürstner (MPI Mülheim)*
10:00	SL3	Rich metal, poor metal: Gold vs Iron as catalysts for direct benzene C-H bond functionalization. *Pedro J. Pérez (CIQSO - Universidad de Huelva)*
10:30	01	Metal-Catalyzed C–H Functionalization Processes. *Arkaitz Correa (UPV-EHU)*
10:45	02	C–H Functionalization of Amines with Aryl Halides by Nickel-Photoredox Catalysis. *Derek T. Ahneman (Princeton University)*
11:00		Coffee Break

11:30	SL4	New Reactivities of Gold Complexes: It is All a Question of Ligand Design! *Didier Bourissou (CNRS-UPS)*
12:00	SL5	Adventures in Catalysis: from Mechanisms to Applications. *Franziska Schoenebeck (RWTH Aachen)*
12:30	03	Isolation of Key Aryl-Co(III) Intermediates in Co-Catalysed C(sp^2)-H Functionalisations: New Insights into Alkyne Annulation Reaction Mechanisms. *Oriol Planas (Universitat de Girona)*
12:45	04	An efficient and sustainable synthesis of NHC gold complexes. *Alice Johnson (ISQCH, CSIC-Universidad de Zaragoza)*
13:00	05	Silver(I) N-heterocyclic complexes for C-C bond activation of alkylnitriles and catalytic application in oxazoline synthesis. *Rachael Heath (University of Bern)*
13:15	06	Introducing Sodium Magnesiates to NHC Chemistry: Accessing Abnormal, “Paranormal” and Anionic NHC Complexes. *Alberto Hernán-Gómez (University of Strathclyde)*
13:30		Lunch
15:00	PL3	New direction in homogeneous catalysis using N-heterocyclic silylene ligands. *Matthias Driess (Technische Universität Berlin)*
16:00	SL6	Gold perfluoroalkyl complexes and organometallic metalloligands. Synthesis, reactivity and self-assembly processes. *Juan Gil Rubio (Universidad de Murcia)*
16:30	07	Boron ate complex: an old dog with new tricks. *Amadeu Bonet (University of Hull)*
16:45	08	Metallomesogens based in triphenylene-carbene structures. *Ana Beatriz Miguel-Coello (Universidad de Valladolid)*

17:00		Coffee Break
17:30 19:00		Poster Session (P80 to P158)

Friday, September 9

09:00	PL4	Fluorine Chemistry Customized for Drug Discovery. *Véronique Gouverneur (University of Oxford)*
10:00	SL7	Molecular catalysts for the conversion of CO_2 and biomass. *Thibault Cantat (CEA Saclay)*
10:30	09	Light-Driven Reductive Processes using Water and Electron-donors as a Source of Hydrides. *Alicia Casitas (ICIQ Tarragona)*
10:45	010	Detangling Catalyst Modifications Reactions from the Oxygen Evolution Reaction by On-Line Mass Spectrometry. *Paula Abril (ISQCH, CSIC-Universidad de Zaragoza)*
11:00		Coffee Break
11:30	SL8	Water-Soluble Palladium and Platinum N-Heterocyclic Carbene Complexes: From Catalysis to Nanomaterials. *Ernesto de Jesús (Universidad de Alcalá)*
12:00	SL9	Phosphinous acids: cooperative ligands for metal-catalysed nitrile hydration. *Victorio Cadierno (Universidad de Oviedo)*
12:30	011	Well-defined organometallic dinuclear gold complexes - application in dual-gold catalysis. *Jarl Ivar van der Vlugt (University of Amsterdam)*
12:45	012	Iron: A New Player in the Z-Selective (Cross) Dimerization of Terminal Alkynes Catalysed by Transition Metal Complexes. *Orestes Rivada-Wheelaghan (Okinawa Institute of Science and Technology Graduate University)*

13:00	013	Computational investigation of Pd-catalysed selective arylation of aldehydes. *Amalia I. Poblador-Bahamonde (University of Geneva)*
13:15	014	Advances in Computational BioInorganics: Predicting Interactions of Coordination Complexes with Biomolecular Scaffolds. *Jean-Didier Maréchal (Universitat Autònoma de Barcelona)*
13:30		Lunch
15:00	SL10	Dynamic kinetic resolution and desymmetrization approaches to the atroposelective synthesis of axially chiral heterobiaryls. *José M. Lassaletta (Instituto de Investigaciones Químicas, CSIC-US)*
15:30	015	Metal-ligand cooperative system in azolate-pincer complexes: bifunctional catalysis. *Elena Avila (Instituto de Investigaciones Químicas, CSIC-US)*
15:45	016	Building New Bridges Between Metal- and Bio-Catalysis: Unprecedented Concurrent Cascade Approach to Chiral Alcohols in Aqueous Media. *Joaquín García-Álvarez (Universidad de Oviedo)*
16:00	PL5	Homogeneous catalysis and fuel cells: an emerging partnership. *Shannon S. Stahl (University of Wisconsin)*
17:00		Closing ceremony
17:30		GEQO members meeting
21:00		Conference Gala Dinner

PL – Plenary Lectures

SL – Session Lectures

O – Oral Communications

POSTERS

P1 Expanding the substrate scope for asymmetric reduction and C-X coupling reactions using a theoretically-guided optimization of new ligand catalysts. Application to high value chiral compounds. *Montserrat Diéguez*

P2 Asymmetric reactions using 1,1'-disubstituted olefins as challenging substrates. *Oscar Pamies*

P3 Silane-thioether compounds: ligands as substrates, substrates as ligands. *Miguel A. Huertos*

P4 Cobalt Catalysed Light-driven Olefin Reduction. *Carla Casadevall*

P5 First Corannulene-bridged bis-N-Heterocyclic carbenes: Synthesis and Coordination. *Carmen Mejuto*

P6 Measuring Which Ligand Does Best in Difficult C–C Couplings. *Estefania Gioria*

P7 Origin of Regioselectivity in Rh-Catalyzed anti-Markonikov Hydroamination of Alkenes. *Gregori Ujaque*

P8 Aurophilic trapping agents in water: a great scarcely explored world. *Laura Rodríguez*

P9 Selective Hydrothiolation of Alkynes Catalysed by N-Donor-Functionalised 1,2,3-Triazol-5-ylidene Rhodium(I) Complexes. *Gregorio Guisado-Barrios*

P10 Hapticity of benzindenyl molybdenum complexes. *Jan Honzicek*

P11 Exploring the versatility of Pd-catalysed reactions in aza-heterocyclic synthesis: domino processes and C-H insertion reactions. *Ferran Pérez-Janer*

P12	Coinage Metal PCP-Pincer complexes with Carbodiphosphorane Moiety. *Christina Poggel*
P13	Biological behaviour of cyclometallated platinum(IV) complexes. *Margarita Crespo*
P14	Synthesis and Reactivity of the Unsaturated Anion$[Mo_2Cp_2(\mu\text{-}PtBu_2)(\mu\text{-}CO)_2]$-. *Melodie Casado*
P15	Design and characterization with GPC of silicone surfactants. *Adrian Lopez*
P16	Unexpected Formation of Early Late Heterobimetallic Complexes from Transition Metal Frustrated Lewis Pairs. *Andy Chapman*
P17	Enantioselective hydroformylation by a Rh-catalyst entrapped in a supramolecular metallocage. *Cristina Garcia-Simon*
P18	Trapping a highly reactive nonheme iron intermediate: stereoselective oxygenation of strong C-H bonds and alkenes. *Joan Serrano-Plana*
P19	Environmentally benign catalytic reactions based on non-precious transition metal complexes – Divergent coupling of alcohols and amines. *Matthias Mastalir*
P20	Anion and ancillary ligand effects on Iridium-based light emitting electrochemical cells. *Gustavo Espino*
P21	Iridium-catalyzed $^3O_2$ photoexcitation and photo-oxidation reactions. *Marta Martínez-Alonso*
P22	Fc-based N-heterocyclic carbenes for the design of redox-switchable catalysts. *Susana Ibáñez*
P23	Reactividad de paladaciclos derivados de iminofosforanos. *Adolfo Fernández-Figueiras*

P24	Síntesis de compuestos derivados de paladio. Aplicaciones en catálisis. *Fatima Lucio*
P25	NHC-stabilized Rh nanoparticles: Surface study and effect on the H/D exchange reaction of phosphorus and oxygen containing compounds. *Francisco Martinez*
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P27	From tetrametallic $[Ir(+1.5)]_4$ chains to bimetallic Ir(0)-Ir(II) mixed-valence complexes. *María Pilar Del Rio*
P28	Compuestos ciclopaladados con fosfinas derivadas del ferroceno. *Paula Munín*
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P30	Suzuki-Miyaura Cross-Coupling of 2-Pyridyl Boronates. *Alba Collado*
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P32	Stereospecific control of metal-centred chirality with κ_4-tetradentate ligands. *Daniel Carmona*
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P39	New chelating diphosphines. Synthesis and applications in Rh-catalysed hydroformylation. *Daniel Herrera*
P40	Síntesis y Reactividad de nuevos complejos vinilideno y alenilideno solubles en agua derivados del fragmento $\{CpRu(PPh_3)\}^+$ con derivados metilados de PTA (PTA = 1,3,5-triaza-7-fosfaadamantano). *Isaac de los Ríos*
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COMMITTEES

ORGANIZING COMMITTEE

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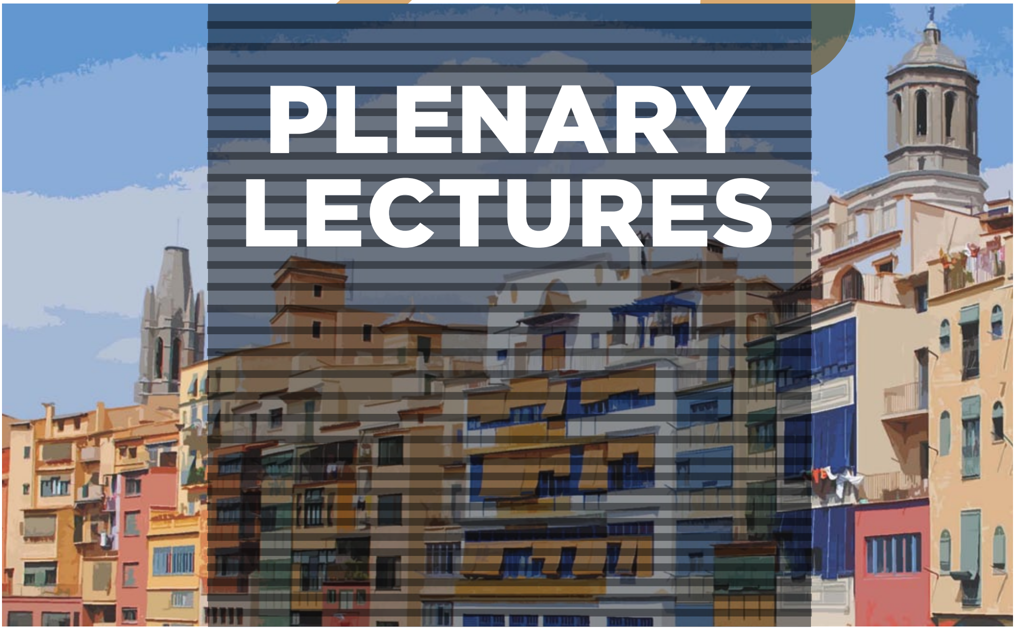

PLENARY LECTURES

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Synthetic single-site iron nitrogenases

Jonas C. Peters

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Nitrogen reduction to NH_3 is a requisite transformation for life. While it is widely appreciated that the Fe-rich cofactors of nitrogenase enzymes facilitate this transformation, how they do so remains poorly understood. A central element of debate has been the site(s) of dinitrogen coordination and reduction. The synthetic inorganic community placed an early emphasis on Mo because Mo was thought to be an essential element of nitrogenases, and because pioneering work by Chatt and his coworkers established that well-defined Mo model complexes could mediate the stoichiometric conversion of coordinated N_2 to NH_3. Catalytic N_2-to-NH_3 conversion was later demonstrated using a molecular Mo catalyst by Schrock.

It is known, however, that Fe is the only transition metal essential to all nitrogenases, and recent biochemical and spectroscopic data have implicated Fe as the likely site of N_2 binding in FeMo-co. These observations motivate a search for functional Fe catalysts. In this talk, I will discuss a tris(phosphine)borane supported Fe complex that catalyzes the reduction of N_2 to NH_3, wherein >40% of the H^+/e^- equivalents are delivered to N_2. This catalytically functional model system establishes that a single Fe site may be capable of stabilizing the various N_xH_y ligands generated en route to NH_3 formation. Geometric flexibility at Fe imparted by a hemi-labile axial donor may be critical for catalysis, and the interstitial C-atom recently assigned in the nitrogenase cofactor may serve a similar hemi-labile role. To further build on this idea, I will discuss more recent data for various Fe complexes aimed at improving the catalysis and providing new mechanistic data that is pertinent to the catalysis.

From Alkylidynes via Alkynes to Carbenes: Mechanistic Studies and Synthetic Implications

Alois Fürstner

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This lecture intends to showcase some unconventional ways of harnessing the reactivity of alkynes via highly selective metal-catalyzed transformations. After a short review of our work in the area of triple bond metathesis, some unorthodox addition reactions to internal alkynes will be discussed in detail. In addition to the use of carbophilic Lewis acids based on gold or platinum, unprecedented metal catalyzed *trans*-hydrogenation, *trans*-hydroboration and *trans*–hydrostannation reactions will be presented. The discussion will focus on the mechanistic aspects of these transformations. They are thought to proceed via metal-carbene intermediates, some of which could be isolated and fully characterized. A few selected applications to target-oriented synthesis are meant to showcase the current state of development.

PL3

New direction in homogeneous catalysis using n-heterocyclic silylene ligands

Matthias Driess

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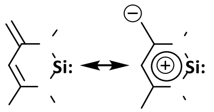
Activation of small molecules by using non- and semi-metals instead of precious metals is a contemporary challenge in molecular science. Recently, we developed two new types of zwitterionic silylenes **1** and **2** which show an unprecedented reactivity pattern with respect to small molecule activation based on silicon. [1,2] The facile oxygenation of **1** with N_2O or CO_2 in the presence of donor ligands coordinated to the divalent silicon led to isolable silanone complexes **3** which are also capable for facile activation of small molecules including ammonia, water, and hydrogen sulfide. Furthermore, the remarkable rich reactivity pattern of **1** and the first silicon(II)-based pincer arene ligands **4**, **5** and **6** can be used as a new generation of steering ligands in homogeneous catalysis. [3-7] I wish to discuss selected features on the reactivity of **1**-**6** and in particular their advantageous use in catalytic transformations.



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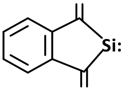

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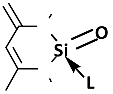

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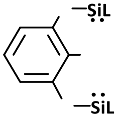

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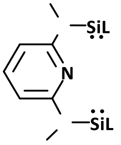

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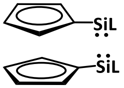

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Fluorine Chemistry Customized for Drug Discovery

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The impact of fluorine chemistry in the life sciences is enormous. As many as 30−40% of agrochemicals and 20% of pharmaceuticals on the market are estimated to contain fluorine. ^{18}F-labeled compounds are also critically important for Positron Emission Tomography [PET]. As a result, there is an increasing demand for facile methods allowing for the fluorination of a large variety of structurally complex and functionalized targets using either ^{19}F-reagents or the cyclotron produced radioisotope ^{18}F. This lecture will discuss our recent contributions to late stage fluorination and ^{18}F-radiochemistry; new methods expanding the radiochemical space available for PET imaging will be presented as well as our approach to bridge the gap between fundamental research in radiochemistry, drug discovery and clinical applications. The emphasis will be on our approach towards method development merging organometallic chemistry with radiochemistry.

Homogeneous catalysis and fuel cells: an emerging partnership

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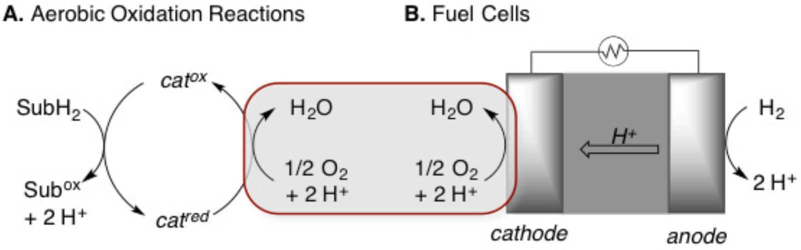
Over the past 15+ years, we have been developing and investigating homogeneous catalytic aerobic oxidation reactions that proceed via two sequential half-reactions: (1) oxidation of the organic substrate ($SubH_2$) by an oxidized catalyst (cat^{ox}), followed by (2) oxidation of the reduced catalyst (cat^{red}) by O_2. This general mechanism closely resembles the two redox half-reactions in fuel cells, and we have recently begun developing and investigating independent electrochemical half-reactions that employ soluble electrocatalytic mediators. Examples include the use of organic nitroxyls and NO_x-based cocatalysts for O_2 `reduction [1], and organic nitroxyl catalysts [2] and` Cu/nitroxyl-cocatalysts for alcohol oxidation [3]. The emerging results highlight substantial synergies among the fields of homogeneous catalysis, organometallic chemistry and electrocatalysis. For example, the insights from homogeneous catalysis have led to significant lowering of the “overpotential” and enhancement of rates in challenging electrocatalytic reactions, while electrochemical studies of independent half-reactions have provided unprecedented insights into the mechanisms of important homogeneous catalytic reactions.



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SESSION LECTURES

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Converging strategies in homogeneous and heterogeneous catalysis

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In the present talk, I will review several aspects of the interplay between homogeneous and heterogeneous catalysis with different applications showing that computational chemistry can be employed to derive a unified theory in Catalysis.

Applications of N-Heterocyclic Carbenes and N-Heterocyclic Imines in Main Group Chemistry

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N-heterocyclic carbenes (NHCs) have received a great deal of attention and have now been employed in a broad range of fields. For example, they have been employed as versatile ligands for transition metals, main group elements, even lanthanides and actinides. Also, the application of NHCs in organocatalysis has been proven as an attractive metal-free method to synthesize a variety of important species. Meanwhile, we have been interested in the synthesis, structure and reactivity of compounds containing low-valent main group elements with unusual structures and unique electronic properties, with the goal of finding novel applications. This presentation will focus on novel low-valent silicon compounds stabilized by NHCs. For instance, the hydrosilylene [R(H)Si:],[1] silyliumylidene ion $[RSi:]^+$,[2,3] and sila-acylium ion $[RSi{=}O]^+$[4] were successfully isolated by employing NHCs as ligands. Recently, we also focused on low-valent main group compounds using N-heterocyclic imines (NHIs) as ligands.[5] Taking advantage of thermodynamic as well as kinetic effect of NHIs, various elusive species including the iminosilylene $[R_2Si:]$,[6] germylene-germyliumylidene $[R_2Ge_2]^+$,[7] stannylenoid $[R_2Sn(Cl)Li]$,[8] cationic thiooxoborane $[B{=}S]^+$,[9] and aluminium telluride [RAl=Te][10] were isolated. The synthesis and reactivity of these compounds towards organic small molecules will also be presented.

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SL3

Rich metal, poor metal: gold vs iron as catalysts for direct benzene c-h bond functionalization

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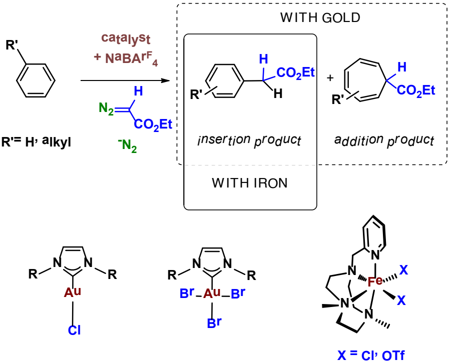
All metals from group 8 to 11 in the Periodic Table are known to promote the catalytic transfer of carbene units from diazo compounds. Gold remained undiscovered for this transformations until nearly a decade ago, when our group described the potential of gold(I) complexes of type (NHC)AuCl (NHC = N-heterocyclic carbene ligand) to abstract and transfer a carbene group of type $C(H)CO_2Et$ from ethyl diazoacetate to the C-H bonds of benzene [1]. The reaction was accompanied by the formation of cycloheptatrienes in the so-called Buchner reaction (see Scheme).

In the search for other catalysts to avoid the formation of undesired products, thus leading to very selective transformations into the *insertion* derivative, we have discovered, in a joint collaboration with the group of Costas, that an iron(II) compound bearing the tetradentate pytacn ligand (pytacn = 1-(2-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane) induces the same transformation with the exclusive formation of the targeted product [2]. Mechanistic studies with both metal-based systems will be also discussed.



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SL4

New Reactivities of Gold Complexes: It is All a Question of Ligand Design!

Abderrahmane Amgoune, Didier Bourissou

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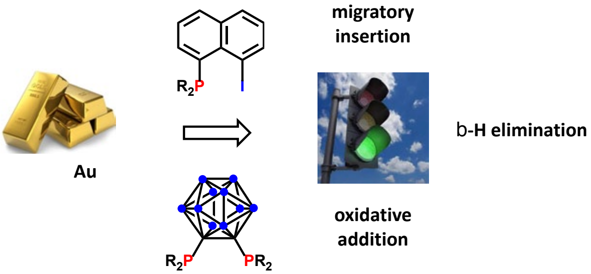
Over the last few years, our group has been developping new polyfunctional ligands for transition metals. We are particularly interested in original metal / ligand interactions (such as the coordination of Lewis acids as σ-acceptor ligands[1] and in new reactivity patterns of the coinage metals.[2]

This presentation will focus on organo gold complexes. With the aim to open new avenues in gold catalysis, we have challenged the presumed reluctance of gold to undergo several key elementary transformations. Thanks to rationale ligand design, we have shown that gold complexes can in fact undergo oxidative addition,[3] migratory insertion[4] and β−H elimination under very mild conditions. Our main achievements in this area will be discussed. The specific properties of gold and the precise role of the "ancillary" ligands will be emphasized.



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Adventures in Catalysis: from Mechanisms to Applications

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Detailed understanding of catalytic transformations is key to designing better catalysts. This talk will give insights on case studies and reactivity designs recently undertaken in our laboratory. A combination of experimental and computational tools were applied to study and/or predict the favored reaction mechanisms, active catalytic species, ligand and additive effects of selected transformations relating to C-C bond formations, C-H functionalizations and the introduction of fluorine containing groups, catalyzed by palladium, nickel and/or Cu complexes of the oxidation states 0, I, II or III. As a result of these investigations, novel reactivities have been uncovered. The lecture will also discuss the power and limitations of computational tools in the study of organic and organometallic reactivities, and outline the advantages of a combined experimental/ computational approach.[1]

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Gold Perfluoroalkyl Complexes and Organometallic Metalloligands. Synthesis, Reactivity and Self-Assembly Processes

J. Gil-Rubio[1], V. Cámara[1], M. Blaya[1], N. Barquero[1], D. Bautista[2], N. Masciocchi[3], J. Vicente[1].

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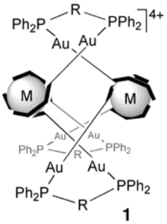
The catalytic, photophysical and biological properties of organogold complexes[1], together with the recent discoveries of new types of gold compounds and reactions[2], are encouraging research in this field. This contribution focus on two different aspects of organogold chemistry: The use of organogold complexes as building blocks in Supramolecular Chemistry, and the chemistry of perfluoroalkyl gold complexes.

We have investigated the reactivity of gold(I) metalloligands functionalized with chelating groups (bipyridyl or terpyridyl) toward metal ions [3]. Depending on the structure of the metalloligand and the reaction conditions, new types of supramolecular complexes such as helicates (**1**) or heteronuclear rod-like oligomers (**2**) are formed by coordination-driven self-assembly. The rules that govern these assembly processes and the structures of the final aggregates, both in the solid state and in solution, will be discussed in detail.

In parallel, we have explored the synthesis and reactivity of gold perfluoroalkyl complexes[4]. In this regard, synthetic methods leading to new types of gold(I) and gold(III) perfluoroalkyl complexes (**3**–**6**) will be presented. The reactivity of these complexes will be also disclosed, focussing on photochemical oxidative addition and reductive elimination reactions.



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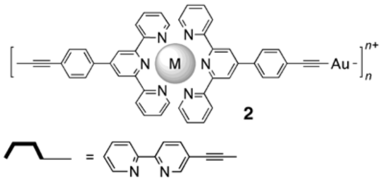

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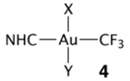
M = Fe, Co, Zn

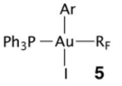
$L-Au-R_F$

3

L = PR_3, NHC,
CNR, $C_6F_5^-$,

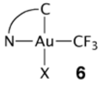


$NHC-\overset{X}{\underset{Y}{Au}}-CF_3$ **4**



$Ph_3P-\overset{Ar}{\underset{I}{Au}}-R_F$ **5**

$R_F = C_nF_{2n+1}$



$\overset{C}{\underset{X}{N-Au}}-CF_3$ **6**

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Molecular catalysts for the conversion of CO_2 and biomass

T. Cantat

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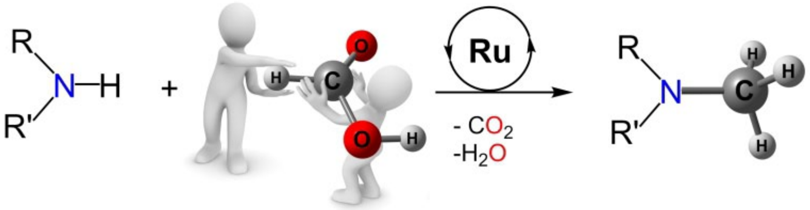
While greenhouse gases emissions are reaching alarming levels, fossil fuels still represent 80% of the world energy portfolio and 95% of our chemical commodities rely on non-renewable resources, namely hydrocarbons. In this context, utilizing CO_2 as a C_1 building block to produce platform chemicals as an alternative to petrochemistry has a double advantage of reusing CO_2 while sparing fossil resources and avoiding CO_2 emissions from their use. We have developed a strategy relying on the simultaneous use of a functionalizing reagent and a reductant that can be *independently* adjusted to perform the reductive functionalization of CO_2. The so-called *diagonal approach* will be discussed and exemplified with novel catalytic processes to convert CO_2 to formamides, N-heterocycles, methylamines and methanol, using hydroboranes, hydrosilanes or formic acid as reductants. These new catalytic reactions rely on the use of simple organocatalysts or Zn, Fe and Ru organometallic complexes. The mechanisms at play in these transformations will be presented, based on DFT calculations and isolation of reactive catalytic intermediates.[1-9] Utilization of these reduction catalysts will be exemplified in a novel strategy aiming at the depolymerization of wood lignin for the isolation of well-defined aromatics.[10]



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Water-Soluble Palladium and Platinum N-Heterocyclic Carbene Complexes: From Catalysis to Nanomaterials

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Catalytic reactions in water involving metal complexes and organic substrates have been growing in importance over the past few decades.[1] In this area, some time ago we observed the synthetic potential of organoalkoxysilanes to couple with aryl bromides in high yields in Pd-catalyzed reactions performed in the aqueous phase.[2] The efficient activation of the more challenging aryl chlorides was further achieved by using N-heterocyclic carbene ligands (NHCs) functionalized with ionic groups. Although the applications of water-soluble NHC complexes are progressing rapidly, there is as yet little information available concerning basic aspects of the chemical reactivity of these complexes in water.[3] In this presentation, we will discuss some of the results recently obtained by our group on the synthesis and reactivity in aqueous phase of palladium and platinum NHC complexes in oxidation states 0 and II. Metal-carbene bonds are fairly stable in water under most conditions, although hydrolysis can be promoted under some circumstances. Methyl NHC complexes of Pd(II) or Pt(II), for instance, evolve under thermal treatment in water by C-C reductive coupling eliminations (or intramolecular C-H activations) with no or minor hydrolysis of Pd-C bonds.[4] The solutions resulting from these thermal treatments contain metal nanoparticles which are highly soluble and stable in water as a result of the coordination of NHC ligands to their surface (confirmed for palladium by the first observation of Knight Shift in a ^{13}C carbene resonance). Solvation and other solvent effects on reactivity will also be discussed. We will highlight the role of the strong hydration of small anions in several stoichiometric or catalytic processes. In addition, studies currently underway on palladium(0) complexes reveal that this solvent is able to stabilize highly reactive (NHC)Pd(0) species, an unprecedented result that might explain the high efficiency showed by NHC Pd complexes to catalyze a variety processes in aqueous media.

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Phosphinous acids: cooperative ligands for metal-catalized nitrile hydration

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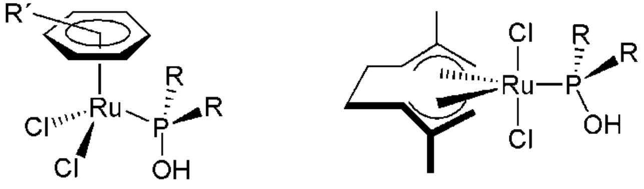
Amide bond forming reactions are among the most important and widely studied transformations in organic chemistry, but they also present a contemporary challenge because of the industrial need for cleaner and more atom-economical protocols. Nitrile hydration ideally represents the simplest method for the sustainable preparation of primary amides. However, strong acids and bases combined with harsh reaction conditions have been traditionally employed to promote the process, lowering its selectivity and applicability. In this context, significant efforts have been for long time devoted to the search for homogeneous catalysts able to promote the selective conversion of nitriles to amides employing directly water as solvent under neutral conditions [1].
Ruthenium complexes are particularly effective nitrile hydration catalysts, and promising results in water have been described with the help of hydrophilic phosphine ligands [2]. However, high temperature regimes (≥ 100 ºC) and metal loadings (5 mol%) are usually needed to achieve good conversions. During the last years our group has been deeply involved in this chemistry [1,2] and, as a significant improvement, we have recently developed a series of Ru(II) and Ru(IV) complexes (see figure) able to catalyze the selective hydration of organonitriles in water under remarkably milder conditions (≤ 60 ºC), and featuring a high activity at a low metal loading (1 mol%) [3]. A summary of these results will be presented in this talk, along with mechanistic studies that allowed to unravel the key role played by the auxiliary phosphinous acid ligands PR_2OH during the catalytic reactions.



R = aryl or alkyl group

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Dynamic kinetic resolution and desymmetrization approaches to the atroposelective synthesis of axially chiral heterobiaryls

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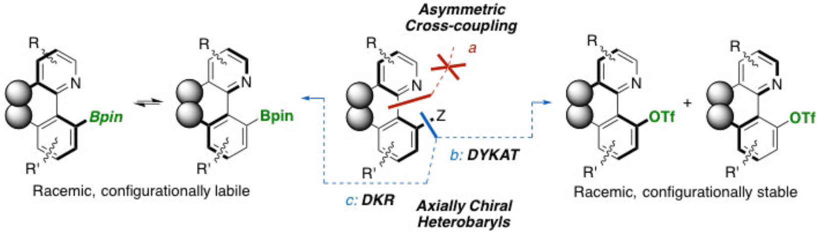
In the field of asymmetric carbon–carbon and carbon-heteroatom cross–coupling reactions, the synthesis of functionalized, configurationally stable heterobiaryls remain as one of the most challenging targets. Our previous contribution in this field centered on the use of hydrazone-based N/N and P/N ligands for the coupling of unfunctionalyzed and formyl(acyl)-substituted electrophiles, respectively.[1] However, these approaches failed for the coupling of heterocyclic derivatives, probably due to problems associated with the coordination ability of the substrates, the stability of the required organometallics, and/or the lower configurational stability of the desired heterobiaryls. Considering, however, the high potential that functionalized heterobiaryls hold in the field of asymmetric catalysis, we started a program to explore new strategies based in dynamic kinetic resolution (DKR) of borylated heterobiaryls[2] (*via* cross-coupling) and dynamic kinetic asymmetric C–C and C–X (X = P, N) cross–couplings (DYKAT) from heterobiaryl electrophiles will be discussed.[3] In this lecture, the collected results and the mechanistic aspects related with these reactions will be discussed.



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Metal-Catalyzed C–H Functionalization Processes

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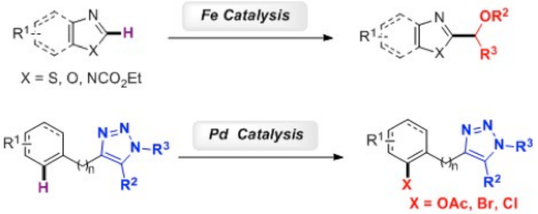
Sustainable development constitutes a matter of genuine concern for our society and scientific community and clearly represents one of the key factors for scientists when designing new chemical processes.[1] In this respect, direct functionalization of molecules containing C(sp^3)–H and C(sp^2)–H bonds stands out today as one of the most challenging and relevant areas in modern organic chemistry. Notably, C–H functionalization offers numerous attractive advantages such as reducing the reliance on existing functional groups while improving atom economy and energy efficiency.[2] In this communication novel catalytic approaches for the direct α-heteroarylation of ethers with azoles[3] as well as triazole-directed C–H oxygenation[4] and halogenation of arenes will be disclosed.



Scheme 1. Metal-catalyzed functionalization of C(sp^3)–H and C(sp^2)–H bonds.

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C–H Functionalization of Amines with Aryl Halides by Nickel-Photoredox Catalysis

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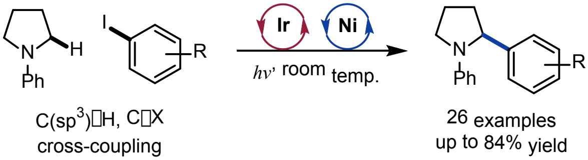

The direct and selective functionalization of C(sp^3)–H bonds is a powerful strategy for the elaboration of organic molecules. Toward this goal, we have used a combination of nickel and photoredox catalysts to enable the direct functionalization of α-amino C–H bonds with aryl halides. This direct C–H, C–X coupling employs readily available starting materials to generate benzylic amines, a well-represented motif among bioactive molecules. A key mechanistic feature of the reaction is the direct arylation of α-amino radicals mediated by a nickel catalyst. Notably, the scope of this coupling is complementary to existing C–H activation and photoredox methodologies. The cross coupling protocol tolerates a range of electronically diverse (hetero)aryl halides and even a vinyl triflate. This protocol has also been demonstrated with complex aryl halides, highlighting the opportunity for its use in late-stage functionalization. Finally, the use of a chiral ligand generates enantioenriched product, validating the possibility for asymmetric C–H functionalization in this system.

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Isolation of Key Aryl-Co^{III} Intermediates in Co-Catalysed C(sp^2)-H Functionalisations: New Insights into Alkyne Annulation Reaction Mechanisms

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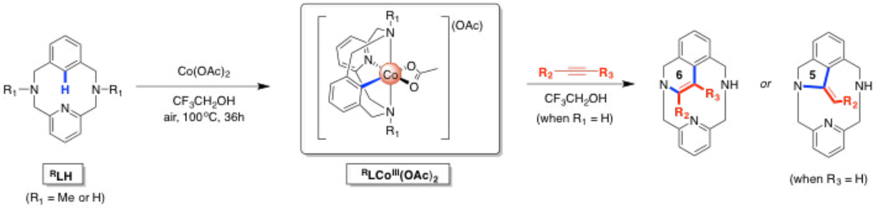
Selective functionalization of inert C-H bonds is currently attracting significant interest due to the desire to develop new simplified synthetic protocols for the preparation of complex pharmaceuticals, agrochemicals and natural products gathers pace.[1] One reaction of particular focus at the current time is the selective annulation reaction of alkynes to substrates with ubiquitous inert C-H bonds, using Co as catalyst.[2,3,4,5] Unfortunately, the mechanisms of these reactions are still relatively poorly understood, with little experimental evidence for intermediates, although generally organometallic Co^{III} species are implicated.[6] In the field of Co-catalysed alkyne annulation protocols (through direct C-H activation), the most solid evidence so far of reaction intermediates has been provided by succinct NMR[4] or MALDI-TOF[2] characterisation.

This contribution describes the preparation and characterisation of stable aryl-Co^{III} compounds (^{R}LCo^{III}(OAc)$_2$; NMR, HRMS, XAS) through C(sp^2)-H activation within a 12-membered macrocyclic ligand (^{R}LH). Subsequent insights obtained from the application of the isolable aryl-Co^{III} intermediates in alkyne annulation reactions, in which they are proposed as key reaction intermediates are disclosed, including new and important results pointing towards different reaction mechanisms for internal and terminal alkynes.



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An efficient and sustainable synthesis of NHC gold complexes

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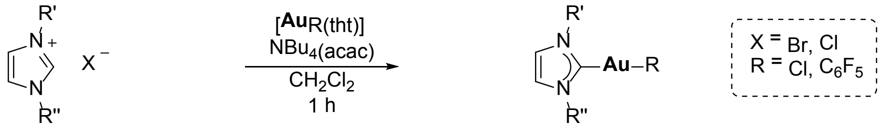
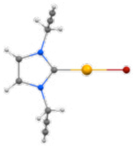
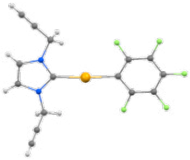
N-Heterocyclic carbenes (NHCs) are of ever-increasing interest due to the multiple and diverse applications of their corresponding transition metal complexes. Their strong sigma donor capacity makes them excellent ligands and generally they form very stable complexes. NHC gold complexes have diverse catalytic, biological, medicinal and optical properties[1-3], however, for these to be fully exploited, the complexes must be accessible and therefore simple, economical and efficient syntheses are vital.

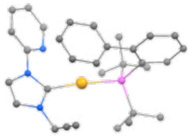
A new method for the synthesis of NHC gold complexes has been developed in which tetrabutylammonium acetylacetonate, NBu_4(acac), is used to deprotonate imidazolium salts to form the NHCs. Reactions are carried out at room temperature, in air and with short reaction times and high yields. This method has been shown to work with both sterically small as well as bulky NHCs and any gold precursor of the form [AuR(L)] where L = labile ligand. It is the only currently known method with such versatility.



A series of propargyl functionalised NHC gold complexes have been prepared from their corresponding imidazolium salts using the NBu_4(acac) method. The propargyl side arms provide an additional coordination site whilst also giving the complexes a degree of water solubility. The emissive and biological properties of the complexes have been studied.







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O5

Silver(I) N-heterocyclic complexes for C-C bond activation of alkylnitriles and catalytic application in oxazoline synthesis

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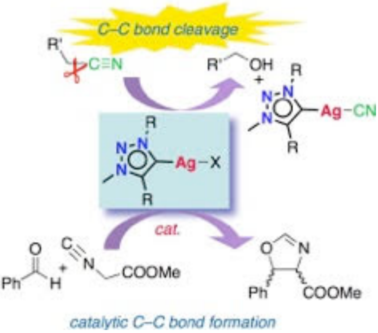
N-heterocyclic carbenes (NHCs) have become increasingly prevalent ligands in the fields of organometallic chemistry and homogeneous catalysis [1]. A convenient route to form NHC transition metal complexes is the *in situ* generation of an Ag–NHC complex from reaction of azolium salts with Ag_2O, followed by transmetallation with a different metal [2]. However, to date little attention has been paid to the Ag–NHC intermediates regarding complex formation and potential catalytic applications [3].



We show that generation of Ag–NHC complexes from azolium salts in refluxing CH_3CN results in a selective C–C bond cleavage and the formation of [(NHC)Ag(CN)] complexes. This bond activation can also be extended to other alkyl nitrile reagents [4].

Furthermore, we will demonstrate the catalytic properties of a series of Ag–NHC complexes in oxazoline formation *via* aldol condensation. These highly active systems disclose new possibilities for applications of easily accessible silver carbene complexes.

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Introducing Sodium Magnesiates to NHC Chemistry: Accessing Abnormal, "Paranormal" and Anionic NHC Complexes

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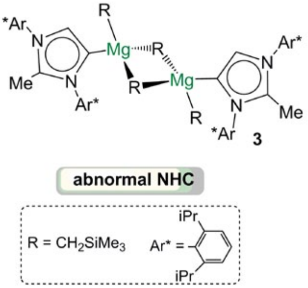
Recent breakthroughs in organometallic synthesis have established alkali-metal magnesiates as a versatile and efficient family of heterobimetallic reagents, finding extensive applications in key transformations such as deprotonative metallation reactions.[1] Remarkably, despite several studies assessing the structural complexity of these systems, using an array of anionic ligands or neutral Lewis bases, the synthesis of alkali-metal magnesiates supported by N-heterocyclic carbenes (NHC's), one of the most relevant and ubiquitous ligands in modern synthesis, has hardly being touched upon.[2]

Merging together these two current topics in synthesis, here we report our findings investigating the synthesis of a new family of magnesium compounds containing neutral, anionic, abnormal and "paranormal" NHC's ligands using a mixed-sodium-magnesium approach.[3] The ability of some of these novel magnesium/magnesiate systems to act as transfer reagents towards transition metal complexes has also been assessed.



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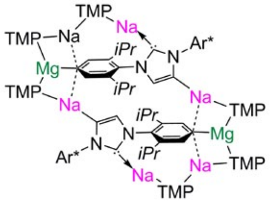
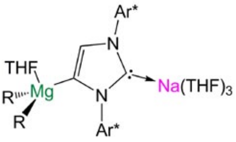
abnormal NHC



paranormal NHC



anionic NHC

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Boron ate complex: an old dog with new tricks

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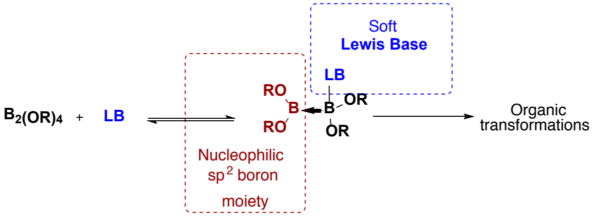
Organoboron compounds are used as universal connectors in organic chemistry to access major functional groups. Indeed, organoboron are present in more than the 30% of coupling reactions to prepare drug candidates. The formation of boron ate complexes, which is the salt formed by reaction of a Lewis acid with a Lewis base whereby the central atom increases its valence, arises as a powerful methodology for the synthesis boron compounds, the transmetallation of boryl units to transition metals complexes and their transformation in other functional groups.[1] The concept lies in the interaction between a Lewis Base and the empty *p* orbital of the boron moiety which polarizes the bond making the neighbour group more nucleophilic, increasing their reactivity.

The versatility of the boron–carbon bond would be useless without practical routes to organoboranes, then the development of new methodologies to introduce boron compounds is key to find new reactivities.[2] Even more important, it can lead to find new asymmetric induction methods that can replace current unsustainable methodologies based on toxic and expensive transition metals or provide new tools when the scope of the reaction is expanded.

In our group, we aim to develop new methods for the activation of diboron reagents and their use in organic synthesis using green and sustainable methods, which include soft Lewis bases and Earth-abundant transition metals. Here I present the recent discoveries in our group, including the organocatalytic use of amines, organic and inorganic salts and iron catalyse nucleophilic boron addition. The results presented in this conference shown that these new methodologies overcome some of the current limitations in terms of substrate scope and functional group tolerance.



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O8

Metallomesogens based in triphenylene-carbene structures

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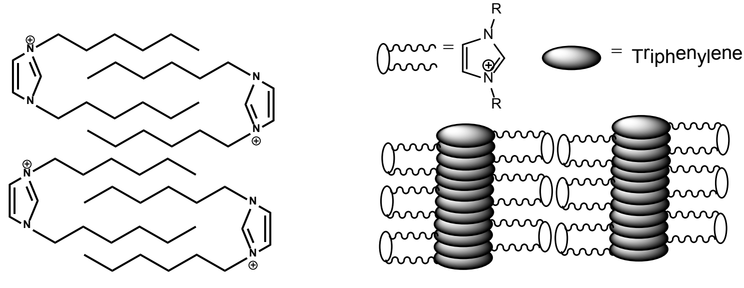
There have been a high interest in understand the structure-properties relation of the Discotic Liquid Crystals (DLCs) in order to get the desirable properties in the new compounds [1]. The DSCs are suitable to use as anisotropic semiconductors, organic lighting emitting diodes (OLEDs) among other applications. In our research group we have synthetized several types of molecules based in hexasubstituted triphenylene as mesogenic core with different functional groups as ligand for transition metals [2] leading to new columnar metallomesogens.

To find other systems and to improve the understanding of the structures, we have prepared two mesogens based in imidazolium salts functionalized with one or two triphenylene which have also been used as precursors of N-heterocyclic carbene ligands to several transition metals. The imidazolium salts very often show a packaging where the chains in the nitrogen atoms place perpendicular to the imidazole plane leading to lamellar mesophases (Scheme 1). Thus, the p-p interactions between triphenylenes in our system, would help to form this packaging, forming lamellar columnar phases (Scheme 1). Also, the possibility of metal-metal interactions out of the main columnar structure should help to fix the structure. We have prepared several carbene complexes containing group 10 and 11 metals, all of them have mesogenic behaviour and luminescent properties based in the triphenylene core.

Scheme 1.



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Light-Driven Reductive Processes using Water and Electron-donors as a Source of Hydrides

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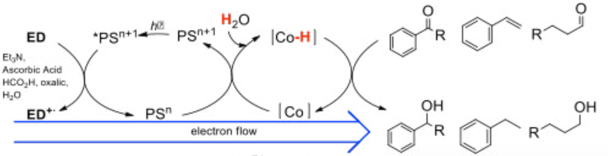
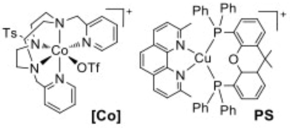
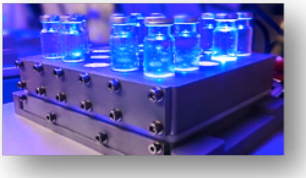
Photogeneration of metal hydride bonds from well-defined complexes in water has been mainly devoted to the synthesis of solar fuels in the field of artificial photosynthesis.[1,2] The development of new synthetic strategies using light-driven water reduction molecular catalysts, especially those based on earth-abundant first-row transition metals, will open the venue to more sustainable methodologies in comparison, for instance, to stoichiometric equivalents of reducing agents such as alkaline hydrides and silanes used nowadays.[3,4] In this regard, photogenerated M-H complexes can be engaged in synthetic reductive processes based on both hydride and hydrogen atom (HA) transfers, depending on the conditions, ligands and organic substrates employed. Parallel photoredox screening platform for high-throughput experimentation allows to speed up the development of more robust and selective catalysts for the reduction of C=O and C=C bonds. More specifically, the use of aminopyridine cobalt complexes enables the efficient reduction of a wide range of aryl ketones, aldehydes and aryl alkenes under mild conditions. Mechanistic studies suggest a chameleon-like nature of the *in situ* photogenerated Co-H reaction intermediate which can perform as hydride donor or HA donor depending on the nature and redox potential of the substrate.







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Detangling Catalyst Modifications Reactions from the Oxygen Evolution Reaction by On-Line Mass Spectrometry

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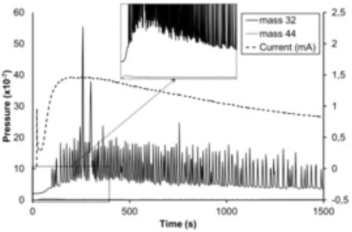
With global energy demand rising, the need for sustainable and non-polluting energy sources is becoming increasingly necessary and considerable effort has been made to split water in order to produce environmentally friendly hydrogen as a green and sustainable energy carrier. Within this process, the water oxidation reaction is especially challenging.[1] Oxidation of water, which is carried out by photosystem II of green plants, is a four-electron process: $O_2(g) + 4H^+(aq) + 4e^-$ ® $2H_2O$ with a redox potential $E^0 = +1.23 - (0.059 \times pH)$ V. In addition to this large thermodynamic requirement, the formation of O_2 is kinetically difficult requiring thus the participation of a catalyst to proceed. Iridium complexes have been extensively studied as catalysts for this reaction with cerium ammonium nitrate or periodate as the most popular sacrificial chemical oxidants.[2] However, under these experimental conditions identification of the active catalyst can be an issue. In contrast, oxidation by electrochemical techniques allows for better defined reaction conditions since the relevant oxidation potential is directly related to the applied electrode potential, leaving no doubt about the thermodynamic driving force.[3]

In this communication, the synthesis and full-characterization of the anionic iridium(III) complex $[Ir(Cl)_3(pic)(HOMe)]^-$ (Hpic = picolinic acid), isolated as the potassium and 2-carboxymethylpyridinium salts, will be presented. Their catalytic activity for water oxidation under electrochemical conditions by dropcasting them onto a pyrolytic graphite (PG) electrode will also be discussed. In addition, amperometry experiments at different potentials were carried out in order to ensure that the maximum activity strongly correlates with the actual potential that is applied, while the nature of the gaseous products as a function of applied potential and time has been confirmed by on-line electrochemical mass spectrometry (OLEMS, see Figure).



The observance of CO_2 evolution combined with XPS measurements after short term electrolysis clearly indicates the formation of iridium oxide with a critical particle size.[4]

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O11

Well-defined organometallic dinuclear gold complexes - application in dual-gold catalysis

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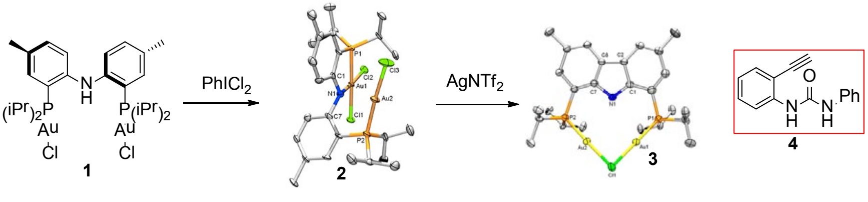
Gold catalysis has flourished the past 15 years and is now applied in a wide-variety of transformations. More recently, dual-activation of substrates has added a new scope of reactions to the abilities of Au-catalysts. This is achieved by activation of alkyne bonds in a combined σ,π-fashion, instead of “classic” π-activation.[1][2] An alternative approach is separate σ- and π-activation of different substrates which then can further react.[3] Examples of bimetallic Au^{I}-complexes applied in this cooperative Au-Au catalysis are very limited and the effect of enforced Au-Au proximity is therefore still underexplored.

Based on our earlier work in Group 10 chemistry with the ditopical PNP ligand,[4] we were interested to apply this multi-purpose scaffold in Group 11 chemistry, particularly aiming for well-defined dinuclear Au complexes (Au^{I}-Au^{I}, Au^{I}-Au^{III} and Au^{III}-Au^{III}) and to study their potential in organometallic chemistry and as catalysts in dual-activation of bifunctional substrates. The versatile coordination chemistry of Au with PNP and the related POP analogues provides many surprises, which will be disclosed. A key observation was the isolation of a bis-gold σ,π-activated phenylacetylide complex supported by a single diphosphine ligand. We also discovered highly unusual ligand-based redox-chemistry for these dinuclear complexes.[5]

This species is a potent precatalyst for the regioselective heterocyclization reaction of urea-functionalized alkynes, outperforming known mononuclear catalysts for the formation of the 5-membered anti-Markovnikov product. We will present the fascinating organometallic and coordination chemistry of these dinuclear species. We will address synthetic and mechanistic aspects related to the catalytic studies and pinpoint the benefits of these well-defined precatalysts over conventional Au-catalysts. Results using POP ligands will also be included.



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O12

Iron: A New Player in the Z-Selective (Cross) Dimerization of Terminal Alkynes Catalysed by Transition Metal Complexes.

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In recent years, our group has developed several Fe(II) pincer complexes and studied their catalytic performance in environmentally benign hydrogenation processes towards different substrates.[1] Pursuing new reactivity and driven by the abundance, low price, and low toxicity of iron, we have developed the efficient homo-coupling of terminal alkynes and cross-dimerization of arylacetylenes with silylacetylene catalysed by the well-defined iron complex, [Fe(H)(BH4)(iPr-PNP)].[2] Catalysis take place at room temperature, with no need of base or other additives, achieving the corresponding Z-selective dimerized products in excellent (79-99 %) yields. These results make iron a new player in the well-known transition metal-catalysed coupling of alkynes to 1,3-enynes [3].

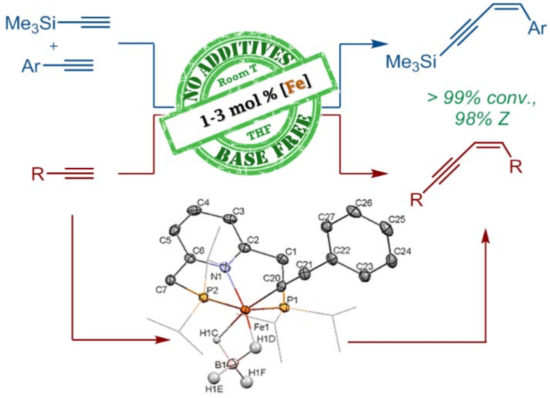

Figure 1. Homo-coupling of terminal alkynes and cross-dimerization of arylacetylenes with silylacetylene

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O13

Computational investigation of pd-catalysed selective arylation of aldehydes

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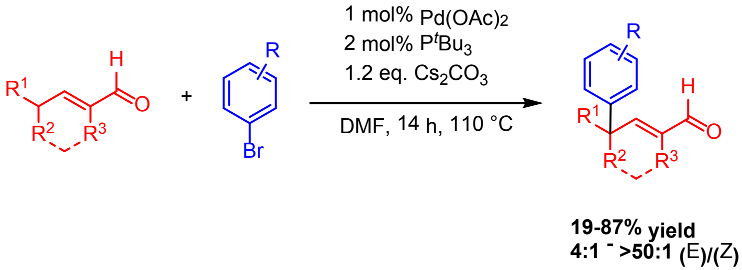
The a-arylation of enolizable carbonyl compounds have significantly advanced, and in this context, aldehydes have revealed as particularly challenging substrates [1]. The scope of this Pd-catalyzed a-arylation reaction has been extended to the remote g-arylation based on the vinylogous analogy [2]. Experimentally, Mazet and co-workers developed an intermolecular Pd-catalyzed γ-arylation of γ-branched α,β-unsaturated aldehydes that led to the corresponding gamma-arylated products in good yields and good selectivities. Mechanistic studies of this reaction suggest the involvement of η3-Pd-allyl intermediates that equilibrates before the reductive elimination step [3].



Prompted by these results, we decided to investigate the mechanism of this transformation by mean of computational tools [4]. DFT calculations were thus performed in order to:

1) Elucidate the nature of the Pd-intermediates involved in the reaction and their equilibration prior the reductive elimination step,
2) Explain the γ-regioselectivity observed and
3) Rationalize the isomerization of the double bond functionality observed in the final products.

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Advances in Computational BioInorganics: Predicting Interactions of Coordination Complexes with Biomolecular Scaffolds

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The interaction of man made coordination complexes with biological scaffolds is gaining a pivotal position at the interface between chemistry and biology as biometallic hybrids are frequently used in the development of biosensors, metallodrugs, metallopeptides and artificial metalloenzymes. Despite the major successes in the last decades in developing efficient systems, the prediction and analysis of the molecular behaviour of this type of systems still represents a complex exercise.

Molecular modelling has shown to be a major ally in the study of bioinorganics system although dealing with transition metals always requires specific *savoir faires* and subtle balances are needed between accuracy of electronic features and size of the models. So far, though, the particular problem of predicting how coordination complexes bind to biomolecules is rather orphan of computational chemistry and structural bioinformatics insights.

In the recent years, our group designed, tested and applied a series of computational strategies in the field of artificial metalloenzymes.[1,2] In this field, we browse from standalone protein-ligand dockings to multi-scale approaches. If our work allowed to better understand the molecular mechanism of different types of biometallic systems,[3] it also resulted in overcoming molecular challenges for the characterization of physically sound models resulting from the binding of coordination complexes with biomolecules.

Here, the underpinning concepts of our strategies are contextualized and discussed. Our latest advances obtained from pure computational works and in collaboration with experimentalists are also exposed.

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Metal-Ligand Cooperative System in Azolate-Pincer Complexes: Bifunctional Catalysis

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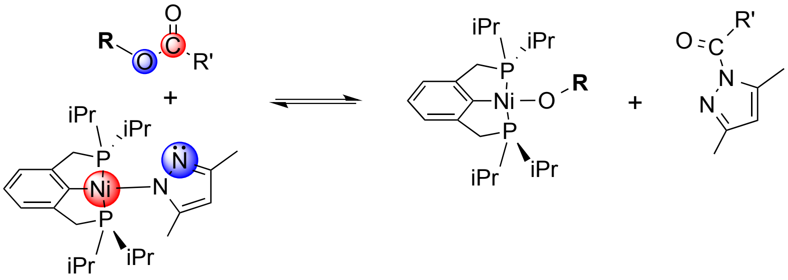
In this contribution we discuss the reactivity of Nickel (II) complexes containing terminally bound azolate (pyrazolate, imidazolate or 1,2,4-triazolate) and tridentate pincer ligands. Azole heterocycles are known to act as organocatalysts in acyl transfer reactions1.In our compounds, the pincer ligand saturates three coordination positions of the square-planar metal center, enforcing the terminal coordination of the azolate. This leaves a nitrogen atom with significant nucleophilic character in the vicinity of the 16e- nickel atom, which retains residual Lewis acidic character. This situation is akin to Frustrated Lewis pairs (FLP)2, which emerged in the past decade as an innovative tool for the development of new catalytic transformations.

In order to evaluate the cooperative metal/ligand effect and to extend the concept of FLP to catalysis, we have studied the ability of our compounds to activate esters affording reactive combinations of nickel alkoxides and acylazolates (Scheme 1). We have exploited this reactivity pattern in the catalytic transesterification of alkyl carbonates, or the generation of reactive nickel species from unsaturated molecules (heterocumulenes, alkynes...), as potential intermediates in synthetically useful catalytic processes.



Scheme 1

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O16

Building New Bridges Between Metal- and Bio-Catalysis: Unprecedented Concurrent Cascade Approach to Chiral Alcohols in Aqueous Media

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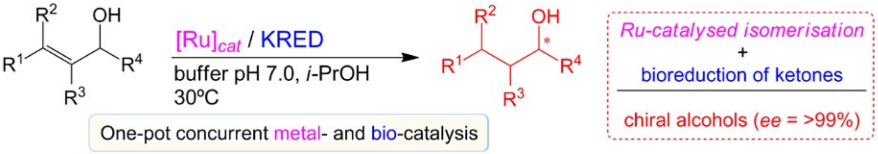
New cleaner and more efficient one-pot multistep cascades in green solvents (*i.e.* water) are emerging as exciting alternatives to highly-costly and tedious step-by-step processes, which also minimise chemical waste, save time and simplify practical aspects [1], being enantioselective one-pot processes one of the most recalcitrant challenges to solve. In this sense, the combination of metal- and bio-catalysts working *hand in hand* in water has recently attracted considerable attention [2].

In our previous work, we reported the first example of coupling of the ruthenium catalysed isomerisation of allylic alcohols with a ω-transaminase (ω-TA) [3]. Although the resulting amines were isolated in very high yields and enantiomeric excesses, the process had to be accomplished in a sequential fashion (two steps) due to the inactivation of the metal catalyst by both the ω-TA and the cofactor (pyridoxal-5´-phosphate). Building on, but going significantly beyond these previous studies, in this communication [4] we present a genuine chemo-enzymatic one-pot concurrent procedure which provides enantiomerically pure alcohols by combining the Ru(IV)-catalysed isomerisation of racemic allylic alcohols with the bioreduction of the *in situ* generated carbonyl compounds promoted by ketoreductases (KREDs). It is important to note that in this process, both the metal- and bio-catalyst are able to coexist and work simultaneously from the beginning of the reaction, constituting a pivotal contribution to the field of chemo-enzymatic concurrent cascade processes.



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Expanding the substrate scope for asymmetric reduction and c-x coupling reactions using a theoretically-guided optimization of new ligand catalysts. Application to high value chiral compounds

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The asymmetric hydrogenation is one of the most efficient and atom-economical tools to prepare chiral molecules. However, the enantiodiscrimination of simple olefins, is still challenging and requires more sophisticated ligand design. On the other hand, new articles are continuously being published to solve the problem of using other "exotic" nucleophiles for Pd-catalyzed asymmetric allylic substitution. In addition, for both processes ligands rarely tolerate a wide range of substrates and different ligands are required for different substrates to optimize enantiopurity. Ligands with wide substrate scope and suitable for a large number of nucleophiles are desirable for synthesizing more complex chiral organic molecules. The discovery of "privileged ligands" easy to handle (solid, robust and air stable) and prepare from simple starting materials and good for a broad range of substrates and nucleophiles is a relevant issue. Our group has contributed in this field with an improved generation of ligands.[1] In this communication I will present our progress in this field. Relevant tandem reactions for the synthesis of more complex molecules and the use of environmentally friendly solvents will also be discussed.

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Asymmetric reactions using 1,1'-disubstituted olefins as challenging substrates

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In most asymmetric transformations involving olefins as prochiral reagents (i.e. epoxidation, hydrogenation, etc.), 1,1-disubstituted olefins are systematically challenging substrates.[1] This is mainly because the chiral transition metal catalyst has difficulty in controlling not only the face selectivity coordination (due to the presence of the two relatively similar substituents at the geminal position) but also the specific attack at the desired terminal position rather than at the more substituted α-position. We have recently showed the positive effect of introducing a biaryl phosphite moiety into the ligand design to expand the substrate scope in the Ir-catalyzed hydrogenation of minimally functionalized olefins to a range of simple 1,1-disubstituted olefins.[2] In this communication, I will present our latter results in the asymmetric hydrogenation, hydroboration and hydroformylation of this elusive substrate class.

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Silane-thioether compounds: ligands as substrates, substrates as ligands

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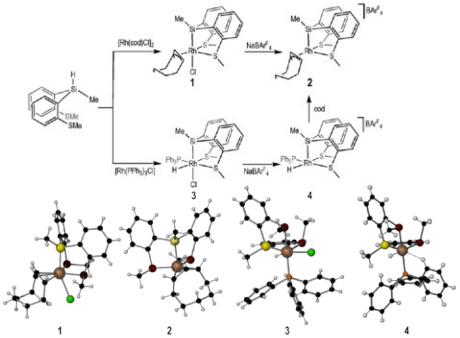
The metal catalysed addition of organic and inorganic silicon hydrides to multiple bonds, has proved to be an efficient method for the formation of organosilicon compounds, and represents one of the most important reactions in the silicon industry. Because these reactions involve the activation of Si–H bonds, we have decided to synthetize silane-thioether compounds and study their behaviour as ligands. Our interest in transition-metal complexes with such ligands is due to the strong *trans* influence of the σ-silyl ligand and to the thioether moieties (σ-donors and weak π-acceptors) being able to exchange with other ligands or molecules.[1,2] Herein we report the preparation and characterization of Rh(III) complexes by reaction of multidentate pro-ligands $SiMe_2H(o\text{-}C_6H_4SMe)$ and $SiMeH(o\text{-}C_6H_4SMe)_2$ with $[Rh(cod)Cl]_2$ [3] and $[Rh(PPh_3)_3Cl]$ [4]. Furthermore, the multidentate nature of $SiMeH(o\text{-}C_6H_4SMe)_2$ has been a key to perform and study the unusual catalytic dehydrogenative coupling of tertiary silanes, where the silane acts as ligand and as substrate.



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P4

Cobalt Catalysed Light-driven Olefin Reduction

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A prerequisite for a sustainable society is the development of new efficient, cheap and greener synthetic methods. Among all the possibilities, the use of sun light as a source of energy is envisioned as one of the most sustainable alternatives. Herein we report the expansion of the catalytic activity of cobalt complexes such as [Co(Py$_2^{Ts}$tacn)(OTf)](OTf), initially developed for the light-driven water reduction to hydrogen,[1] in combination with photoredox catalysts[2] and sacrificial electron donors towards new organic transformations using light as a source of energy and water as a source of protons. In addition, mechanistic studies are also performed to get more insights on the mechanism involved by characterisation of intermediates, kinetics and DFT studies.

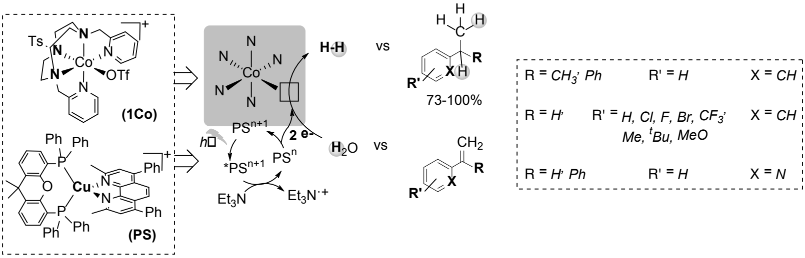

Figure 1. Expansion of the catalytic activity of [Co(Py2Tstacn)(OTf)](OTf) (1Co).

We have been able to reduce a wide range of monosubstituted and disubstituted aromatic olefins with either electrowithdrawing and electrodonating groups to their corresponding alkanes, using [Co(Py$_2^{Ts}$tacn)(OTf)](OTf) as catalyst, [Cu(bathocuproine)(Xantphos)](OTf) as photosensitizer,[3] Et$_3$N as electron donor, light as a source of energy and water as a source of protons. In addition, several modifications of the metal centre have shown different selectivity towards H$_2$ formation or olefin reduction.[4]

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P5

First Corannulene-bridged bis-N-Heterocyclic carbenes: Synthesis and Coordination.

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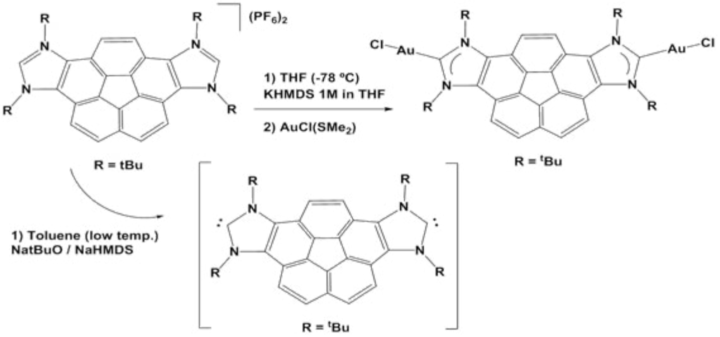
Corannulene is one-third the size of C_{60} and the smallest subunit of the buckyball motif that still maintains a curved surface. The curvature of this compound gives unique electronic properties that are not observed in planar polyaromatic hydrocarbon (PAH) analogues, such as pyrene, naphthalene and coronene.[1] A wide variety of mono- and multifunctionalized derivatives have been described, which were used as precursors for numerous classes of materials.[2] We have been recently interested in the preparation of a wide variaty of bis-NHCs connected by polyaromatic linkers.[3] These ligands, not only gave rise to catalysts with unusual high activity, but also allowed us to prepare new species with interesting photophysical properties.[4] Based on our previous experience, we now report the prepartion of a bis-NHC with a coroanulene linker. The preparation of the free bis-NHC and its coordination to several metal fragments will be described. The low electron-donating character of this ligand will be used for the preparation of catalysts with properties different from those shown by other 'classical' NHC ligands.



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Measuring Which Ligand Does Best in Difficult C–C Couplings

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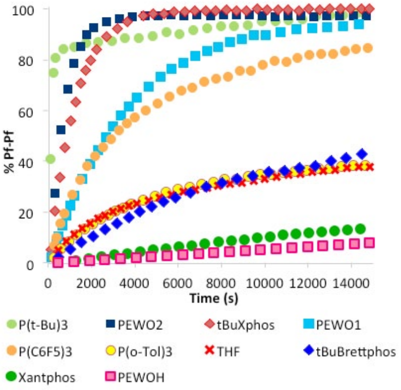
Reductive elimination is one of the most decisive step in Pd catalysed cross-coupling reactions because it is typically irreversible and this pulls forward the whole catalytic cycle.[1,2] Through several years valuable knowledge about reductive elimination have been developed mostly based on theoretical studies of the barriers for the different pathways it could take.[3,4] This work develops an experimental system to test ligand ability to promote difficult coupling processes.

$$\underset{(\mathbf{1})}{cis\text{-}[Pd(C_6F_5)_2(THF)_2]} + 2L \xrightarrow[T = 25\ ^{o}C]{\text{Toluene}} \underset{(\mathbf{2})}{F_5C_6{-}C_6F_5} + PdL_2$$



A Pd complex, *cis*-$[Pd(C_6F_5)_2(THF)_2]$,[5] (**1**) is an excellent meter to easily evaluate the relative ability of different ligands to promote challenging couplings. It only requires monitoring the formation of the coupling product $C_6F_5–C_6F_5$ (**2**). Our protocol is useful to rank experimentally the ability of ligands to promote electronically difficult couplings as isolated from other steps; in addition, it happens to detect some side reactions.

Testing several common ligands used in Pd catalysis, this ability was ranked in the order P^tBu_3 > PEWO2 ≈ ^{t}BuXPhos > $P(C_6F_5)_3$ ≈ PEWO1 > P(*o*-Tol)$_3$ ≈ THF >> Xantphos ≈ PEWOH >> PPh_3 according to the coupling initial rates, whereas their efficiency in the long term is ranked ^{t}BuXPhos ≈ $PtBu_3$ ≈ PEWO2 > PEWO1 > $P(C_6F_5)_3$ >> THF ≈ P(*o*-Tol)$_3$ > Xantphos > PEWOH >> PPh_3.

The scale of relative ΔG‡(Pf-Pf) values is hoped to help to the understanding of problems associated to difficult couplings. Other ligands may be incorporated in the future.

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P7

Origin of Regioselectivity in Rh-Catalyzed anti-Markonikov Hydroamination of Alkenes

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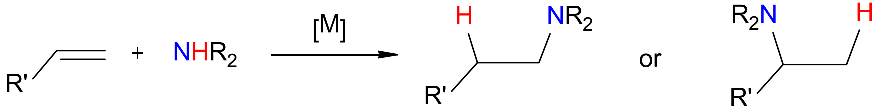
The addition of amines to unsaturated molecules is one of the most economical pathways (in terms of price and atom economy) for synthesis of N-containing compounds such as amines, imines and enamines.[1] This reaction is thermodynamically feasible but activation energies required use to be quite demanding, thus requiring the use of catalysts. Transition metals are proven to be very efficient. Regarding the regioselectivity, anti-Markovnikov hydroamination of olefins was named as one of 10 challenges for homogeneous catalysis (Scheme 1).[2] Progress has been made, but a lot of work is still needed.



Scheme 1. Schematic representation of the regioselective addition of amines to terminal alkenes.

The catalytic cycle for the hydroamination of unsaturated bonds have been analyzed in our group by means of computational calculations.[3] In the present comunation the Rh-catalyzed anti-Markonikov addition of amines to alkenes will be presented. The two main proposed mechanisms of hydroamination reaction mechanisms (amine activation and alkene activation) will be evaluated. One of the major competitive side reactions yielding the enamine product, oxidative amination, will be also investigated.

The origin of the regioselectivity for the addition process (Markovnikov vs anti-Markovnikov nucleophilic attack) will be analyzed in detail. Interesting correlations between catalyst-alkene coordination mode and the regioselective outcome will be discussed. [4]

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P8

Aurophilic trapping agents in water: a great scarcely explored world

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Gold(I) complexes represent an emerging area of investigation within supramolecular and nanomaterials chemistry, due to the establishment of weak Au(I)···Au(I) aurophilic interactions.[1] These interactions can modulate and govern the resulting assemblies and properties in very different potential applications.[2] Our recent reports on hydrogelators and vesicular structures must be highlighted among the resulting supramolecular structures obtained with low molecular weight gold(I) complexes.[3-6]

In the present communication, we would like to present the use of aurophilic hydrogelators as trapping agents in water as a new and scarcely explored field that will open a wide range of new applications in these investigation areas. Among all the possibilities, we have selected two of them: i) the possibility to solubilize metal nanoparticles in water (Figure 1A);[7] ii) the possibility to trap aromatic molecules in water and induce their phosphorescence emission at room temperature and in solution, due to the heavy atom effect (Figure 1B).

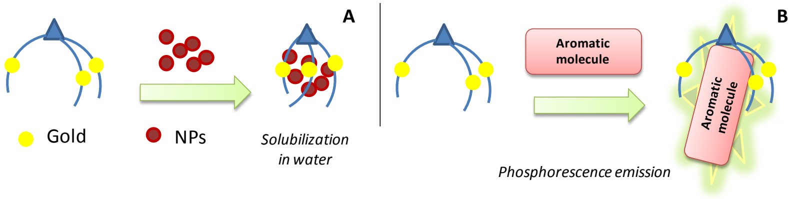

Figure 1. Schematic representation of the use of aurophilic hydrogelators as trapping agents.

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Selective Hydrothiolation of Alkynes Catalysed by N-Donor-Functionalised 1,2,3-Triazol-5-ylidene Rhodium (I) Complexes

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Vinyl sulfides [1] are important targets in organic synthesis since they are valuables intermediates in the synthesis of pharmaceutically and biologically active molecules, organic materials and intermediates. They are accessible through alkyne functionalization strategies, with catalysts developed to this end for increased atom-economy and milder reaction conditions.[1] In this context, we recently reported an anionic CNC-pincer ligand, [2] featuring an amido and two strong sigma-donating 1,2,3-triazol-5-ylidene moieties. The corresponding Rh(I) oxygen adducts, are very active and highly selective towards both the dimerization and hydrothiolation of alkynes, yielding gem- enynes and α-vinyl sulfides, respectively at low catalyst loading.[3] However, in most cases, the regioselective outcome of vinyl sulfide formation from the corresponding aryl alkynes and sulfides still remains a major challenge. Therefore, the development of more efficient and easy tunable catalysts is highly desirable.

Herein the synthesis, characterization and catalytic activity of a series of N-donor functionalised triazol-5-ylidene rhodium (I) complexes towards the hydrothiolation of alkynes using aryl sulfides will be described (Figure 1).

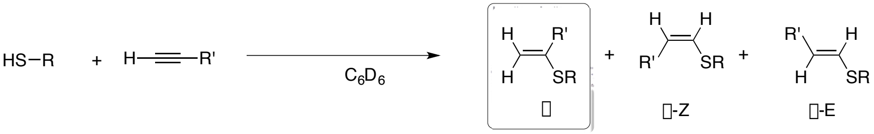

Figure 1

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P10

Hapticity in benzindenyl molybdenum complexes

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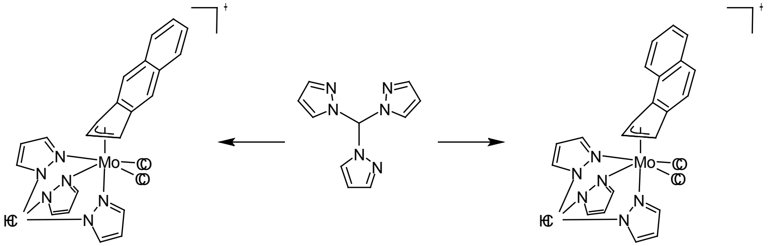
The ability of cyclopentadienyl ligand to adjust its hapticity, *i.e.* the number of contiguous carbon atoms involved in bonding to the central metal, gives rise to processes known as “haptotropic shifts” [1]. Electronically saturated transition metal complexes with η^5-bonded extended aromatic systems (*e.g.* indenyl or fluorenyl) exhibit substantial increase in the reaction rates of substitution reactions and activation of the coordinated ligands [2]. Although haptotropic shifts of cyclopentadienyl, indenyl and fluorenyl ligands have been deeply investigated, revealing various distinct coordination modes, the rearrangements of the congeners with other conjugated π-systems stay almost unexplored even though they are of the particular importance due to the consequent implications for the design of catalytic systems [3].



This study deals with molybdenum(II) compounds bearing benz[*e*]indenyl and benz[*f*]indenyl ligand [(η^5-$C_{13}H_9$)Mo(CO)$_2$(η^3-C_3H_5)]. Although these species are isostructural, their reactivity is influenced by position of annulated benzene ring due to different aromatic stabilization of polycyclic ligands. Both allyl complexes were found to be suitable precursors of various molybdenum(II) compounds. The main attention was given to reactivity with tridentate ligands. In case of tris(pyrazolyl)methane, novel species with η^3-bonded benzindenyl ligand were isolated and characterized by spectroscopic methods and X-ray diffraction analysis; see Scheme. These complexes represent the first example of η^3-coordination mode reported for given polycyclic ligands.

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P11

Exploring the versatility of pd-catalysed reactions in aza-heterocyclic synthesis: domino processes and C-H insertion reactions

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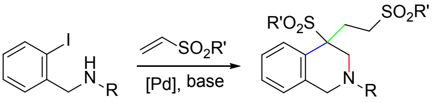
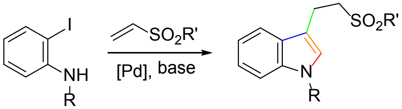
During the past years we have been exploring different ways to increase the versatility of Pd-catalysis in C-C bond-forming reactions, for example, by controlling the ambiphilic character of organopalladium intermediates in intramolecular coupling reactions with carbonyl derivatives.[1]

Continuing our search for new methodologies to increase the potential of organopalladium chemistry in the synthesis of aza-heterocycles, we have recently investigated the integration of the Pd-catalysed α-arylation reaction into multistep domino processes. These studies have allowed us to develop efficient methodologies for the synthesis of highly functionalized tetrahydroisoquinolines[2] and indoles[3] by means of aza-Michael/Pd-catalysed α-arylation/Michael addition domino processes, which are based on the use of sulfones both as electrophiles and nucleophiles.



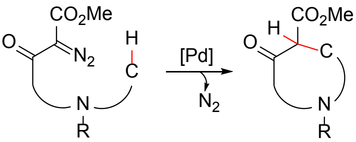
aza-Michael/Pd^0-catalysed □-arylation/
Michael addition domino sequence



aza-Michael/Pd^0-catalysed □-arylation/
Michael addition/□-elimination domino sequence

To further generalize the application of these synthetic methodologies, we have also explored the use of other electron-withdrawing groups in the domino α-arylation/ Michael addition strategy.

In parallel, we have investigated the feasibility of palladium as a catalyst for the carbenoid C-H insertion from diazocarbonyl derivatives, and the use of this methodology for the synthesis of aza-heterocycles.[4]



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P12

Coinage Metal PCP-Pincer complexes with Carbodiphosphorane moiety

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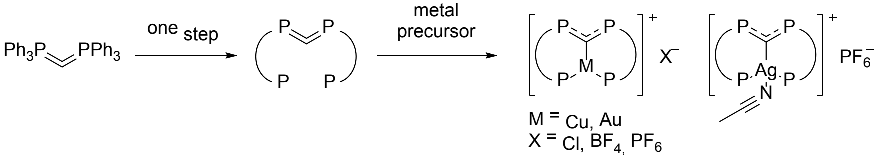
Carbodiphosphoranes (CDP) and related compounds of the general type $L^1 \rightarrow C \leftarrow L^2$ are of significant interest with regard to their reactivity and mode of bonding – the nature of the central carbon atom in particular has been investigated thoroughly.[1,2] Furthermore, the monodentate and especially the multidentate ligands show a diverse range of coordination modes.[3] The first PCP-CDP-pincer ligand $C(Ph_2PCH_2PPh_2)_2$ and its group 10 complexes were described by the group of Peringer, who found a rich structural diversity due to the high flexibility of the ligand backbone.[4,5]

Our goal was the design of more rigid PCP-CDP-pincer ligands for transition metal complexes that are suitable for catalytic applications. Within the scope of our studies, we developed a ligand that can be synthesized in a one step reaction from hexaphenylcarbodiphosphorane.



Reactions of this new ligand with coinage metal precursors yielded monocationic complexes with either trigonal (Cu, Au) or distorted-tetrahedral (Ag) coordination modes. If reacted with two equivalents of CuBr, the ligand stabilizes a dinuclear complex with a Cu-Cu-bond length of 2.75 Å. Reactivity studies and DFT calculations were performed to gain further insights into their properties.

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Biological behavior of cyclometallated platinum(IV) complexes

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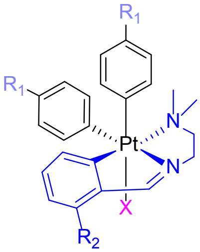
Platinum(IV) complexes are considered promising candidates as new anticancer agents capable of overcoming some of the problems associated with the existing platinum(II)- chemotherapeutics. In spite of the great number of platinum(IV) compounds prepared and tested so far [1], cyclometallated platinum(IV) compounds have received little attention.

This work focuses on three cyclometallated platinum(IV) compounds in which a meridional [C,N,N'] terdentate, two aryl and one halido ligands complete the octahedral coordination around the platinum. These compounds were evaluated against a panel of human adenocarcinomas (A-549 lung, HCT-116 colon, and MCF-7 breast) cell lines. Moreover, in order to evaluate whether reduction of these compounds to produce platinum(II) compounds similar to cisplatin is feasible, electrochemical studies based on cyclic voltammetry were also carried out for these compounds.



1a: X = Br; R_1 = F, R_2 = H
1b: X = Br; R_1 = Me; R_2 = H
1c: X = Cl; R_1 = Me; R_2 = Cl

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P14

Synthesis and Reactivity of the Unsaturated Anion $[Mo_2Cp_2(\mu\text{-}P^tBu_2)(\mu\text{-}CO)_2]^-$

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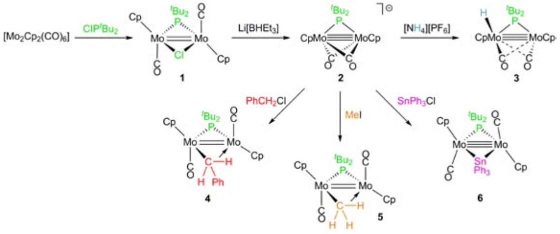
During the last years our research group has developed new synthetic routes to binuclear complexes of the group 6 metals (Mo and W) with M–M multiple bonds stabilized by bridging phosphide ligands ($\mu\text{-}PR_2$). This allowed us to start an extensive study on the reactivity of complexes such the 30-electron anions $[M_2Cp_2(\mu\text{-}PCy_2)(CO)_2]^-$ (M = Mo, W) or the hydrides $[M_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2]$ [1, 2], which revealed that the nature of metal center has an important influence on the chemical behavior of these unsaturated species. As an extension of this research, in this study we aim to evaluate the influence that the nature of the bridging phosphide ligand may have on the structure, stability and reactivity of these unsaturated molecules. In particular, we decided to study the effect of incorporating the quite bulky di*tert*butylphosphido ($\mu\text{-}P^tBu_2$) ligand.

The unsaturated anion $[Mo_2Cp_2(\mu\text{-}P^tBu_2)(\mu\text{-}CO)_2]^-$ (**2**) was prepared using a route similar to that used for the anions with other PR_2 bridges [1, 2], that its via two-electron reduction of the chlorocomplex $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(CO)_2]$ (**1**), which in turn is easily accessible through a one step process using commercially available reagents. The unsaturated anion **2** proved to be a versatile precursor of different unsaturated complexes through its reaction with several electrophiles, since it displays two nucleophilic sites located at the dimetallic unit and the oxygen atoms of the bridging carbonyl ligands. More importantly, its protonation produces the stable 30-electron hydride $[Mo_2Cp_2(H)(\mu\text{-}P^tBu_2)(\mu\text{-}CO)(CO)]$ (**3**), a complex displaying an unusual terminal disposition of the hydride ligand which is in contrast with the bridging disposition found for its PCy_2 bridged analogue [1b]. Other unsaturated derivatives like the agostic alkyl complexes **4** and **5** proved to be much more stable than their PCy_2-bridged counterparts, thus enabling further studies on their chemical behaviour, currently under way.



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P15

Design and characterization with GPC of silicone surfactants.

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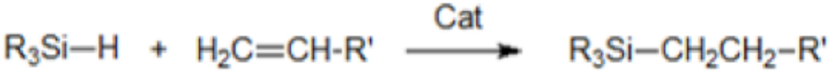
The properties of polyurethane foams depend on the silicone surfactant additive [1], among others. The chemical structure of these surfactants (polyether-polysiloxane copolymers) plays an important role on the properties of polyurethane foams [2] [3]. In order to synthesize silicone surfactants, we have reacted silicone-hydride reactive silicones with allyl polyether, this reaction is the hydrosilylation reaction [4,5].



$$R_3Si{-}H \;+\; H_2C{=}CH{-}R' \xrightarrow{\text{Cat}} R_3Si{-}CH_2CH_2{-}R'$$

Our work describes the design of different chemical structures of silicone surfactants by changing the molecular weight and the ramification of silicone-hydride reactive silicones. To make these reactive silicones, we have used two pathways, the cationic equilibration [6] and AROP [7].

Finally, the characterization of the obtained silicone surfactants have been carried out using gel permeation chromatography (GPC). We have used this technique as the main tool of our work, in order to determinate the different molecular weights of each species, considering that the molecular weight is a major effect in the final properties of polyurethane foams.

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Unexpected Formation of Early Late Heterobimetallic Complexes from Transition Metal Frustrated Lewis Pairs

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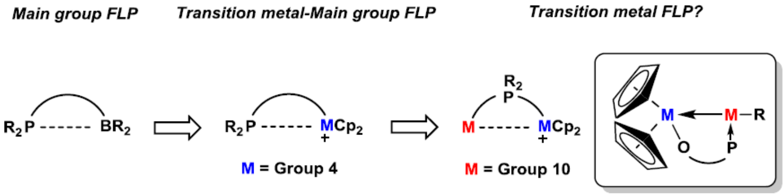
Frustrated Lewis pair (FLP) chemistry, in which Lewis acid–base pairs act cooperatively to activate small molecules such as hydrogen and CO_2, is one of the most exciting recent developments in main group chemistry, not least because of the promise of catalysis with such FLPs. We [1] and others [2] have extended this chemistry to transition metal systems, replacing the main group Lewis acid with an electrophilic group 4 fragments to give highly reactive FLPs based on metallocene phosphinoaryloxide complexes. With examples of transition metals replacing either the main group Lewis acidic or Lewis basic component of an FLP now established, we are intrigued by the possibility of having both the Lewis acidic and basic functions as transition metals. This possibility is, of course, reminiscent of early late heterobimetallic complexes, which have been studied for many years [3]. In this communication we present some exciting preliminary results we have discovered in our attempts to prepare 'metal-only' FLPs [4]. Reaction of transition metal "frustrated" Lewis pair precursors of the type $[Cp_2Zr(Me)(OC(CF_3)_2CH_2PtBu_2)]$ with the low valent platinum species $[Pt(norbornene)_3]$ leads to the unexpected formation of a heterobimetallic species $[Cp_2Zr\{Pt(Me)\}(OC(CF_3)_2CH_2PtBu_2)]$. Single crystal X-ray analysis reveals an unusual T-shaped geometry at the platinum center. Treatment of this compound with PMe_3 yields $[Pt(PMe_3)_4]$ and regenerates the zirconium precursor. Treatment with $[(Et_2O)_2H][B(C_6F_5)_4]$ results in rapid protonolysis and loss of methane to generate an extremely unstable cationic heterobimetallic compound. Analogous observations are made with titanium–platinum species starting from Ti-Cl precursors. We propose the chemistry is best rationalized as a formal insertion of Pt(0) into a Zr–C or Ti–Cl bond.



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P17

Enantioselective hydroformylation by a Rh-catalyst entrapped in a supramolecular metallocage

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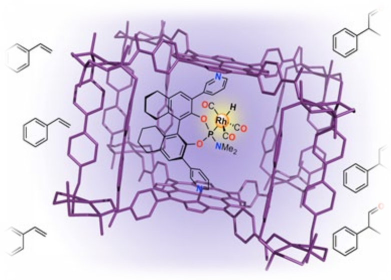
Compared to man-made chemical catalysts, enzymes display greater performance in terms of rate enhancement, stabilization of the transition state or restricted substrate motion. Most of these effects are induced by the enzyme protein secondary structure. Supramolecular self-assembly is a powerful tool for the development of molecular reaction vessels, which may mimic the cage-like structure of enzymes.[1] Here we report the regio- and enantioselective hydroformylation of styrenes upon embedding a chiral Rh complex in the self-assembled metallocage cage **4**·(BArF)$_8$.[2] The catalyst that results converts styrene derivatives into aldehyde products with much higher chiral induction in comparison to the non-encapsulated Rh catalyst and its template analogue.[3] Enhanced enantioselectivity is rationalized by the modification of the second coordination sphere that become possible upon catalyst inclusion inside the cage, being one of the few examples in achieving enantioselective outcome via indirect through-space control of the chirality around the catalyst centre.[4] These results are a showcase for the future development of asymmetric catalysis by using size-tunable supramolecular capsules.



Acknowledgements

XR, MC and JNHR thank the European Research Council, XR and MC thank MINECO and DIUE of the Generalitat de Catalunya and ICREA-Acadèmia awards.

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Trapping a highly reactive nonheme iron intermediate: stereoselective oxygenation of strong C-H bonds and alkenes

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Oxygenation of nonactivated alkyl C-H bonds constitutes a very challenging reaction owing to their notorious chemically inert character. Consequently, highly reactive species are necessary to break these bonds.[1] In nature, C-H hydroxylation is mainly performed by iron-dependent enzymes, which create highly electrophilic species via finely controlled partial reduction of the O_2 molecule. In particular, oxidation of C-H bonds is carried out by high-valent oxo-iron species both in heme enzymes (e.g. cytochrome P450)[2] and in non-heme enzymes (e.g. α-ketoglutarate dependent hydroxylases and halogenases).[3]

Mononuclear iron-peroxide species have been also detected and proposed as the C-H oxidizing species in the anticancer drug Bleomycin, and their implication in the reaction mechanism of cytochrome P450 has been largely debated. However, while several synthetic models of mononuclear iron-peroxide species have been described,[4] their oxidative reactivity against organic substrates has proved to be sluggish at best. Mononuclear ferric species with hydroperoxo, alkylperoxo and acylperoxo ligands have been prepared and have been shown uncapable of attacking strong C-H bonds and olefines.[5] This work constitutes the first example where a synthetic nonheme iron species responsible for stereospecific and site selective C-H hydroxylation is spectroscopically trapped.[6] This intermediate can also perform oxygen atom transfer (OAT) to olefinic substrates with exceedently fast rates and very remarkable is a true competent OAT intermediate with relevance in nonheme iron catalyzed epoxidations.[7]

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Environmentally benign catalytic reactions based on non-precious transition metal complexes – Divergent coupling of alcohols and amines

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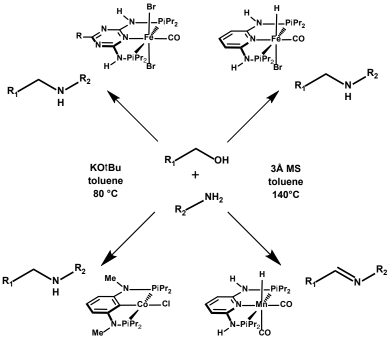
Since alcohols are readily available by a variety of industrial processes and can be obtained renewably via fermentation or catalytic conversion of lignocellulosic biomass, the direct acceptorless coupling of alcohols and amines is one of the most promising, green synthesis pathways for the preparation of amines and imines. In this process, only water and H_2 are produced as byproducts. This reaction has been accomplished in recent years mainly with precious-metal-based catalysts. However, the limited availability of such metals, their high price, and their toxicity will diminish their attractiveness in the long run and more economical and environmentally friendly alternatives have to be found. Accordingly, in order to develop greener and more cost-effective chemical processes it is highly important to replace precious metal catalysts by earth abundant non-precious metal catalysts.[1-3]



We present here new Mn(I), Fe(II), and Co(II) PNP and PCP pincer complexes and describe their catalytic activity towards the coupling of alcohols and amines. This methodology is based on the so-called borrowing hydrogen strategy and yields in the case of Mn(I) selectively imines, while in the case of Fe(II) and Co(II) amines are formed.

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Anion and ancillary ligand effects on Iridium-based light emitting electrochemical cells

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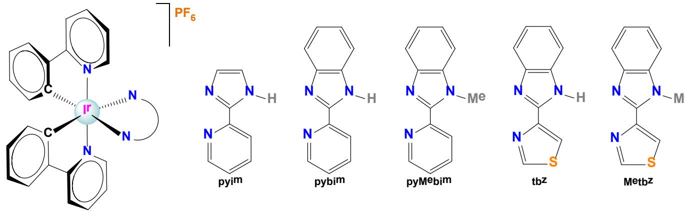
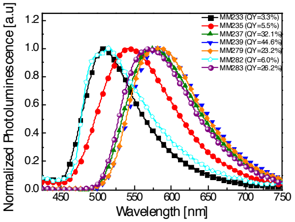
Heteroleptic Ir(III) complexes of the type $[Ir(C\text{^}N)_2(N\text{^}N)]PF_6$ show promising photoluminescent (PL) properties in the field of light-emitting electrochemical cells (LECs). In particular, these complexes allow a modular fine-tuning of the emission colour and PLQY, by introducing little changes in both the cyclometalated and the ancillary ligands which result in variations in the energy band gap [1]. Counterion modifications can also alter the emission colour [2]. Nonetheless, the presence of chloride ions results in significant reductions in the performance of ionic transition metal complexes (iTMC) in LECs [3].





In this work, we present a series of cationic Ir(III) complexes with general formula $[Ir(ppy)_2(N\text{^}N)](PF_6)$ where N^N = arylazole (see structures). The complexes were fully characterised by NMR, IR, mass spectrometry and elemental analysis. Furthermore, electrochemical measurements and theoretical calculations were performed so as to support and explain the observed photophysical properties (see emission spectra). The study revealed an hypsochromic shift (52 nm) in the emission for complex with pyim compared to that with pybim, whereas a bathochromic shift (13 nm) and an increase in the PLQY was observed when N-H was replaced with N-Me in the benzimidazole scaffold. In addition, the -Me presence was proved to enhance the features of the LECs.

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Iridium-catalyzed $^3O_2$ photoexcitation and photo-oxidation reactions

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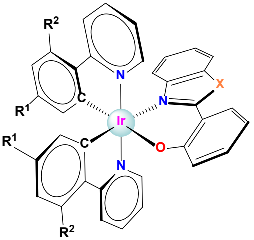
In the present communication, we disclose the synthesis and characterization of six neutral Ir(III) bis-cyclometalated complexes resulting from the combination of two different hydroxy-benzoazolate ligands (O^N) and three different cyclometalated ligands (C^N) (see Figure 1). Moreover, we have concluded that the photophysical properties of the described complexes depend mainly on the ancillary ligand (O^N) with a minor influence corresponding to the C^N ligand. For instance, the photoluminescent quantum yields are very high for those complexes with *hPhbim* and moderately high or low for those complexes with *hPhbtz*. Besides, the emission wavelengths of the Ir(III) molecules are also strongly dependent on the specific O^N ligand, since *hPhbim* causes a marked blue-shift (between 68 and 80 nm) compared to *hPhbtz*. As expected [1], the emission properties of these derivatives are O_2-sensitive (Figure 2). Consequently, they behave as efficient photo-sensitizers of $^3O_2$, and show catalytic activity in photooxidation reactions, such as the conversion of thioanisole to methyl phenyl sulfoxide.



[1a]: $R^1 = R^2 =$ H, C^N = **ppy**; X = NH, O^N = **hPhbim**
[2a]: $R^1 =$ Me, $R^2 =$ H, C^N = **tpy**; X = NH, O^N = **hPhbim**
[3a]: $R^1 = R^2 =$ F, C^N = **dfppy**; X = NH, O^N = **hPhbim**
[1b]: $R^1 = R^2 =$ H, C^N = **ppy**; X = S, O^N = **hPhbtz**
[2b]: $R^1 =$ Me, $R^2 =$ H, C^N = **tpy**; X = S, O^N = **hPhbtz**
[3b]: $R^1 = R^2 =$ F, C^N = **dfppy**; X = S, O^N = **hPhbtz**

Figure 1. Molecular structures of the synthesized bis-cyclometalated Ir(III) complexes.

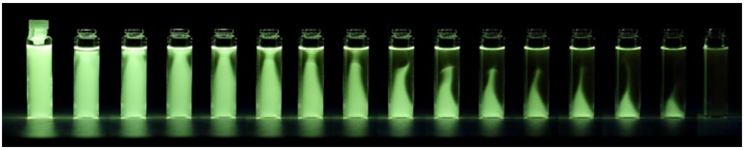


Figure 2. Sequence of photographs illustrating the quenching of photoluminescence under UV light (365 nm) for complex **[2a]** as a result of O_2 diffusion during a period of 2 min.

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Fc-based N-heterocyclic carbenes for the design of redox-switchable catalysts

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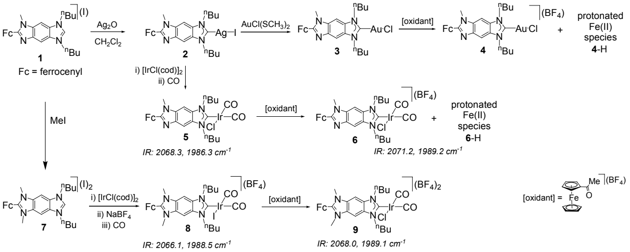
In traditional design of homogeneous catalysts, the choice of a ligand is based on its steric and electronic properties. This is due to the notion that the ligand plays a spectator role. However, some of the properties of a metal complex may be influenced by essentially ligand-based reactivity.[1] For example, the introduction of a *redox-active* functionality within a ligand framework potentially allows the reactivity and selectivity of complexed metal centers to be modulated through the electrochemical switching of the redox center.[2] In a typical reaction, a redox-switchable catalyst facilitates a given transformation at a given rate when the ligand is in the neutral form. In this context, we have designed imidazolium salts **1** and **7**, in which the redox-active fragment is connected to the NHC ligand precursor unit through a polyaromatic system. Ferrocenyl-imidazolium salt **1** has been used for the preparation of related ferrocenyl-NHC Ag(I), Au(I) and Ir(I)-based complexes (Scheme 1). Aiming to oxidize complexes **3** and **5**, the two complexes were reacted with acetylferrocenium tetrafluoroborate that is quantitatively transformed in acetylferrocene, yielding mixtures of the oxidized compounds **4** and **6** along with the protonated Fe(II) species **4**-H and **6**-H, respectively. In order to avoid the protonation of the ligand and to quantify the modification of its donating character upon the introduction of a positive charge, dicationic salt **7** was prepared and used as precursor in the preparation of complex **8**. Complex **8** was also oxidized using acetylferrocenium tetrafluoroborate, generating complex **9** that was analyzed by IR spectrum. The catalytic activity of the Au(I) complexes has been studied in two benchmark gold-catalyzed reactions, namely hydroamination of phenylacetylene with arylamines and cyclization of alkynes with furans, in which the addition of an oxidant to the reaction vessel afforded a significant improvement. In particular, the introduction of the oxidant activates the otherwise completely inactive Au(I) complex towards the cyclization reactions.



Scheme 1

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Reactividad de paladaciclos derivados de iminofosforanos

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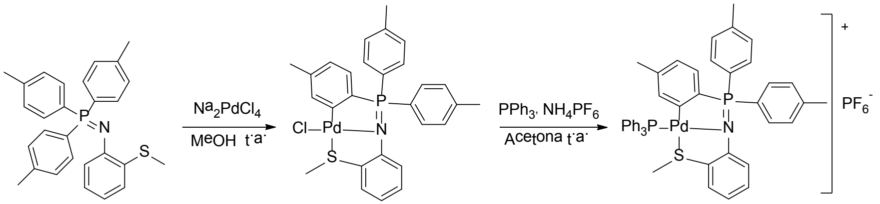
Los iminofosforanos, compuestos de fórmula general $R_3P{=}NR$, se pueden considerar como análogos nitrogenados de los iluros de fósforo. El enlace P=N está fuertemente polarizado de forma que el átomo de nitrógeno soporta una carga parcial negativa por lo cual son buenos dadores σ y malos aceptores π. Al reaccionar con sales metálicas se pueden obtener compuestos ciclometalados análogos a los derivados de las bases de Schiff, cuyas propiedades como catalizadores[1] así como anticancerígenos[2] los convierten en compuestos de un elevado interés en investigación. En la presente comunicación se describe la preparación, caracterización y estudio estructural de nuevos ciclometalados de paladio derivados de iminofosforanos y su reactividad frente a fosfinas terciarias con uno o más átomos donadores, tal como se puede observar en el ejemplo que se muestra en el esquema siguiente,



Agradecimientos

Los autores agradecen a la Xunta de Galicia (Galicia, Spain), la ayuda financiera recibida GRC2015/009.

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Síntesis de compuestos derivados de paladio. Aplicaciones en catálisis

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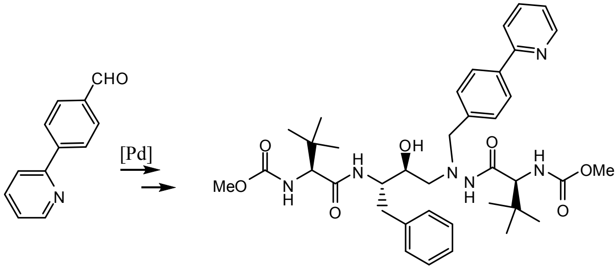
En 2010 A. Suzuki fue galardonado con el premio Nobel de Química, compartido con R. Heck y E. Negishi, por sus aportaciones al estudio de las reacciones de acoplamiento de C–C [1], las cuales son de gran importancia en síntesis orgánica y en procesos industriales. Los compuestos de paladio, y en particular los paladaciclos, presentan como una de sus características más significativas la de poder ser utilizados como catalizadores en tales procesos [2] con eficiencia variable en función de los ligandos y de su estructura. Nuestro grupo de investigación tiene una cierta experiencia en el estudio de este tipo de compuestos, tanto en lo referente a su síntesis como a su posterior caracterización [3]; por ello, la investigación llevada a cabo en la actualidad se centra en la aplicación de los paladaciclos en la reacción de Suzuki [4], entre otras por su alta aplicabilidad en la síntesis de medicamentos.



Atazanavir **2b**

Figura 1.- Aplicaciones de la reacción de Suzuky-Miyaura en la síntesis de Atazanavir [5]

En esta comunicación se describe la síntesis y caracterización de una serie de compuestos organometálicos de paladio con ligandos tiosemicarbazonase y la posterior utilización de los mismos en reacciones de acoplamiento cruzado con formación de enlaces C–C.

Agradecimientos

Los autores agradecen a la Xunta de Galicia (Galicia, Spain), la ayuda financiera recibida GRC2015/009.

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NHC-stabilized Rh nanoparticles: Surface study and effect on the H/D exchange reaction of phosphorus and oxigen containing compounds

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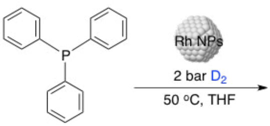
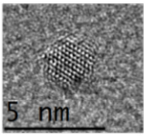
In catalysis, metal nanoparticles (NPs) display the advantages of both homogeneous and heterogeneous catalysts, as they are extremely active, their reactivity can be modulated and they can be recovered and reused. [1] Recently, Ru@PVP NPs have been efficiently used as catalysts in H/D exchange reactions to selectively label nitrogen-containing compounds with various degrees of deuterium incorporation and substrate tolerance and even with enantiospecificity at stereogenic centers in the case of chiral amino acids and derivatives. [2, 3] More recently, we have reported the application of Ru@PVP NPs in the H/D exchange of aromatic compounds containing phosphorus atoms, obtaining selective deuteration at the *ortho* position of the aromatic ring with phenyl- or phenyl-alkylphosphines. However, hydrogenation of the aromatic ring in the case of triphenylphosphine oxide indicated the coordination of this substrate by the aromatic ring by p–interactions. [4]

Since several studies have demonstrated that stabilizers play an important role on catalysis, significant efforts have been made in the synthesis of ligand-stabilized nanoparticles to rule the properties of these nanocatalysts. [5] 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. [6,7]

Here we report the synthesis and characterization of Rh NPs stabilized by NHC ligands and their application in H/D exchange of compounds containing phosphorus and oxygen atoms.





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Ru- Rh- and Ir-based catalytic transfer hydrogenation of quinolines and hcooh decomposition

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Gabriel García-Herbosa,[1] Aránzazu Carbayo,[1] Félix A. Jalón,[2]
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In the present communication, we disclose the synthesis, characterization and catalytic activity in hydride transfer processes of twelve cationic Ir(III), Rh(III) and Ru(II) half-sandwich complexes (Cp* or *p*-cymene) with different types of N,N- or P-donor ligands (see Figure 1). It is known that this type of complexes can act as catalysts in transfer hydrogenation reactions of various aromatic N-heterocycles in aqueous HCO_2H/HCO_2Na [1]. Herein, we conclude that our complexes show good activity as transfer hydrogenation catalysts of different types of quinolines and ketones, with a metal hydride as the key species in the process. Moreover, in some cases, quinolines can undergo catalytic hydroformylation of amine groups in addition to the hydrogenation process. On the other hand, these metal complexes can decompose formic acid to H_2 and CO_2. In mechanistic studies performed by NMR, we can observe the strongly dependence of the metal centre on the hydride stability, and also a high dependence on the ancillary ligand to generate H_2 once the hydride has been formed.

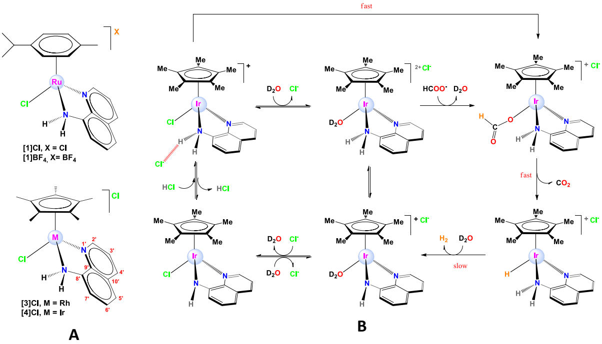

Figure1. A: Two of the twelve synthesized catalysts, with 8-aminoquinoline as (N^N) ligand. **B:** Species involved in the reactivity of **[4]Cl** against HCO_2H/HCO_2Na in D_2O.

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From tetrametallic $[Ir(+1.5)]_4$ chains to bimetallic Ir(0)–Ir(II) mixed-valence complexes

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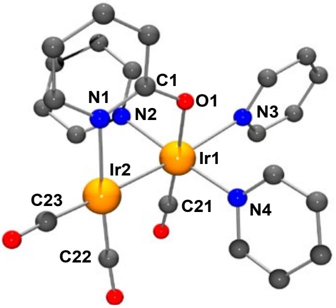
Compounds containing discrete chains of metal-bonded atoms are interesting because of their potential applications as nanoscale devices.[1] During the recent years we have been working on the feasibility of connecting electroactive components to a new family of '*iridium blues*' (multinuclear mixed-valence chains)[2] for transporting charge from one end to the other through the electronic delocalization along the metal backbone. Related with that subject, we reported the binding of π-conjugated systems such as acetylides or bis(acetylides) to the tetranuclear $[Ir(+1.5)]_4$ chain $[\{Ir_2(\mu\text{-OPy})_2(CH_3CN)(CO)_4\}_2](PF_6)_2$ (**1**) (OPy = 2-pyridonate) via replacement of one axial acetonitrile ligand by the terminal alkyne in the presence of a base.[3]



To our surprise, all the attempts to coordinate a simpler molecule such as pyridine to the ends of the chain **1** were unsuccessful. The dissolution of the complex in pyridine leads to the cleavage of the backbone with the formation of a dinuclear mixed-valence Ir(0)–Ir(II) complex (see Figure) instead of the expected replacement of the labile acetonitrile by pyridine. This type of complex is not very common; just a few examples reported by Nocera et al. are known.[4] However two-electron mixed-valence M^n–M^{n+2} complexes are considered highly valuable compounds since they have been proposed as key promoters of multielectron/multiproton transformations.[5]

In this communication we will discuss some geometric and electronic properties of $[(CO)_2Ir^0(\mu\text{-OPy})Ir^{II}(Py)_3(CO)](PF_6)$ (**2**) along with the most relevant reactivity considerations.

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Compuestos ciclopaladados con fosfinas derivadas del ferroceno

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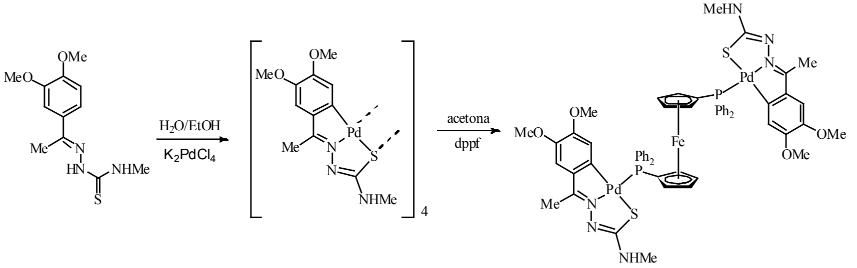
La síntesis, aislamiento y caracterización del ferroceno[1] y sus derivados marcaron un hito importante en la evolución de la Química Organometálica moderna. Una parte significativa de esta química la constituye el conjunto de paladaciclos con tiosemicarbazonas, y en particular aquéllos que contienen derivados del ferroceno. Se trata en este caso de ligandos tridentados [*C,N,S*] que originan compuestos con anillos aromáticos y metalaciclos fusionados, conteniendo el complejo final dos metales diferentes, tanto en lo referente a su naturaleza como también en las características del enlace que forman con el ligando. En la presente comunicación se describe la preparación, caracterización y estudio estructural de nuevos complejos de paladio con ligandos tiosemicarbazona, que incorporan fosfinas terciarias derivadas de ferroceno con modos de coordinación variable en función de las características de la reacción de síntesis, como se muestra en el ejemplo siguiente,



Agradecimientos

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P-C Bond Formation Promoted by Rhodium Complexes

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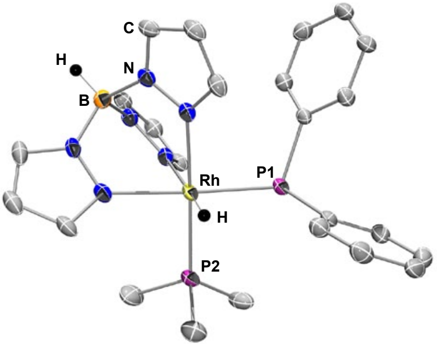
Complexes with a terminal phosphanido (M-PR_2) functionality bound to a single late transition metal center have been proposed as intermediates in relevant processes such as dehydrocoupling[1] and hydrophosphanation[2] reactions. The former provides an easy way to diphosphanes, phosphacycles and unique oligophosphanes. The later represents an atom-economical route to a very important class of compounds such as organophosphanes. Moreover, safety, selectivity and 'green synthesis' are major advantages of dehydrocoupling and hydrophosphination catalysis. A key step postulated in both processes is the activation of the P-H bond, commonly proposed to occur by oxidative addition at late-transition metal centers. Indeed, a combination of the tripodal trispyrazolylborate and the basic trimethylphosphane ligands on rhodium allowed the easy cleavage of the P-H bond to give the novel terminal phosphanido complex [RhTp(H)(PMe_3)(PPh_2)] (**1**, see Figure).[3]

In this communication, we will showcase the ability of complex **1** in promoting C–P bond formation reactions as a direct consequence of the nucleophilicity of the phosphanide ligand in the complex. In this contex we will discuss stoichiometric reactions of **1** with chloroalkanes, activated olefins and alkynes.



In addition, the activity and selectivity of **1** in the effective catalytic hydrophosphanation of unsaturated substrates as well as the proposed catalytic cycle will be commented.

Finally, the ability of non-activated olefins such as ethylene to undergo insertion reactions into Rh-H and Rh–P bonds enlighten the substrate-control over outer- or inner-sphere mechanisms in hydrophosphanation, which will be shown with relevant compounds isolated in preparative reactions.

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P30

Suzuki-Miyaura Cross-Coupling of 2-Pyridyl Boronates

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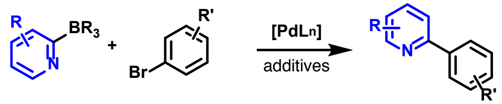
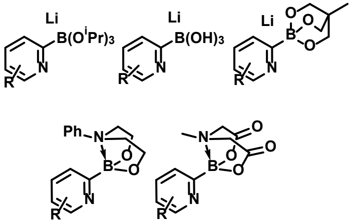
Suzuki-Miyaura cross-coupling is one of the most widely used strategies for the formation of C-C bonds. [1] Since firstly described, many research groups have further developed this protocol to access milder conditions, low catalyst loadings and challenging substrates. However, some challenges still remain in this field. One of them is the efficient coupling of electron deficient 2-heteroaryl species.

Due to the ubiquity of 2-pyridyl moieties in pharmaceutical and natural products,[2] many efforts have been devoted to the development of methods to synthesise molecules containing this motif. The use of 2-heteroaryl boronic acids in Suzuki-Miyaura cross-coupling usually affords low or no conversion at all. This reactivity has been attributed to instability of the boronic acids and protodeboronation occurring in the media. To overcome this issue, different 'masked boronates' have been synthesises and used as cross-coupling partners. [3]

Interested in the mechanism of this important transformation, we have performed kinetic analyses on the Pd-catalysed cross-coupling of a range of 2-pyridyl-boronate systems and aryl bromides. The reactions have been monitored by NMR spectroscopy and the influence of different bases, additives and co-catalysts, such as Cu salts, has been studied.





Masked boronates

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P31

Novel chiral Rh catalysts for asymmetric hydroformylation heterogenised via π-π stacking interactions

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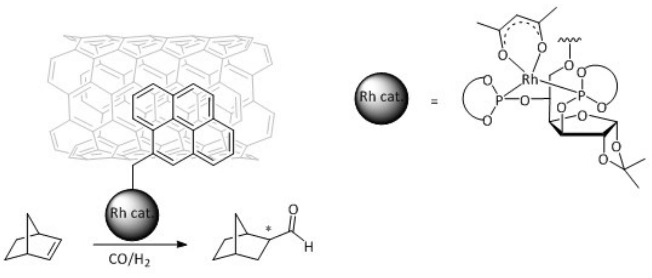
Homogeneous catalysis has been successfully employed to large number of processes to achieve high activity and selectivity, as well as high level of mechanistic understanding.[1] Nevertheless, the heterogenisation of the related catalysts for their recovery and reuse is still nowadays a goal to be achieved to improve the sustainability of catalytic processes.[2]

The use of non-covalent interactions is an attractive strategy to attach homogeneous catalysts onto a solid support since it usually does not require additional synthetic efforts and maintain the structure of the ligand scaffold.[3] Recently, carbon materials such as graphene or carbon nanotubes emerged as promising supports due to their unique properties and large surface area.[4] Furthermore, they provide the possibility to immobilise catalysts via covalent or non-covalent interactions such as π-π stacking, which allow the grafting of molecules containing large polyaromatic systems onto these materials.[5]

In this work, we report the synthesis and characterization of rhodium complexes bearing pyrene tagged chiral 1,3-diphosphite ligands derived from D-glucose. The non-covalent immobilisation of these species onto various types of carbon nanotubes was explored to obtain heterogenised catalysts, which were subsequently tested in the asymmetric hydroformylation of bicyclic alkenes [6]. Finally recycling experiments in batch and flow mode were carried out to analyse the robustness of these systems.



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P32

Stereospecific control of metal-centred chirality with κ^4-tetradentate ligands

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The development of the asymmetric catalysis as a powerful branch of the catalysis has been boosted by the fact that the two enantiomers of a chiral compound may have significantly different properties. The typical asymmetric metallic catalyst is a chiral Lewis acid in which the quirality source is an enantiopure organic ligand. The prochiral substrates coordinate the metal and therefore, the greatest level of chiral induction would be expected for chiral-at-metal complexes. However, the development of this type of catalysts is very limited mostly due to the paucity of preparative methods for configurationally stable metallic complexes. As far as we know, only bis- or tris-chelate octahedral complexes have been resolved and, subsequently, applied as catalysts to asymmetric processes [1].

We have started a research project aiming to develop chiral catalytic precursors with stereogenic metal centres based on tetradentate ligands. The chosen ligands are tertiary amines containing arene, pyridine and phosphane substituents (Figure 1). Their geometry and connectivity allow for a κ^4 coordination in all cases.

Figure 2 shows the geometries that an octahedral ion may adopt bearing this type of ligands. When two of the three substituents are equal (N_2P in Figure 2), a pair of enantiomers as well as an achiral complex can be formed. With three different substituents (CNP in Figure 2), three pairs of enantiomers can be obtained.

In a first step, we will try to stereoselectively prepare and resolve octahedral metallic complexes with this type of ligands. In the present poster, the results achieved in this area will be disclosed.

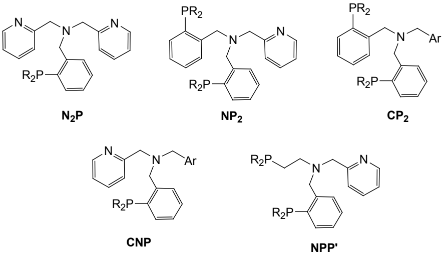

Figure 1

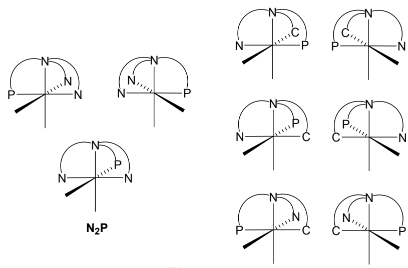

Figure 2

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P33

Metallic Brønsted acids as catalysts

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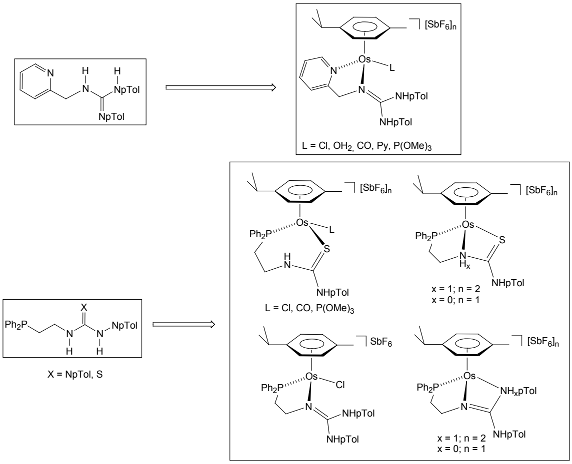
Ureas and thioureas are organocatalysts that activate electrophiles either through hydrogen bond interactions or by acting as Brønsted acids. Their activity can be increased by incorporating electron withdrawing substituents and catalytic asymmetric versions have been developed by using chiral groups as substituents. Over the last years, this type of catalyst has been successfully applied to a variety of organic reactions.

The principles that are the basis of success for these catalysts can be also met by transition metal complexes. Ligands containing NH groups may increase their acidity by coordination to a metallic Lewis acid and, in the case of chiral metallic fragments, these protons could enantioselectively activate electrophiles. The resulting metallic species have been classified by Yamamoto and Futatsugi as Lewis acid assisted Brønsted-acid catalysts (LBA). They can also be called "metallo-organocatalysts". So far, only a few number of examples of this type of catalyst have been reported [1,2].

In the present poster, we show the results obtained in the preparation and characterisation of half-sandwich osmium complexes with ligands containing NH groups with the capability for acting as Brønsted acids (see scheme). Furthermore, we also present some preliminary results about their catalytic applications.



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P34

Easy C–C, C-N and C-P Coupling Processes in the Reactions of Unsaturated Benzylidyne-Bridged Complexes

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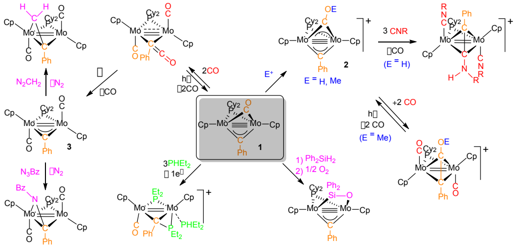
The chemistry of carbyne (≡CR) complexes is an intensively studied area within the organometallic field. Usually these compounds display a high reactivity derived from the multiple nature of their M–C bonds and they are also involved in several processes of industrial relevance such as the Fischer-Tropsch synthesis of hydrocarbons from syngas or the metathesis of alkynes. Furthermore, when bridging two metal atoms the chemical reactivity of the carbyne ligand can be significantly increased by the combined presence of multiple metal-metal bonds.

In this area, we have recently set forth high yield routes for the preparation of unsaturated benzylidyne complexes of formulae $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_x]$ (x = 1, 2),[1] which allowed us to initiate a systematic study of their reactivity.[1,2] Herein we report the results of their reactions toward several organic molecules which in most cases involve actively the carbyne group. The 30-electron carbyne **1** undergoes unusual C–C and C-P coupling processes under mild conditions, but mainly from cationic derivatives following from alkylation or oxidation steps. In its neutral state, complex **1** is rather unreactive toward small unsaturated organic molecules such as alkynes or diazoalkanes; however, the 32-electron carbyne **3** is more reactive towards these reagents and it displays a multisite reactivity. Thus, its reaction with N_2CH_2 gives an alkenyl derivative following from selective C–C coupling of the carbyne and methylene groups, while its reaction with N_3CH_2Ph gives an iminoacyl derivative following from C-N coupling between the carbyne and a nitrene group. Finally, complex **1** reacts with Ph_2SiH_2 to give an intermediate silylene complex which does not undergo C-Si coupling, but instead undergoes easy oxidation with air to generate an unprecedented silanone containing complex, a reaction sequence in which the carbyne ligand acts as a mere spectator group.



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Synthesis and supramolecular properties of Pt(II) complexes bearing pyrene-based NHC ligands

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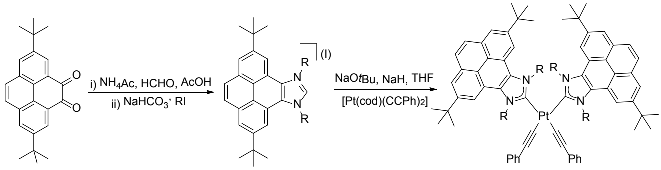
The processes of molecular recognition and self-assembly, which are governed by weak and specific non-covalent intermolecular interactions, are of fundamental importance for the formation of higher organized chemical systems.[1] These non-covalent interactions, including hydrogen bonding, ion paring and π-stacking interactions, play an important role in biological processes. In this context, we have been particularly interested in studying the effect of π-stacking interactions in homogeneous catalysis in those cases in which the catalysts contain polyaromatic NHC-based ligands. We have demonstrated that the activity of such complexes is strongly modified by these supramolecular interactions.[2] Aiming to further explore the nature and the magnitude of these supramolecular interactions, we have prepared a series of pyrene-based bis-carbene Pt(II) complexes and have studied their interaction with aromatic substrates using host-guest chemistry methods. As depicted in Scheme 1, complexes **2** were prepared starting from previously reported pyrene-imidazolium salts **1**.[3]



1a R = Me
1b R = Et
1c R = *n*-Pr

2a R = Me
2b R = Et
2c R = *n*-Pr

Scheme 1

Complexes **2** form stable host-guest adducts with a variety of aromatic molecules such as 1,2,4,5-tetracyanobenzene (TCNB) through attractive π-π interaction between the aromatic guest molecule and the pyrene part of the complex. These complexes, with a cavity of flexible size, can be therefore regarded as molecular tweezers.[4] ^{1}H NMR spectroscopy has been used to study the magnitude of the interaction of complexes **2** with TCBN. The calculated association constant (K_a) shows that the adduct **2a**-TCNB is thermodynamically more stable than those with complexes **2b** and **2c**.

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P36

Impact of electronic and steric tuning of the ligand structures on the generation of Fe(IV)O complexes

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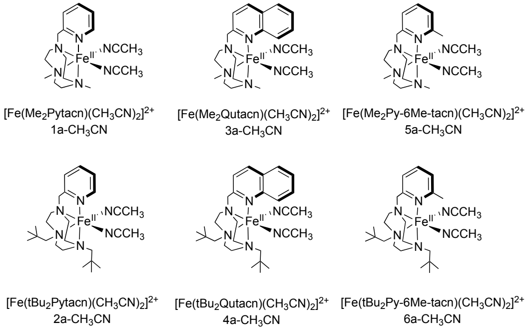
The vast majority of non-heme iron oxygenases enzymes characterized to date contain a cis-labile binding sites and because of this synthetic iron(IV)-oxo complexes based on tripodal tetradentate ligands are specially relevant as biomimetic models. However, they have been proved to be extremely less stable then their pentadentate counterparts; thus rendering their study more difficult. Indeed, most of the reported studies have been performed using pentadentate N_5 ligands (N_4Py) or equatorial tetradentate N_4 ligands, with two labile sites in a trans configuration (tmc).[1]

Recently, the preparation of oxo-Fe(IV) species bearing the tripodal tetradentate ligand 1-(2'-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane (Pytacn) was reported by Costas et al.[2,3] The $[Fe^{IV}(O)(Pytacn)(NCMe)]^{2+}$ complex could be isolated and exhibits a remarkable stability at room temperature with a half-life time of 2.2 h at 15 ºC.[3]

Now, a family of tetradentate ligands, which contains a functionalized triazacyclononane ring with distinctive electronic and steric properties, has been prepared and the corresponding Fe(II) complexes synthetized (Scheme 1), to be used as precursors to generate Fe(IV)O species in situ.

The introduction of bulky terbuthyl groups and the substitution of the pyridine ligand with a quinoline are aimed at evaluating putative electronic and steric effects on the generation of Fe(IV)O intermediates and on the reactivity of these species.



$[Fe(Me_2Pytacn)(CH_3CN)_2]^{2+}$
1a-CH_3CN

$[Fe(Me_2Qutacn)(CH_3CN)_2]^{2+}$
3a-CH_3CN

$[Fe(Me_2Py\text{-}6Me\text{-}tacn)(CH_3CN)_2]^{2+}$
5a-CH_3CN

$[Fe(tBu_2Pytacn)(CH_3CN)_2]^{2+}$
2a-CH_3CN

$[Fe(tBu_2Qutacn)(CH_3CN)_2]^{2+}$
4a-CH_3CN

$[Fe(tBu_2Py\text{-}6Me\text{-}tacn)(CH_3CN)_2]^{2+}$
6a-CH_3CN

Scheme 1. Structure of the Fe(II) precursor complexes used in the present study.

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P37

Highly Efficient and Selective Hydrogenation of Aldehydes: A Well-Defined Fe(II) Catalyst Exhibits Noble Metal Activity

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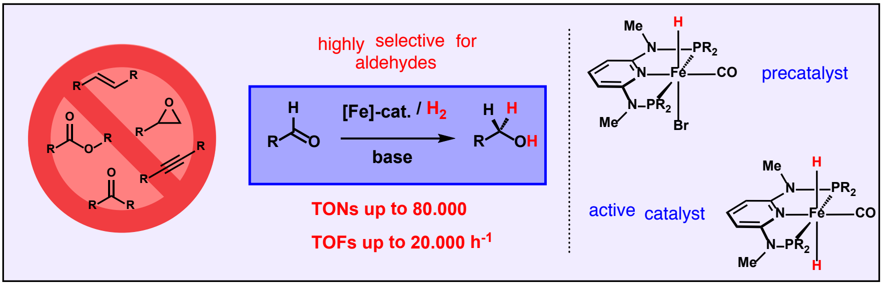
The synthesis and application of [Fe(PNP^{Me}-*i*Pr)(CO)(H)(Br)] and [Fe(PNP^{Me}-*i*Pr)(H)$_2$(CO)] as catalysts for the homogeneous hydrogenation of aldehydes is described. These systems were found to be the most efficient catalysts for this process reported to date and constitutes a rare example of a catalytic process which allows for the selective reduction of aldehydes in presence of ketones and other reducible functionalities. In some cases, TONs and TOFs of up to 80000 and 20000 h^{-1}, respectively, were reached. Based on stoichiometric experiment and computational studies, a mechanism which proceeds via a trans-dihydride intermediate is proposed. The structure of the hydride complexes was also confirmed by X-ray crystallography.



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P38

Post-polimerization functionalization of va-polynorbornenes via palladium-catalyzed cross coupling reactions: buchwald-hartwig amination and suzuki reactions.

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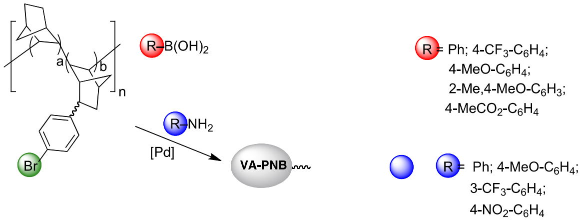
Vinylic addition polymerization of norbornene (VA-PNB) leads to an aliphatic backbone where the bicyclic structural unit of the monomer is intact. This leads to a robust material suitable as support of reagents, functional groups that carry out a specific property, or catalysts [1]. The attachment of a functional group to VA-PNBs is not a simple task since the vinylic addition polymerization of functionalized norbornenes is a difficult reaction and most catalytic systems fail to do so. We devised a different route to synthesize these materials by direct vinylic polymerization of bromoalkylnorbornenes followed by reaction with nucleophiles [2]. Here, we report the synthesis of bromoaryl VA-PNBs and a new route for the subsequent functionalization of these polymers using palladium-catalyzed cross coupling reactions.

The bromoaryl VA-PNBs were prepared 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 the polymers as well as Buchwald-Hartwig amination reactions to give the substituted diaryl or arylamino VA-PNBs. In all cases the bromo substitution ranges from 75 to 100%. The first step in the catalytic cycle, the oxidative addition of the polymeric bromoaryl substituents to palladium, has been demonstrated and pendant Pd-aryl complexes on the VA-PNBs have been prepared and characterized. This work shows that Pd-catalyzed couplings can be applied efficiently to the functionalization of polymers of interest.



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P39

New chelating diphosphines. Synthesis and applications in Rh-catalysed hydroformylation

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We have recently developed the synthesis of a new family of triarylphosphines containing both trifluoromethyl and carboxylic acid groups [1,2]. These ligands were prepared by hydrolysis of the trifluoromethyl group using fuming sulphuric acid and boric acid (figure 1). Although the hydrolysis of trifluoromethylbenzene was reported long time ago, [3] this strategy was never applied to the synthesis of phosphines, and it offers an alternative method for the preparation of carboxylic aryl phosphines [4].

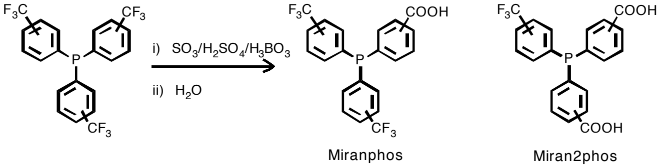

Figure 1. General synthesis of carboxylated triarylphosphines. Miranphos and Miran2phos family

Herein, we present an application of the Miranphos type ligands [5], obtained from the above mentioned procedure. The carboxylic acid moiety of the ligands has been used to synthesize new chelating diphosphines with a diamide backbone (figure 2). These new diphosphine ligands have been used in the rhodium-catalysed hydroformylation of 1-octene showing good linear to branched ratios. In order to understand this behaviour, different studies have been carried out, including molecular mechanics calculations of the bite angle and high pressure NMR and IR experiments.

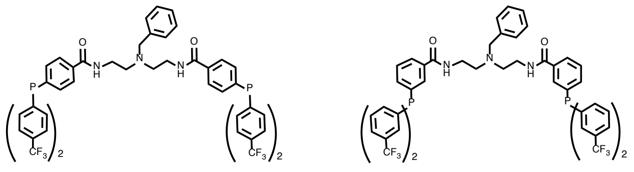

Figure 2. Diamide *p*- and *m*-Miranphos derivative diphosphines.

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P40

Síntesis y Reactividad de nuevos complejos vinilideno y alenilideno solubles en agua derivados del fragmento $\{CpRu(PPh_3)\}^+$ con derivados metilados de PTA (PTA = 1,3,5-triaza-7-fosfaadamantano)

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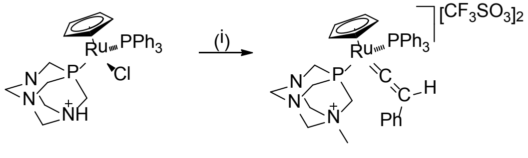
Los complejos carbeno insaturados, especialmente los complejos vinilideno y alenilideno, han demostrado su utilidad en la síntesis de compuestos orgánicos, tanto a nivel estequiométrico como a nivel catalítico [1]. A pesar del amplísimo número de complejos vinilideno de rutenio sintetizados, existen pocos ejemplos de vinilidenos solubles en agua. Estos, han mostrado su eficiencia como catalizadores en bifase en procesos como por ejemplo reacciones de metátesis de olefinas cíclicas (ROM) o isomerización de enoles [2]. Aún más escasos son los ejemplos de complejos alenilideno solubles en agua, alguno de ellos sintetizados por nuestro grupo de investigación [3]. En los últimos tiempos, uno de los puntos de interés de nuestro grupo de investigación ha sido la obtención de complejos semisandwich de Ru(II) conteniendo ligandos derivados de 1,3,5-triaza-7-fosfaadamantano [4]. Los complejos sintetizados pueden, en presencia de un abstractor de haluros y en disolventes polares, disociar el ligando cloruro permitiendo la reacción con 1-alquinos y alquinoles para dar finalmente los vinilidenos y alenilidenos deseados. En esta comunicación se presenta la síntesis, caracterización y reactividad de nuevos derivados vinilideno y alenilideno solubles en agua conteniendo el fragmento $\{CpRuCl(PPh_3)\}^+$ y derivados metilados de PTA.



(i) $^{+}$Ag[CF$_3$SO$_3$]’ $^{+}$ PhCCH’ $^{-}$AgCl

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P41

Cobalt Complexes Mediating Photo- and Electrocatalytic Reduction Reactions

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Currently, one of the most appealing research areas is the discovery and study of new photo- and electrochemical catalytic transformations based on earth-abundant elements.[1] In this regard, we have developed fast and efficient molecular complexes for the reduction of water to hydrogen, ketones, aldehyde and olefins.[2] Despite the fast development of the field, the mechanistic comprehension and the key structural factors of the activity of homogeneous catalysts is not entirely understood.

With this aim, we have developed robust and modular homogeneous catalytic systems in which the electronic and structural properties can be easily tuned. Here, we present a new family of well-defined catalysts for water reduction based on cobalt with robust tetra- and pentadentate ligands. Electrocatalytic studies show high currents and low overpotentials (>150 mV). More importantly, mechanistic studies suggest a proton-couple electron-transfer (PCET) process as the key feature that enables this excellent reactivity. The activity can be easily modulated and improved by tuning the electronic properties of the ligand. Under optimized conditions, more than 8500 catalytic cycles per catalyst (TON) and 55000 TON/h^{-1} were obtained under light-driven conditions. Dynamic Light Scattering (DLS), Nanoparticle Tracking Analysis (NTA) and Hg poisoning studies discarded nanoparticles as active catalytic species. By a combination of experimental and computational studies, we will discuss the mechanistic insights and their implications in the high TOF observed.

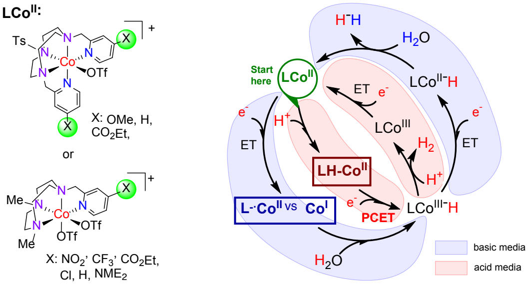

Figure 1. General scheme for the reduction of water to hydrogen.

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P42

Bioactive amino acid and peptide gold complexes

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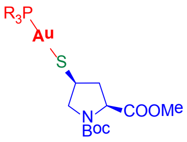
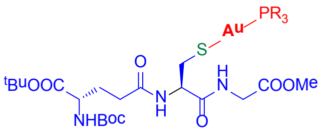
Gold compounds have been traditionally used in medicine, and some gold(I) drugs, like auranofin, are being employed clinically in the treatment of rheumatoid arthritis since last century. However, in the last decades gold complexes have attracted great attention because their excellent anticancer properties in vitro and in vivo, superior in many cases to cisplatin. Consequently, a large number of gold(I) complexes bearing several type of ligands such as thiolates (auranofin analogues), phosphines or carbenes, among others, have been reported [1]. Amino acids and peptides are two important classes of biomolecules which display a wide range of biological activities [2], and could also be employed as useful biocompatible ligands [3] to deliver the gold(I) atom to its biological target.

In this context, and with the aim of preparing more active and selective gold drugs, we have prepared diverse gold(I) complexes with amino acids and peptides. The introduction of these molecules in the complexes might decrease the undesired toxic side-effects (they are biocompatible ligands) and they could serve as good carriers to deliver the gold atom to the biological target.

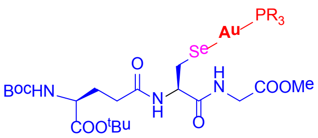
Several gold(I) bioconjugates with amino acid or peptide derivatives, as those shown in Figure 1, have been prepared. Structural modifications, as changes of the type of phosphine ligand or changes in the number of gold(I) atoms per molecule have been performed in order to establish a Structure-Activity Relationships (SAR) for this class of compounds. The cytotoxicity of the new complexes has been studied *in vitro* against several human tumor cell lines. All the complexes exhibit strong cytotoxicity with very low IC_{50} values.



4-mercaptoproline



glutation derivative



selenoglutation derivative

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Heterometallic [$AlMMe_3(OR)$] aluminates: study of their reactivity towards CO_2

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Group 13 elements attract wide attention not only because of their rich chemistry, but also due to the important applications that those elements exhibit in areas as diverse as organic synthesis, electronic materials, structural materials and catalysis.[1] In particular, aluminium derivatives play an essential role in a vast array of catalytic reactions. As an example, aluminoxanes acting as co-catalysts constitute a key part in the Ziegler-Natta olefin polymerization processes, being one of the more important activators in industrial processes.[2] As well, aluminium heterometallic compounds are appealing species, as the joint effect of two different metals in the same compound frequently leads to improved catalytic properties, especially when connected by an oxygen atom.[3]

One of our research interest is focused on the study of new heterometallic *ate* species containing aluminium and alkali metals.[4] We are interested in preparing derivatives with functionalized aryloxide groups. In this particular study phenols with functional groups placed in both *ortho* positions were chosen as ligand precursors. The reaction of alkali metal phenolates and $(AlMe_3)_2$ allowed us to prepare heterometallic derivatives where the $AlMe_3$ moieties remained intact coordinated to the alkali metal by the oxygen atom of the phenolate (see Figure 1). These species have a very interesting reactivity in activation reactions of C-H bonds and small molecules such as CO_2.

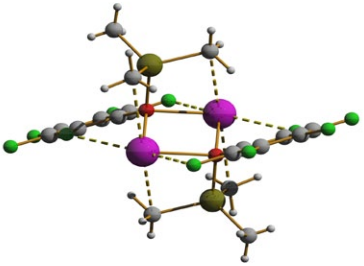

Figure 1

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P44

Novel PNP-pincer based Mn(I) catalysts – Selective hydrogenation of aldehydes under mild, basefree conditions

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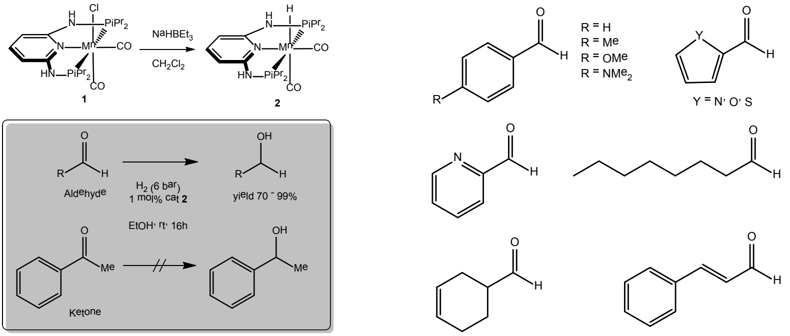
In recent years, pincer complexes of non precious metals have shown numerous applications in various catalytic reactions. Yet, the performance of some examples is comparable to those of noble metals. Especially, elements of the 1st row transition metals witness a rising focus throughout this research area. However, little case studies of manganese catalysts in low oxidation states are reported so far [1-2]. A new type of Mn(I) complexes based on a PNP pincer ligand system have been successfully applied for hydrogenation of aldehydes. Over a spectrum of a dozen of substrates, the yield of the corresponding alcohols ranged from 70 to 99%. Also a high degree of tolerance to functional groups was shown throughout the substrate scope.



Herein we report on the synthesis and catalytic activity of new Mn(I) PNP pincer complexes, based on the 2,6-diaminopyridine scaffold. The catalysts 2 shows very good results for a variety of substrates at low catalyst loadings (1 mol%) even under mild conditions. Moreover, the hydrogenation was highly selective for aldehydes, since conjugated double bonds and ketones remained untouched.

In the present work we also keep the importance of mechanistic studies in mind, so that theoretical calculations support the clarification of the proposed mechanism.

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P45

C-H bond oxidation reactions catalyzed by bioinspired manganese complexes

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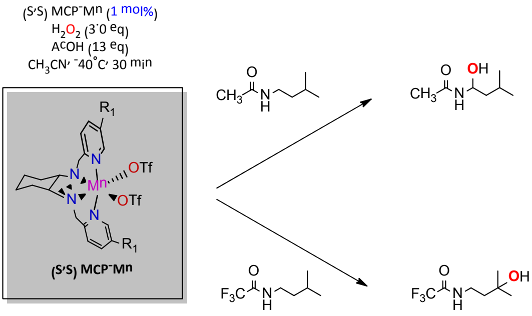
The selective functionalization of aliphatic C-H bonds represent one of the main challenges of modern synthetic organic chemistry and accordingly increasing efforts have being devoted towards this research goal. Oxidation of C-H bonds mediated by transition metal complexes are fundamental steps in fine and industrial chemistry, and in many biomedical trasformations. The factors that govern selectivity in these reactions have been actively pursued and identified[1]. In most cases C-H site selectivity is dictated by the innate properties of C-H bonds, irrespective of the nature of the oxidant. Inspired by oxidations taking place at oxygenases, the combination of manganese-based catalysts and hydrogen peroxide is an attractive approach for developing oxidation methods because of availability, low cost and low toxicity considerations[2]. Recently, our group reported that the combination of bulky and chiral nature of the tris-(isopropyl)silyl (tips) groups on the pyridine of Fe-$(OTf)_2$^{TIPS}(MCP) complex, led the oxidation of alkyl C-H bonds with remarkable regioselectivity[3]. The present work shows the use of amides as protecting groups of aliphatic amines to achieve C-H bond oxidation reactions with aqueous H_2O_2 using bioinspired manganese catalysts. In particular we propose that the nature of the amide play a key role in the regioselectivity of the reactions.



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P46

Heterogenization of new N- Heterocyclic Carbene ligands with Pyrene tags for the Production of Fine Chemical using Carbon Dioxide as a Reagent

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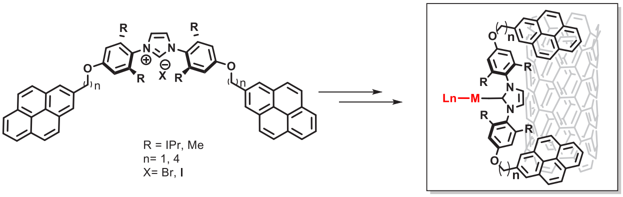
One of the current aims in Catalysis is to combine the advantageous of Homogeneous and Heterogeneous catalysis.[1] Tremendous research efforts are continuously directed towards the development of new systems that merge the high selectivity and activity observed in Homogeneous Catalysis and the recyclability that offers Heterogeneous catalysis.[2] One powerful approach to overcome this challenge is to immobilize homogeneous catalyst on a solid support. The application of these immobilized homogeneous catalysts in conjunction with continuous flow techniques could represent an efficient synthetic methodology to address practical application in Chemical and Pharmaceutical industries.[3]

The immobilization of Homogeneous Catalyst has been achieved via covalent attachment onto solid supports.[1] However, this approach usually required additional synthetic manipulations and significant structural perturbations of the parent catalysts skeletons.[4] As an alternative, non-covalent interactions appear as an ideal strategy to obtain supported catalyst without chemical modifications of the homogeneous catalyst or the solid support.[5]

Herein we report the synthesis and characterization of new pyrene tagged N-Heterocyclic Carbenes ligands and their coordination to metal fragments. The Heterogenization of these metal complexes is performed using carbon supports through π-π stacking interactions.[5] The catalytic performance and recycling of these new hybrid materials have been studied in the production of fine chemical using CO_2.



Scheme 1. A) Functionalized NHC to be used for Heterogenization onto Carbon materials.

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P47

Design of novel low cost and reusable heterogeneous Pd nanocatalyst

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Recently, the polymer and fine chemicals industries focused much interest in the selective hydrogenation of alkynes since the alkenes produced by steam reforming contain some alkynes impurities that poisoned the subsequent polymerization processes. The preferred option to overcome this issue is the catalytic selective conversion of these impurities into alkene useful product.[1]

Several transition metals have been reported for this process in which the main issues are the alkene over-hydrogenation and alkyne oligomerisation.[2] Among these metals, Pd has been identified as the most effective metal in terms of activity and selectivity.

In this context, the application of PdNPs as catalysts enables a maximization of the available metal surface area and consequently enhance the catalyst productivity. To date, most heterogeneous catalysts are used in fine powders forms, which make them difficult to handle.[3] Alternative supports such as textile, paper and cotton were contemplated. Among them, conventional filter paper is of interest for catalyst immobilization since it is cost-effective, biodegradable, accessible and flexible.

In the present work, we describe the preparation and characterization of a novel low cost and reusable heteregeneous catalyst by painting a commercial filter paper with a Pd@CNT ink. This catalyst provided excellent results in the selective hydrogenation of alkynes and alkynols and could be recycled at least 5 times without loss of activity and selectivity.

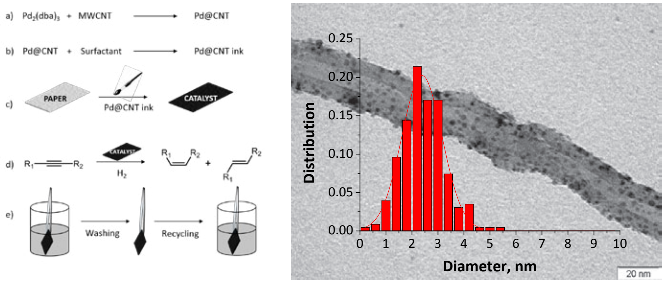

Figure 1. General approach for the preparation of the paper-based nanocatalyst and TEM micrograph of Pd@CNT

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P48

Gold(I) mediated thiourea organocatalyst activation: A synergic effect for asymmetric catalysis

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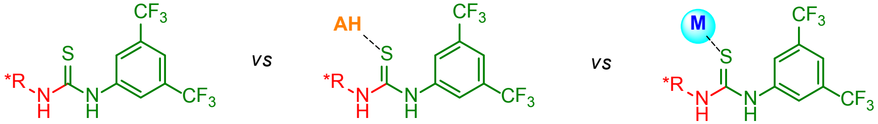
The promising results of the influence of metal assisted thiourea organocatalysts in the asymmetric Friedel-Crafts alkylation of indoles with nitroalkenes are described. The final 3-substituted indole derivatives were obtained with good results because of the cooperative effects between the chiral thiourea and the [AuL$_2$]OTf complex. It is observed that the synergic effect between both species is higher than the effect promoted by each one separately. The higher reactivity and selectivity found in this reaction is attributed to a pioneering gold(I) activation of thiourea catalysts, affording a more acidic and rigid catalytic complex than that provided by the thiourea alone [1-3]. Furthermore, the use of the gold-thiourea organocatalyst allows reducing the catalyst loading to 1-3%. Further modulations of the nature of the metal and the ligands could improve the results [4].



thiourea **I** **thiourea-HA** **II** **thiourea-Metal** **III**

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New development on the chemistry of Group Six PCP Pincer Complexes

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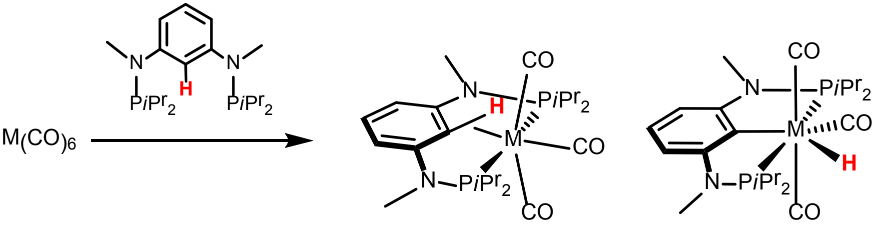
One of the main goals of organometallic and coordination chemistry is the development of a well-designed ligand system that modifies in a controlled manner the properties of the metal centers. During the last decade, pincer ligands are prominent among the ligand systems due to their high stability, activity and variability. Furthermore, numerous applications in various areas of chemistry, including catalysis, have been found for this class of tridentate ligands. Focusing on pincer ligands featuring phosphines as donor groups, we begun to investigate the use of amines as spacers between the aromatic ring and the phosphine moieties. This has resulted in the preparation of a range of new PCP pincer complexes based on the 1,3-diaminobenzene scaffold [1-3].

In the present study, we are focusing on chemistry originating from various group 6 metal complexes. Among the new complexes achieved and studied are seven-coordinate hydrido carbonyl complexes of the type [W(k^3-*P,C,P*-PCP$^{\mathrm{Me}}$*i*Pr)(CO)$_3$H] and six-coordinate complexes of the type [M(k^3-*P,CH,P*-PCP$^{\mathrm{Me}}$*i*Pr)(CO)$_3$] (M = Cr, Mo) featuring a C$_{\mathrm{aryl}}$-H agostic interaction (Scheme 1).



1, M = Cr
2, M = Mo

3, M = W

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P50

Nanoconcentrator: pre-organization of catalysts and substrates in nanospheres

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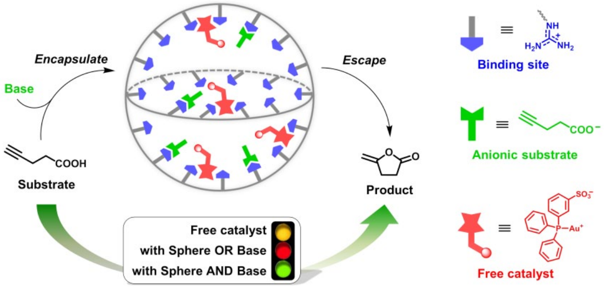
Advances in the field of transition metal catalysis have been dominated by ligand design strategies in which catalyst’s properties are controlled by the ligands attached to the metal center. The design of well-defined second coordination spheres around transition metal complexes provides a novel manner of controlling those properties. A recent example of such a strategy comprises the pre-organization of 24 gold-complexes in a nanosphere leading to extreme high local concentration of gold (1.1 M), resulting in more efficient catalytic transformations.[1] Along these lines, we now report a system that is able to co-encapsulate the catalyst and substrates within a confined space, leading to high local catalyst/substrate concentrations. It consists of a nanosphere endohedrally functionalized with 24 guanidinium moieties, which by means of multiple hydrogen bond interactions strongly binds the catalyst inside the sphere. The remaining guanidinium functionalities can be used to preorganize the substrates by weaker interactions. This strategy leads to improved reaction rates in the gold catalyzed cyclization of acetylenic acid to enol lactone (Scheme 1).[2]



Scheme 1

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Modified peppsi-type palladium catalysts, synthesis, reactivity and catalytic activity in the coupling reactions

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Palladium catalysed cross-coupling reactions belong to the most important methods for construction of single carbon-carbon bonds, in organic chemistry. The significance of the reactions has been recognised by the Nobel Prize in Chemistry awarded in 2010 to Professors Heck, Negishi and Suzuki for ”palladium catalysed co-coupling reactions in organic synthesis”. So far, the studies on cross-coupling reactions have been concentrated on obtaining highly efficient and highly selective processes and on the extension of the range of reagents. A number of precursors being complexes or salts of palladium(II) or palladium(0) have been used as catalysts. The complexes have been often used in the presence of certain ligands, co-catalysts or bases. [1] A group of relatively easy to synthesise complexes showing high stability towards air, humidity and a number of functional groups was described in 2005. [2] They show high catalytic activity in a number of coupling processes often taking place in mild conditions and with no need to use co-catalysts. [3] Although classical PEPPSI complexes contain in their structure NHC donors (imidazol-2-ylidenes or 1,2,4-triazol-5-ylidenes), their mesoionic carbene (MIC) counterparts 1,2,3-triazol-5-ylidenes have received a lot of attention in the last few years. [4] 1,2,3-triazol-5-ylidenes have been postulated as being even better ligands in catalysis because of their strongly donating mesoionic compared with their classical N-heterocyclic carbene (NHC) counterparts of the imidazole-2-ylidene type. A number of important reactions have been catalyzed by transition-metal complexes bearing 1,2,3-triazol-5-ylidenes including the catalytic transfer hydrogenation, cross-coupling and cyclization. In addition, substituted 1,2,3-triazoles can easily be synthesized via the 1,3-dipolar cycloaddition reaction of an azide to an alkyne (click reaction). [4] In this presentation, we will demonstrate the results of research focusing on the synthesis, structure, and reactivity of new PEPPSI-type complexes: palladium (II) 1,2,3-triazol-5-ylidene complexes and $Pd(MIC)_2X_2$ (X = halide) (Figure 1). High catalytic activity of the complexes observed in the coupling reactions of Suzuki, Heck and free-copper reaction of Sonogashira will be further discussed. It will be proved that a simple and efficient synthesis method of the palladium complex was developed. The complex was fully characterized using X-ray crystallography, mass spectrometry, NMR spectroscopy (^{1}H, ^{13}C) and its high catalytic activity will be demonstrated opening the possibility for potential application.

Acknowledgements

Financial support from the National Science Centre (Poland), (UMO-2013/11/N/ST5/01612) is gratefully acknowledged.

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P52

Nickel-Cornered Molecular Cages with Bis-NHC Bridging Ligands

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Metal-assembled structures have shown an increasing interest during the last decade, due to the enormous number of applications [1] that these materials [2] may introduce. The basis for the construction of metal-assemblies are multitopic ligands with two or more binding domains separated by spacers, which by combination with metals may form structures with different shapes and sizes. During the last five years our research group has developed a series of rigid bis-N-heterocyclic carbene (NHC) ligands [3] connected by polyaromatic hidrocarbons. We thought that these ligands should fulfill the requirements for the preparation of metal-cornered species by metal directed self-assembly. Inspired by the work by Hahn and co-workers [4], we now report the preparation of a series of nickel-cornered molecular cages based on three types of bis-NHC ligands with rigid polyaromatic linkers (Figure 1). The structural, spectroscopic and electronic properties of these species have been evaluated, together with their supramolecular interactions with a series of molecular guests.

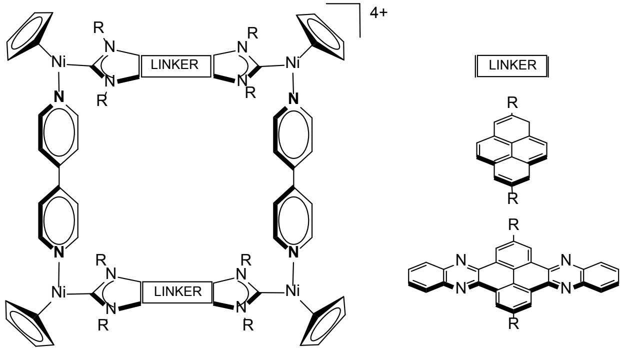

Figure 1

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P53

Cyclopalladated (*E*)-*N*-([1,1’-biphenyl]-2-yl)-1-phenylmethanimines: synthesis and anticancer, antibacterial and antioxidant activities

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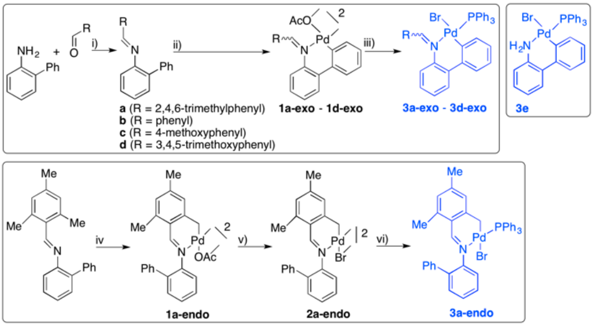
Compounds **3** were obtained according to procedures given in Scheme 1 and were characterized by IR, ^{1}H NMR, ^{31}P{^{1}H}NMR and ESI-(+) mass spectrometry. Compound **3e** was prepared as previously reported [1]. The crystal structures of imine **d** and compound **3c-exo** were also determined by single X-ray diffraction analysis. Some compounds **3** presented *in vitro* a similar anticancer activity than that of *cisplatin* and an antibacterial activity similar to that of the commercial antibiotics Cefexime and Ciprofloxacin. In addition, some compounds **3** presented also a relative high antioxidant activity in realtion to ascorbic acid.



Scheme 1: i) EtOH, reflux, 4 h, ii) Pd(OAc)$_2$, dichloromethane, 24 h, rt, iii) LiBr, PPh$_3$, acetone, rt, 1 h, iv) Pd(OAc)$_2$, acetic acid, reflux, 4 h, v) LiBr, acetone, rt, 1 h, vi) PPh$_3$, acetone, rt, 1 h.

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Novel C_2 P-stereogenic ligands with a hydrazine backbone

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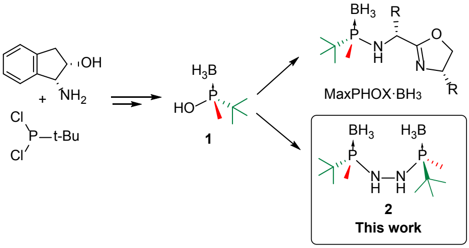
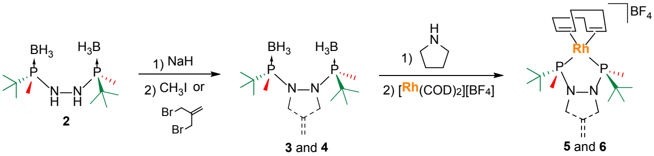
The development of new chiral ligands is of key importance in asymmetric catalysis in order to obtain optically pure compounds.[1] Our group has recently reported a procedure to synthetize valuable P-stereogenic synthons using 1,2-cis-aminoindanol as a chiral auxiliary.[2,3] One of the new synthons, the borane-protected *tert*-butylmethylphosphinous acid (**1**), has been employed in the synthesis of MaxPHOX·BH_3, a very efficient ligand in asymmetric hydrogenation.[4] Using a similar procedure the borane-protected P-stereogenic bisphosphine (**2**) was synthetized starting from **1** using hydrazine in a one-step synthesis (Scheme 1).



Scheme 1. Preparation of the synthon 1 and its transformation into bidentate ligands.

The N,N'-alkylation of **2** was achieved using methyl iodide (**3**) or 3-bromo-2-bromomethyl-1-propene (**4**) and yielding, in both cases, two different atropoisomers in slow exchange. The deprotection with pyrrolidine followed by reaction with $[Rh(COD)_2][BF_4]$ gave two new cationic Rh(I) complexes containing C_2 P-stereogenic bisphosphine ligands with a hydrazine backbone (**5** and **6**) (Scheme 2). In the present communication we will describe the synthesis of the ligands, their coordination to metals as well as the catalytic activity of the new complexes.



Scheme 2. Synthesis of new cationic Rh(I) complexes containing C_2 P-stereogenic ligands.

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P55

Hydroamination of Terminal Alkynes by *cis*-[W(CO)$_4$(pip)$_2$]: A Convenient Tool for New Enamines Synthesis

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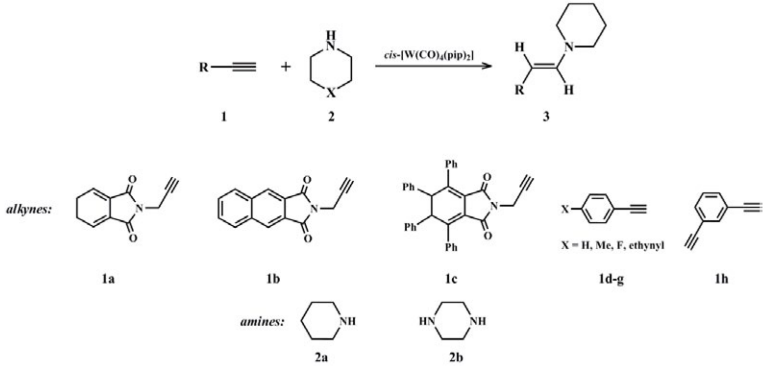
Alkynes are widely available reagents and the catalytic addition of the N−H bond of amines to the triple bond of alkynes, RC≡CH, is of great significance in the synthesis of enamines and the other nitrogen containing compounds. This atom-economical process is mostly catalyzed by complexes based on such metals as Rh, Ru, Pd, Au, Ag, lanthanides or actinides [1].

Recently, we found the highly selective and efficient hydroamination of alkynes with cyclic secondary amines in the presence of *cis*-[W(CO)$_4$(pip)$_2$] [2]. The remarkable results inspired us to test the W(0) complex activity in hydroamination of more complex alkynes; acetylene dicarboxyimide (**1a**-**c**) and phenylacetylene derivatives (**1d**-**h**) with amines (**2a**-**b**) (Scheme 1). Synthesis of *E*-vinyl (**3**) amines were carried out under relatively mild conditions.

All compounds were identified by GC-MS and isolated with high yield. Their molecular structures were revealed in solution by one and two-dimensional ^{1}H and ^{13}C NMR spectroscopy.



Scheme 1

Acknowledgements: This research was supported by a grant from the National Science Centre, Poland (No. 2013/09/N/ST5/00402).

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Pd-catalyzed telomerization of 1,3-butadiene with acetic acid: the role of imidazolium acetate ionic liquid and new trifluoromethylated sulfonated triarylphosphines

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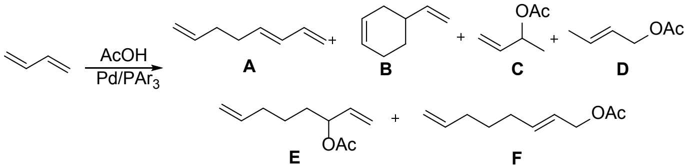
The telomerization of 1,3-butadiene with acetic acid yields branched (E) and linear (F) acetoxyoctadienes, as illustrated in Scheme 1. These unsaturated esters can be used as starting materials for the synthesis of many artificial and natural products. [3] The reaction also leads to the acetoxybutenes (C) and (D), resulting from the catalyzed reaction of the diene and the nucleophile, as well as the butadiene dimers (A) and (B).

A conventional scheme of this reaction employs the catalyst system $[Pd(OAc)_2]_3$/PPh_3/base, eventually leading to very high catalytic activity. [4] The addition of a base in this reaction have a beneficial effect, since it leads to the formation of the acetate, increasing the nucleophilicity of AcOH. [5] Sodium or potassium acetate is generally added as the base, but its role could be taken by an imidazolium ionic liquid (IL) containing acetate anions, which could act, besides of as cocatalyst, as solvent and stabilizer for the catalytic system itself.

We report here the telomerization of 1,3-butadiene by $[Pd(OAc)_2]_3$ in an imidazolium acetate IL, using a variety of new trifluoromethylated sulfonated triarylphosphines recently disclosed by us. [6] Under optimized conditions, a high TON of 14600 with 78% of selectivity to the linear telomere was obtained. [7]



Scheme 1

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Efficient Tungsten(0)-Catalyzed Hydroamination of Terminal Alkynes

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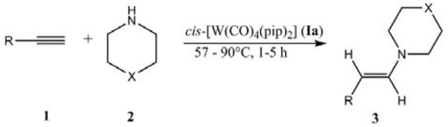
Alkynes are widely available reagents and the catalytic addition of the N−H bond of amines to the triple bond of alkynes, RC≡CH, is of great significance in the synthesis of enamines and the other nitrogen containing compounds. This atom-economical process is mostly catalyzed by complexes based on such metals as Rh, Ru, Pd, Au, Ag, lanthanides or actinides [1-3].

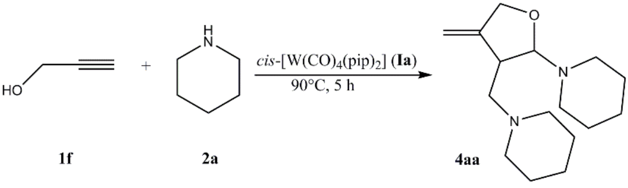
We found the highly selective and efficient hydroamination of alkynes (**1**) with cyclic secondary amines (**2**) in the presence of a tungsten(0) piperidine complex *cis*-[W(CO)$_4$(pip)$_2$] (**Ia**) (Scheme 1) [4]. Synthesis of *E*-vinyl (**3**) amines were carried out under relatively mild conditions, without solvent, in good yield.



R = Ph **1a,** C_6H_4-4-Me **1b,** C_6H_4-4-F **1c,** n-C_4H_9 **1d,** CH_2OMe **1e,** CH_2OH **1f,** CH(OH)Me**1g,** CH_2CH_2OH **1h,** $C(OH)Me_2$ **1i,** C_6H_4-4-NO_2 **1j,** $CH(OEt)_2$ **1k,** C_4H_3S **1l.**
X = CH_2 **2a,** - **2b,** O **2c,** NMe **2d,** NH **2e,** CHMe **2f,** CH_2-2-Me **2g,** CH_2-3-Me **2h,** CH_2-4-Me **2i,** CH_2-2,6-Me **2j,** CH_2-3,5-Me 2**k.**

Scheme 1

As an extension of our continuous study on hydroamination of triple CºC bond, we have now found that in the presence of tungsten(0) catalyst the hydroamination of prop-2-yn-1-ol (**1f**) was accompanied by the hydroalkoxylation/cyclization and elimination of water molecule processes, leading to the construction of tetrahydrofuran ring (Scheme 2).



Scheme 2

All compounds were identified by GC-MS and isolated with high yield. Their molecular structures were revealed in solution by one and two-dimensional ^{1}H and ^{13}C NMR spectroscopy.

Acknowledgements: This research was supported by a grant from the National Science Centre, Poland (No. 2013/09/N/ST5/00402).

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P58

Platinum σ-SiH complexes. Reactivity studies and CO_2 hydrosilation

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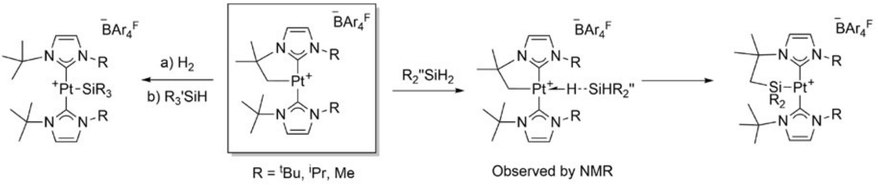
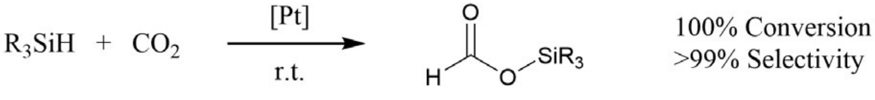
Silane σ-complexes have been proposed as intermediates in a high number of catalytic processes.[1] Although coordination of the silane to the metal center can take place through η^1, η^2-SiH interaction, the first one is very rare, with only one example of an isolated iridium complex.[2] In spite of the relevant role of platinum complexes in hydrosilation reactions, no examples of σ-SiH platinum species are known. The formation of a silane σ-complex renders the silicon atom more electrophilic and therefore susceptible of nucleophilic attack, particularly in the η^1-SiH coordination mode. This polarization can be leveraged in the activation of small molecules such as CO_2, whose stability and inertness make it challenging to transform. Indeed, selective hydrosilation of carbon dioxide is still difficult nowadays because mixtures of products are often obtained, or the reduction process cannot be stopped at any intermediate.[3] In this work, the synthesis of platinum(II) silane σ-complexes stabilized by N-heterocyclic carbenes (NHCs) (with a preferred η1-SiH coordination mode according to DFT calculations) will be described, as well as their reactivity and their role on the selective reduction of carbon dioxide to the formate stage.





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P59

Synthesis and dynamic behavior of chiral nno-scorpionate zinc initiators for the ring-opening polymerization of cyclic esters

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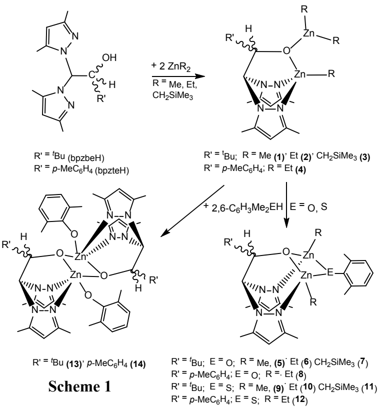

Scheme 1

The reaction of chiral alcohol-scorpionate compounds bpzbeH [bpzbeH = 1,1-bis(3,5-dimethylpyrazol-1-yl)-3,3-dimethyl-2-butanol] or bpzteH [bpzteH = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*para*-tolylethanol] with [ZnR_2] (R = Me, Et, CH_2SiMe_3) in a 1:2 molar ratio afforded the dinuclear chiral zinc alkyls [Zn(R)(κ^2-NNm-O)Zn(R)$_2$] (**1**–**4**) [κ^2-NNm-O = bpzbe, R = Me **1**, Et **2**, CH_2SiMe_3 **3**; bpzte, R = Et **4**]. Subsequent alcoholysis or thioalcoholysis reaction with ArEH (1 equiv; E = O, S; Ar = 2,6-$C_6H_3Me_2$) yielded the chiral dinuclear mixed alkyl-alryloxides/thioaryloxides [(ZnR)$_2$(κN:κN-m-O)(m-EAr)] (**5**–**12**) [κN:κN-m-O = bpzbe, E = O, R = Me **5**, Et **6**, CH_2SiMe_3 **7**; bpzte, E = O, R = Et **8**; bpzbe, E = S, R = Me **9**, Et **10**, CH_2SiMe_3 **11**; bpzte, E = S, R = Et **12**]. The alcoholysis reaction of the previously reported monoalkyls [Zn(Me)(κ^3-NNO)] or [Zn(R)(k-NNm-O)]$_2$ with ArOH (1 equiv, Ar = 2,6-$C_6H_3Me_2$) afforded the chiral aryloxides [Zn(OAr)(κ^2-NNm-O)]$_2$ (**13**–**14**) [κ^2-NNm-O = bpzbe **13**; bpzte **14**] (Scheme 1). The X-ray crystal structures of **3**, **5**, **6** and **14** confirmed a dinuclear structure in all cases, with the alkoxide of the heteroscorpionates in a μ-bridging mode between the Zn(II) centers. Variable-temperature NMR studies were carried out in order to study their dynamic behavior in solution.

Complexes **1**–**9** and **12** can act as single-component initiators for the ROP of *e*-CL and L-/*rac*-LA, and afforded materials with low molecular weights and narrow monomodal molecular weight distributions. MALDI-ToF mass spectra confirmed that for **5**–**8** the initiation occurred through nucleophilic attack by the alkoxide group, rather than the alkyl group, on the lactide monomer. Microstructural analysis of poly(*rac*-lactide) revealed that the mixed alkyl/aryloxide-substituted initiators exert a moderate level of heteroselectivity ($P_s = 0.66$) [1].

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Copolymerization of cyclic esters controlled by chiral nno-scorpionate zinc initiators

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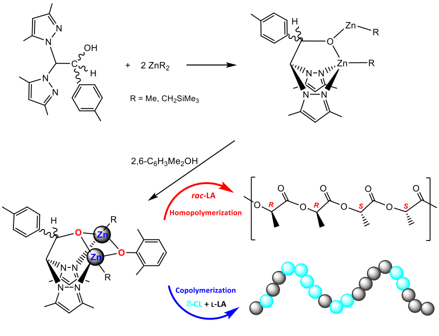

Scheme 1

Reaction of the chiral alcohol-scorpionate compound bpzteH [bpzteH = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*para*-tolylethanol] with [ZnR$_2$] (R = Me, CH$_2$SiMe$_3$) in a 1:2 molar ratio afforded the dinuclear chiral alkyl zinc complexes [Zn(R)(κ^2-NN*m*-O)Zn(R)$_2$] (**1**–**2**) [κ^2-NN*m*-O = bpzte, R = Me **1**, CH$_2$SiMe$_3$ **2**]. Subsequent alcoholysis reaction with ArOH (1 equiv; Ar = 2,6-C$_6$H$_3$Me$_2$) yielded the chiral dinuclear zinc complexes [(ZnR)$_2$(κN:κN-*m*-O)(*m*-OAr)] (**3**–**4**) [κN:κN-*m*-O = bpzte, R = Me **3**, CH$_2$SiMe$_3$ **4**] (Scheme 1). The X-ray crystal structures of **1** and **3** confirmed a dinuclear structure and the alkoxide of the heteroscorpionate ligands in a μ-bridging mode between the two Zn(II) centers.

Trisalkyl and alkyl-aryloxide-containing zinc complexes **1**–**4** can act as single-component initiators for the ring-opening homopolymerization of *e*-caprolactone and L-/*rac*-lactide. Microstructural analysis of poly(*rac*-lactide) revealed that the alkyl-aryloxide **3** exerts a moderate level of heteroselectivity (P_s = 0.68). More interestingly, initiators **3** and **4** also allowed the well-controlled random copolymerization of ε-CL and L-LA, as indicated by the values of the reactivity ratios of the two comonomers (r_{CL} = 1.15 and 0.92, and r_{LA} = 1.37 and 1.05, for **3** and **4**, respectively) and the average lengths of the caproyl and lactidyl sequences (L_{CL} ~ 2.0; L_{LA} ~ 2.5, for both initiators). In addition, the copolymers had monomer contents in close agreement with the composition of the initial monomer feed and the T_g of various copolymers produced by **3** vary in a linear fashion with the molar percentage of L-lactide [1].

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Allylic substitution reactions catalyzed by pd complexes with *P*-stereogenic, C_1-symmetric diphosphorus ligands

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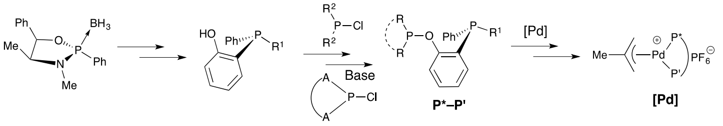
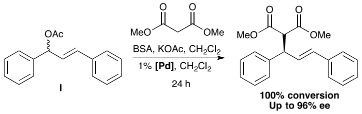
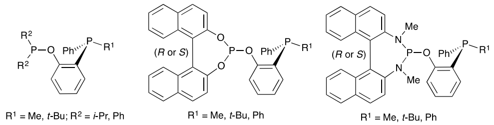
After decades of efforts, the synthesis of new chiral phosphorus ligands continues to be reported at full speed in the literature because they are indispensable in transition-metal asymmetric catalysis. At present all the sources of chirality are actively investigated with the aim to obtain new ligands that lead to improved catalytic results [1]. Despite all this effort, there still are certain types of ligands that remain relatively unexplored, such the *P*-stereogenic ligands [2] or the C_1-symmetric bidentate phosphorus ligands.

In order to contribute to unleash the potential of these ligands, in this contribution we present the synthesis of the uncommon C_1-diphosphorus ligands (**P*–P'**) containing a stereogenic phosphine moiety (**P***) and a phosphinite, phosphite or diamidophosphite moiety (**P'**). The ligands have been prepared by the condensation of an optically pure 2-hidroxyphenylphosphine, prepared by the Jugé-Stephan method [3], with an electrophilic chlorophosphorus precursor in the presence of base [4,5].



With this method, 14 ligands have been prepared and have been coordinated to $[Pd(h^3\text{-}C_4H_7)]$ moieties leading to the corresponding cationic Pd complexes, which have been characterized and used as precursors in asymmetric allylic alkylation and amination reactions.





The ligands were designed to contain one or two chiral elements so the effect of the absolute configurations on the catalysis outcome can be studied. For some of the ligands important *match*/*mistmatch* effects have been found in the enantioselectivity. The matched ligands have produced very high enantiomeric excesses in the alkylation of the model substrate **I**.

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C-F bond activation of fluorinated hydrocarbon CH_3F by actinide mono-cations: a theoretical prediction

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It is well known that the C-F bond in organic compounds is significantly stronger than the corresponding C-C and C-H bonds, and the activation of this bond by metallic mono-cations is a formidable task in organometallic chemistry [1]. Here, relativistic density functional theory (DFT/ZORA) calculations have been performed to investigate the reactivity of actinide mono-cations toward C-F bond activation of fluorinated hydrocarbon CH_3F; the potential energy surface corresponding to the reactions has been studied by means of LT (linear transit) and IRC (intrinsic reaction coordinate) calculations.

We found that the reaction mechanism of the Ac^+ and Pu^+ systems appears as a harpoon-like mechanism, revealing the presence of a transition state (TS) and involving an electron transfer from actinide cation to the fluorinated substrate (see Fig.1for Ac^+) . The other actinide elements (Th^+, Np^+, and U^+) show a slightly different reaction mechanism (insertion-elimination, see Fig.2).

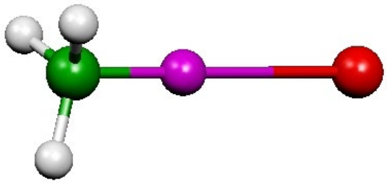

Fig.1. Transition state structure of $CH_3F + Ac^+ \rightarrow AcF^+ + CH_3$. reaction

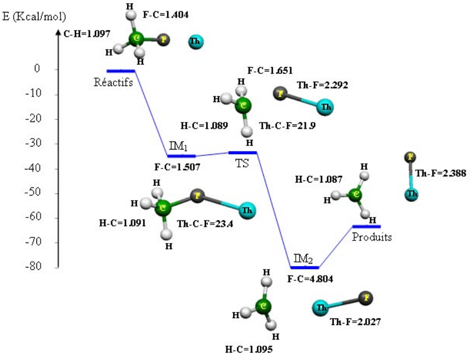

Fig.2. Potential energy surface profile of the $CH_3F + Th^+ \rightarrow ThF^+ + CH_3$. reaction

The crucial role orbital of the metal 5f-orbitals on the reactivity of the actinide mono-cations towards CH_3F is highlighted by the orbital analysis, excepted in the actinium case. Mulliken population analysis (MPA) reveals the major charge transfers and bonding interactions occurring during the reactions.

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Redox properties of mixed sandwich uranium (III) complexes: a relativistic dft study

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The structural and electronic properties of a series of uranium (III) mixed-sandwich complexes of the type [U(COT^{TIPS2})(Cp^{EMe4} = EC_4Me_4, E is N, P or As, and COT^{TIPS2} = $C_8H_6\{1,4\text{-Si}^i\text{Pr}_3\}$) have been explored using density functional theory (DFT) in the framework of the relativistic zeroth order regular approximation (ZORA). The solvent effects are taken into account using the COSMO (Conductor Screening Model) solvation model. A very good agreement has been achieved between the calculated geometrical parameters and the available experimental data [1].

The second step of our work is to study redox behavior of these new mixed sandwich uranium (III) complexes which allows us to estimate the ionization energy (during oxidation process). A very good liner correlation was found between the calculated ionization energies at ZORA/BP86/TZP level and the experimental half-wave oxidation potentials $E_{1/2}$ (see Fig. 1).

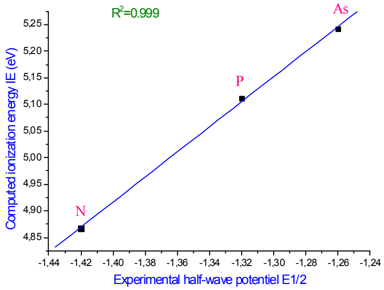

Fig.1. Correlation between computed *IE* and $E_{1/2}$

Our study brings to light the importance of spin-orbit coupling and solvent effect which must be taken into account in order to achieve the best agreement between theory and experiment. Also, the molecular orbital analysis underlines the important role played by the 5f orbitals of the central metal whereas the Mulliken population analysis has permitted us to show the principal charge transfers occurring in a series of molecular systems. An excellent correlation is found between the variations of the uranium Hirshfeld charges and the experimental oxydation potential, result similar to that obtained in previous study [2]. Finally, the Nalewajski-Mrozek bond indices have permitted us to explain well the bond distance variations following redox processes.

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Synthesis of New Water-Soluble Palladium(0) NHCs: Characterization and Study of their Behaviour in Aqueous Medium.

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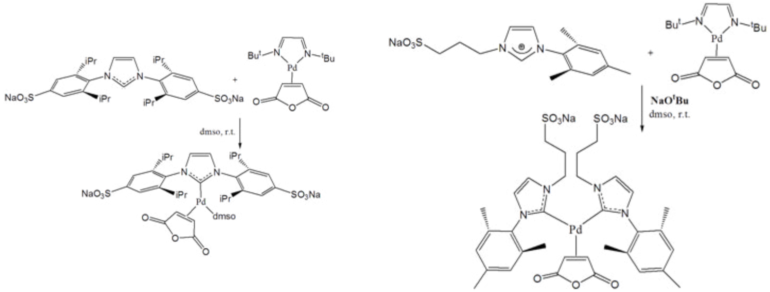
Conventionally, most of the laboratory and industrial syntheses were carried out in organic solvents due to the advantages that this media bring up, such as high solubility of a wide range of reagents. Unfortunately, most of these solvents present toxicity and flammability problems. Hence, during the last years, there has been an increasing interest in engaging aqueous media in organic syntheses.[1] However, there is little knowledge on the role of water in the reaction mechanisms in most of the cases. So, study of the behaviour of the organometallic complexes in aqueous media is of high concern.[2]

New water-soluble Pd(0) mono and bis NHCs complexes have been prepared, where NHC is an anionic sulfonated and sterically hindered N-heterocyclic carbene. A two-step synthetic route was employed for the mono NHC Pd(0) complex, which involves formation of the free carbene by direct deprotonation of the imidazolium salt with sodium *tert*-butoxide and direct reaction with the organometallic precursor. For the bis NHC Pd(0) complex a one-pot, one-step synthetic route was engaged. (Scheme 1)



Scheme 1. Synthesis of Pd(0) NHCs

The stability and chemical behaviour of these Pd(0) NHCs in aqueous solution was investigated, mainly by NMR. It has been seen that the Pd(0) bis-carbene is stable in water for prolonged periods of time, while the mono-carbene evolves to Pd(II) after 24h. Other surveys involve the study of the stability in acidic or basic aqueous media and the interaction with oxidizing and reducing agents.

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Methane C-H bond activation by actinide complexes: a relativistic dft investigation

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In order to bring an understanding of the reactivity of actinide complexes $(Cp^*)_2AnCH_3$ (An=Ac, Th, Pa, U, Np and Pu), leading to the methane C–H bond activation [1], a theoretical study based on the relativistic density functional theory (DFT) through the zero-order regular approximation [2] (ZORA), was carried out. These ZORA/DFT calculations were performed using the Amsterdam Density Functional (ADF2014.01) program package. In GGA approach, Becke an Perdew approximations are considered for exchange and correlation functionals respectively while the triple zeta plus one polarization function (TZP) basis sets were used. After having previously determined the optimized geometry of each complex which allow to know the nature of the bonds between the central metal and the ligands, the reactions $(Cp^*)_2AnCH_3+CH_4$ were explored by performing LT (linear transit) and IRC (intrinsec reaction cordinate) calculations. The first results obtained (energy profiles and activation energies) brougt to light the high reactivity of these complexes towards the activation of the methane C–H bond since the calculated activation energies are low, and show that the mechanism involved in these reactions is characterized by proton transfer between methane and methyl group of the complex (Figure 1).

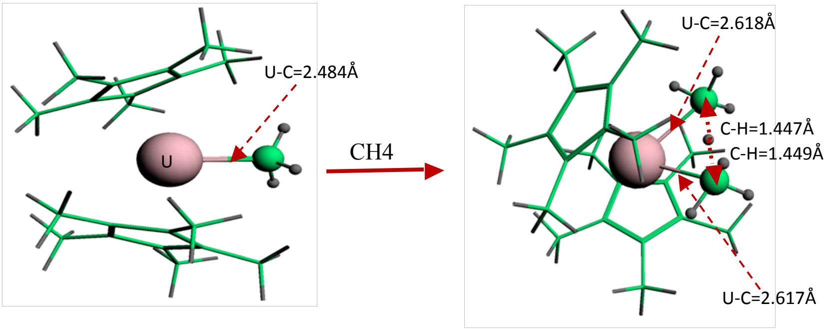

Figure 1. Optimized structures of the complex $(Cp^*)_2UCH_3$ and the transition state of $(Cp^*)_2UCH_3+CH_4$ reaction

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Theoretical investigation on insertion reaction of small molecules with uranium iv complexes

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This work refers to the theoretical study of the reactivity of uranium IV bisthiolate complexes $U(Cp^*)_2(SR)_2$ (R=Me, ^{i}Pr, Ph and ^{t}Bu) towards small molecules [1] (CS_2 and CO_2). This reactivity, experimentally observed on the complex $U(Cp^*)_2(S^tBu)_2$ reacting with CS_2 is achieved by the insertion of the CS_2 into U–S bond of this complex [2]. The theoretical approach used in this study is based on the relativistic density functional theory through the zero-order regular approximation (ZORA). These DFT/ZORA calculations were performed using the Amsterdam Density Functional ADF2014 program package. Previously, the ground state geometries of bisthiolate complexes have been determined in both gas phase and THF solvent. The molecular structures obtained by these calculations were found suitable to the experimental data. Then, the reactivity of these complexes was explored by performing linear transit (LT) calculations using the same DFT approach (ZORA/BP86/TZP). The results thus obtained highlight the insertion of CS_2 (and of CO_2) in the U–S bond of the $U(Cp^*)_2(SR)_2$ (R=Me, ^{i}Pr, Ph and ^{t}Bu), particularly in the case of the $U(Cp^*)_2(S^tBu)_2$ complex reacting with CS_2 where the molecular structure of the insertion product $U(Cp^*)_2(S^tBu)(S_2CS^tBu)$ predicted by these calculations (figure 1) agree well with that found in experiments.

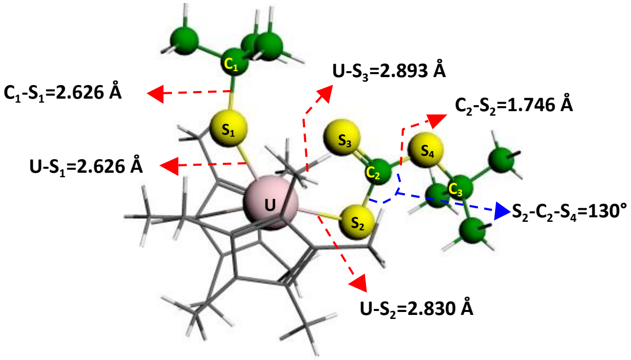

Figure 1. The insertion product $U(Cp^*)_2(S^tBu)(S_2CS^tBu)$

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Targeting C−H bonds in iridium complexes

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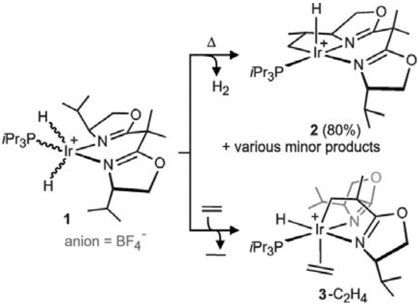
Iridium complexes have been extensively studied in the context of catalytic reactions that form or cleave C−H bonds [1]. The investigations pursuing mechanistic details of these reactions have frequently allowed the observation of iridium(III) hydride intermediates or resting states, but the possible evolution of these species within the catalytic cycles via higher or lower oxidation states often remains matter of discussion [2]. Aimed at contributing to this discussion, we investigated in further detail the previously reported intramolecular C−H activations on C_2-symmetric bis(oxazoline) ligands shown in the scheme, in which the target C−H bond was found to depend on the reaction conditions [3]. Our previous "a priori" rationalization of the processes suggested that such a selectivity divergence could result from the participation of different Ir(I) intermediates depending on the experiment: a three-coordinate species generated via the thermally induced reductive elimination of H_2, or a four-coordinate h^2-alkene complex when using ethylene as hydrogen acceptor.



We present new experiments and calculations indicating that the h^2-alkene intermediate is indeed a feasible alternative in the presence of ethylene, but discarding the participation of three-coordinated Ir(I) species in the thermally induced reaction. Instead, the results show that the actual dihydride precursor and its five-coordinate Ir(III) activation products are capable of undergoing facile C−H bond cleavage reactions that eventually lead to the thermodynamically preferred complex. Thereby, the presence or absence of ethylene drives the intramolecular C−H activation through Ir(I) or Ir(III) intermediates that bring about kinetic or thermodynamic selectivity, respectively.

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Catalytic activity in carbon-carbon bond forming reactions of peppsi Pd-NHC type *N*-heterocyclic carbene complexes

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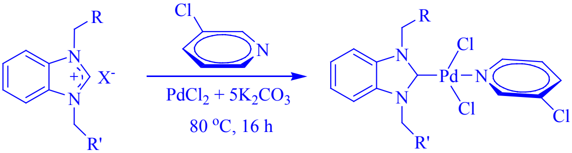
As catalysts, palladium *N*-heterocyclic carbene (Pd-NHC) complexes have displayed remarkable activities in coupling reactions [1-3]. Among various Pd-NHC complexes such as [Pd(NHC)(dmba)Cl] (dmba = *N*, *N*-dimethylbenzylamine) and [Pd(NHC)-(Im)Cl_2] (Im = imidazole) [4], [PEPPSI Pd-NHC] complexes have been seen more popular due to the combination of efficiency and versatility [5]. The synthesis conditions for these complexes are generally mild and do not require an inert atmosphere. The steric and electronic parameters are also easily modified by attaching substituents. PEPPSI Pd-NHC complexes have been used in different coupling reactions such as Mizoroki-Heck cross-coupling [6], Suzuki-Miyaura cross-coupling [7] and arylation reactions [9].



Scheme 1: Synthesis of benzimidazolium salts and their PEPPSI Pd-NHC complexes.

To find more effective catalysts, we synthesized four PEPPSI Pd-NHC complexes in this study. The structures of all compounds were confirmed by various spectroscopic methods (^1H and $^{13}C\{^1H\}$ NMR, UV-VIS, ESI-FTICR-MS, FT-IR) and elemental analysis. These complexes were tested for catalytic activities both in direct arylation and Suzuki-Miyaura cross-coupling reactions. The compounds were found to be very efficient in the symmetric and asymmetric C-C bond formation reactions.

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1-(4-Methoxybenzylideneamino)-5-(4-methylbenzoyl)-4-p-tolylpyrimidin-2(1H)-one and its catalytic activity properties

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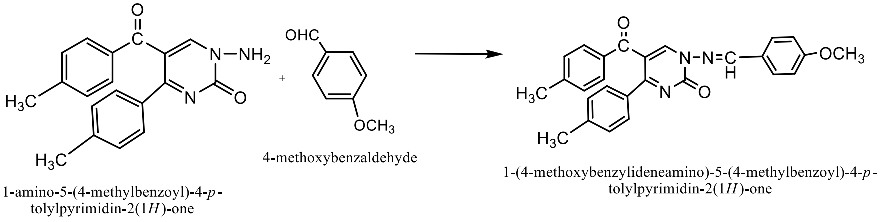
Schiff base ligands with sulphur and nitrogen donor atoms in their structures act as good chelating agents for the transition and non transition of metal ions [1]. There is a continuing interest in the metal complexes of Schiff bases. Because of the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands, they readily coordinate with a wide range of transition metal ions yielding stable and intensely coloured metal complexes, some of which have been shown to exhibit interesting physical and chemical properties [2] and potentially useful biological activities [3].



Scheme 1. Schematic represetation of the synthesis route of the 1-(4-methoxybenzylideneamino)-5-(4-methylbenzoyl)-4-p-tolylpyrimidin-2(1H)-one.

We presented the synthesis, charecterization and antimicrobial activity of one novel schiff bases in this study. For this, 1-amino-5-(4-methylbenzoyl)-4-p-tolylpyrimidin-2(*1H*)-one [4] as a starting material was synthesised to produce 5 1-(4-methoxybenzylideneamino)-5-(4-methylbenzoyl)-4-p-tolylpyrimidin-2(1H)-one [5]. This new Compound's structure was characterised by the FT-IR, ^{13}C NMR, ^{1}H NMR elementary analyses techniques. Also we studied for catalytic avtivities in Suzuki-Myaura cross coupling reactions in aquaus media. Schematic represetation of the synthesis route of the compounds shown in Scheme 1.

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P70

5-(4-Methylbenzoyl)-4-p-tolyl-1-(3,4,5-trimethoxybenzylideneamino)pyrimidin-2(1H)-one and it's antimicrobial properties

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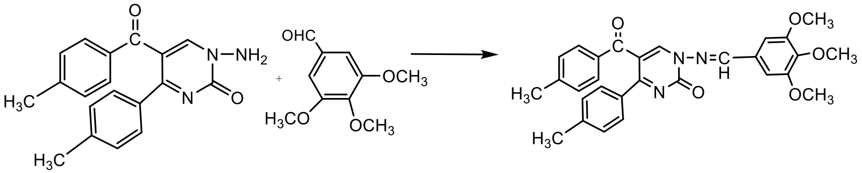
Research on transition metal complexes represents one of the most active areas of material science and chemical research. Major advances have been made in these materials due to their interesting properties. Schiff bases are some of the most widely used organic compounds in this area. They are used as catalysts, pigments and dyes, as polymer stabilisers, and intermediates in organic synthesis [1]. Schiff bases have been shown to exhibit a broad range of biological activities, including antimalarial, antifungal, antiproliferative, antibacterial, anti-inflammatory, antipyretic properties and antiviral [1, 2].



1-amino-5-(4-methylbenzoyl)-4-*p*-tolylpyrimidin-2(1*H*)-one   3,4,5-trimethoxybenzaldehyde   5-(4-methylbenzoyl)-4-*p*-tolyl-1-(3,4,5-trimethoxybenzylideneamino)pyrimidin-2(1*H*)-one

Scheme 1. Schematic represetation of the synthesis route of the 5-(4-methylbenzoyl)-4-p-tolyl-1-(3,4,5-trimethoxybenzylideneamino)pyrimidin-2(1H)-one.

We presented the synthesis, charecterization and antimicrobial activity of one novel schiff bases in this study. For this, 1-amino-5-(4-methylbenzoyl)-4-p-tolylpyrimidin-2(*1H*)-one [3] as a starting material was synthesised to produce 5-(4-methylbenzoyl)-4-p-tolyl-1-(3,4,5-trimethoxybenzylideneamino)pyrimidin-2(1H)-one [4]. This new compound's structure was characterised by the FT-IR, ^{13}C NMR, ^{1}H NMR elementary analyses techniques. Also, we studied for antimicrobial activities. Schematic represetation of the synthesis route of the compounds shown in Scheme 1.

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P71

Chemical fixation of carbon dioxide into cyclic carbonates catalysed by aluminium and lanthanum complexes

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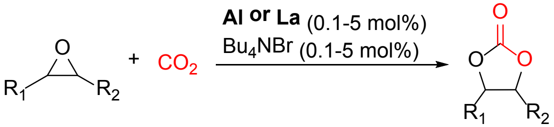
Two important challenges facing the global chemical community over the next two decades are: stabilizing atmospheric carbon dioxide levels to mitigate the effects of climate change; and developing sustainable raw materials for the chemicals industry to replace crude oil.[1] One approach to both of these problems is the development of commercially viable routes to basic chemicals that employ carbon dioxide as the starting materials. Therefore, carbon dioxide is potentially an abundant, economical and sustainable feedstock for the chemicals industry. In the last few decades, much research has been directed towards the use of carbon dioxide chemical feedstock.

The production of cyclic carbonates from epoxides is one of the main industrial processes, which uses carbon dioxide as a starting material. This reaction is 100% atom economical and leads to a five–membered ring cyclic carbonate with important applications as electrolytes in lithium–ion batteries, polar aprotic solvents and as chemical intermediates in organic synthesis.[2] Using this route, cyclic carbonates are currently produced using quaternary ammonium or phosphonium salts as catalysts at high temperature and pressure. In recent years, metallic complexes have been developed as catalysts for this reaction under milder reaction conditions.

In this contribution, we report the use of scorpionate-based metal complexes as highly efficient catalysts for the synthesis of cyclic carbonates from both monosubstituted and internal epoxides and carbon dioxide. Aluminium and lanthanum complexes had excellent catalytic activity towards the synthesis of cyclic carbonates from terminal and internal epoxides displaying a broad substrate scope. A kinetic study has been carried out and based on this, a catalytic cycle has been proposed.[3]



20 examples; up to 99% yield

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P72

Chiral recognition and formation of helicates in one and two-step self-assembly processes with Zn(II) and ditopic bis(pyrazolyl)methane ligands

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The coordination-driven self-assembly of organic and metallic components is an area of intense current interest in inorganic crystal engineering and has led to fascinating structures and to materials of multiple applications. Recently, the concept of secondary building units (SBUs) has been introduced [1] as molecular complexes and cluster entities in which ligand coordination modes and metal coordination environments can be utilized to transform these fragments into extended porous networks using polytopic linkers. In this work, we describe the formation of dimer Zn complexes that act as SBUs for the building of helicates with chiral recognition.

The self-asembly of $Zn(NO_3)_2$ with the new ligands bis(pyrazol-1-yl)(pyridin-3-yl)methane (**1**) and bis(3,5-dimethylpyrazol-1-yl)(pyridin-3-yl)methane (**2**) led to the formation of box-like cyclic dimers: $[ZnL(NO_3)_2]_2$ (L = **1**, complex **3**; L = **2**, complex **4**) with the ligands in a head-to-tail fashion (Figure 1)[2]. In **3** and **4** the pyridine rings exhibit a planar chirality and the two p*R*,p*R* and p*S*,p*S* enantiomers coexist in the crystal. A two-step assembly process using **3** as SBU and sodium 1,4-benzenedicarboxilate (Na_2BDC) as linker leads to the formation of hexanuclear cyclic helicates with distorted trigonal prism form, $[\{Zn_2(\mathbf{3})_2(H_2O)_2\}_3(BDC)_3](BDC)_3$, **5** (Figure 1). The observed chiral recognition makes that the three dimers of the helicate have the same chirality. Chains of helicates of the same chirality are formed and they interdigitate with chains of opposite chirality.

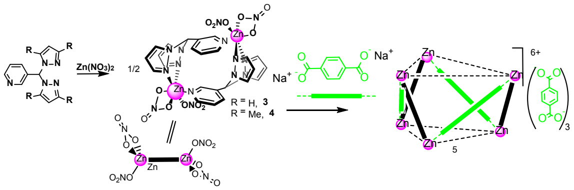

Figure 1

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Assessment of CH-π hydrogen bonds as building material to engineer helical architectures

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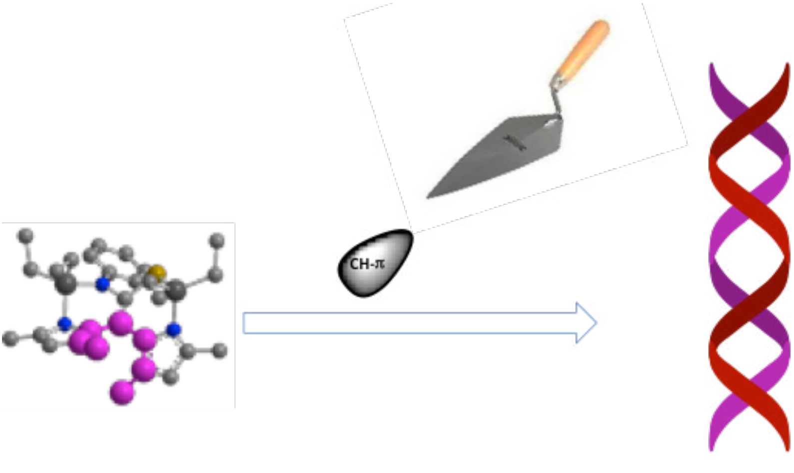
CH-π hydrogen bonds as building material for the construction of supramolecular helixes have been assessed for organometallic helicates.[1,2] The assembly of these organometallic entities, guided by the existence of noncovalent intra- and inter-strand interactions, has been analysed in solution by NMR and in the solid state by X-ray diffraction. A comparative study of the supramolecular structure of the helicates based on X-ray determination and density functional theory (DFT) calculations was performed to shed light on the mechanism of the helical construction.



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Oxygen evolving [Ir(IMes”)] complexes

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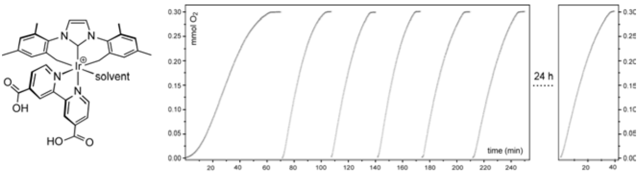
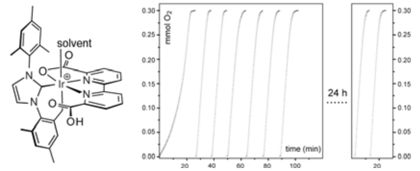
The cationic fragment [Ir(IMes”)]$^+$, which contains a doubly cyclometalated IMes ligand [1], has been used to prepare water-soluble complexes that catalyze the production of oxygen from periodate and water [2]. Catalyst solubility in water is achieved using bipyridine (bipy) auxiliary ligands that contain deprotonable carboxylic groups, whose positions in the bipy skeletons determine both the speciation in aqueous solution and the catalytic activities. Thus, the ligands with carboxylic substituents in positions 4,4’ (above in the figure) or 6,6’ (below) lead to different main species and, once deprotonated, give rise to catalytic profiles evidencing different activities and rate dependences on periodate concentration.





The catalysts need to be activated in the presence of excess periodate and, preferably, visible light, and after activation they become virtually inmortal. They can maintain remarkable turnover frequencies, above 3.5 s^{-1} at 30ºC during months and after thousands of turnovers, as exemplified in the picture, in which every separate run corresponds to the evolution of 1200 molecules of oxygen per molecule of the catalysts.

The molecular nature of the catalysts and the likely source of the oxygen atoms (water or periodate) will be discussed on the basis of analytic, spectroscopic and kinetic experimental information.

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Coordination of Zinc Hydrides to Transition Metal Carbonyls

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Since the first dihydrogen complex was reported in 1984 by Kubas, [1] transition metal complexes featuring E–H bonds (E = H, B or Si) have found great attention not only in coordination chemistry, but also in metal catalysed processes. While the coordination and oxidative addition of H–H, Si–H and B–H bonds to transition metals continues to receive considerable attention, [2,3] only recently have heavier main group hydrides begun to emerge as ligands for transition metal complexes. [4,5]

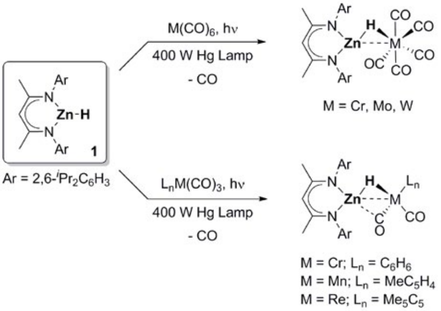

Figure 1.

Recently we reported the synthesis of heterobimetallic complexes generated by the addition of main group hydrides (M–H; M = Al, Zn, Mg) to a Rh(III) intermediate that is formed from the reductive elimination of triethylsilane from [Cp*Rh(H)$_2$(SiEt3)$_2$]. [6]

Herein we describe the synthesis and characterisation of new transition metal complexes containing a neutral Zn–H donor ligand (see Figure 1). The photochemical reaction of transition metal carbonyls M(CO)$_6$ or LnM(CO)$_3$ (M = Cr, Mo, W, Mn or Re) and the beta-diketiminate stabilised zinc hydride 1 leads to ligand exchange at the metal centre and to the formation of new heterobimetallic complexes. In each case, the crystallographic data of the new species indicates the formation of a three-centre two-electron Zn–H–M bond.

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Catalytic applications of new palladium(II) complexes with terphenyl phosphane ligands

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Palladium catalyzed cross-coupling reactions are fundamental tools for the formation of carbon-carbon and carbon-heteroatom bonds.[1] Investigations in this field have been recently focused in the development of well-defined palladium-based catalytic systems stabilized by bulky phosphane or N-heterocyclic carbene ligands (NHCs).[2] These precatalysts ensure an efficient formation of catalytically active Pd(0) species and a better control of the influence of the ligand in the coupling process.

We present herein the synthesis and the structural characterization of Pd(II)-metallacycles stabilized by dialkyl terphenyl phosphane ligands, recently synthesized in our research group (Fig. 1). The catalytic applications of the new precatalyst are also discussed.

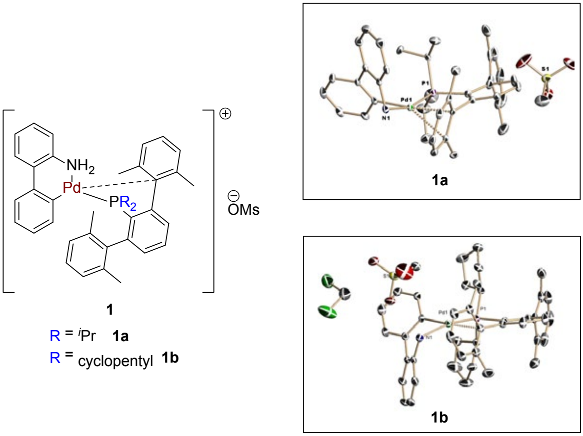

Figure 1. Pd(II) metallacycles prepared in this study

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Synthesis and Reactivity of Nickel Complexes Bearing a Non-Innocent Diphosphine Ketone ligand

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The recent researches on homogeneous catalysis for the hydrogenation of CO_2 or its polar derivatives have only reported a small number of efficient catalysts, often based on precious metals. Heavy metals such as rhodium, iridium, and ruthenium are often toxic, rare, and therefore expensive. Thus, this research targets the development of nickel-based catalysts for these types of reactions. We propose a new class of ligands [1] incorporating a C=O moiety, in a robust pincer-type scaffold, where nickel can be bound in η^2-coordination mode, as described by Dewar-Chatt-Duncanson model (Figure 1; compound **1**). Indeed, this design was believed to match the properties of low oxidation state metals and favours the η^2-(C,O) over the η^1-(O) coordination mode to the electron rich nickel centre. [2,3] Moreover, a five membered chelate cycle (Ni-P-C-C-C) is preferred. This latter is also anticipated to act as a hemilabile and/or cooperative ligand (Figure 1). Consequences of a cooperative-hemilabile behaviour could be beneficial for H_2 activation.

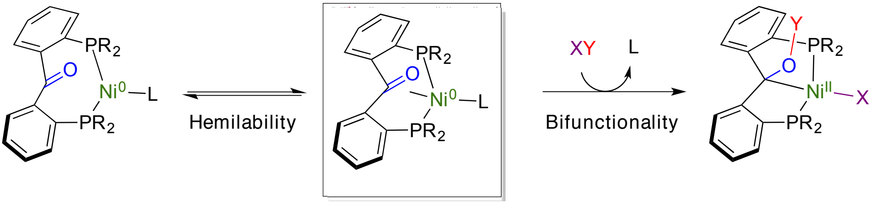

Figure 1: Postulated hemilabile and bifunctional character of an η^2-bound (C=O) ligand to a nickel centre. L = Stabilizing co-ligand.

This presentation involves the synthesis and characterization of nickel complexes displaying unusual electronic structures. A detailed understanding of their reactivity towards different kinds of molecules and their potentials in homogeneous catalysis is described. Therefore, we herein report the preliminary studies for the development of nickel-based complexes, aimed at catalyzing important reactions in organic synthesis, using a bifunctional approach.

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Double Hydrophosphination of Alkynes Promoted by Rhodium: the Key Role of an N-Heterocyclic Carbene Ligand

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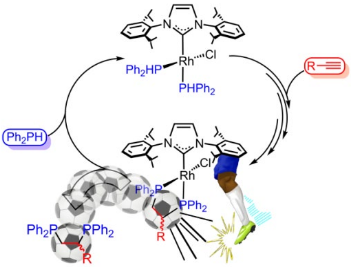
Phosphines are probably one of the most important families of compounds used as ligands for transition metals, therefore the development of synthetic procedures for carbon–phosphorus bond formation is an important task. Transition-metal-catalyzed phosphorus-hydrogen bond addition to unsaturated compounds is probably one of the most straightforward synthetic methods. However, only few examples of catalytic systems has been described, and particularly catalytic double hydrophosphination of alkynes is a really challenging reaction due to the formation of 1,2-diphosphines that form strong bonds with transition metals inhibiting their catalytic properties. To the best of our knowledge only one example of a catalytic system based on a Fe complex able to mediate the double hydrophosphination of alkynes has been described.[1] However, this system is active only with aromatic terminal alkynes, which strongly restricts the applicability of this synthetic method.



Our research group has recently showed how Rh^I-NHC complexes are really active and selective catalysts for different types of hydroelementation of alkynes.[2] In this communication, we report the first example of a Rh^I complex bearing a *N*-heterocyclic carbene (NHC) ligand able to catalyse the regioselective double hydrophosphination of terminal aromatic or aliphatic alkynes including substrates containing heteroatoms or a sensitive moiety as cyclopropane.[3] The experimental studies on the reaction mechanism have shown that the presence of the NHC ligand is fundamental to preserve the activity of the catalyst. We hypothesize that the interplay between the steric hindrance and the high *trans* effect imparted by the IPr is responsible for the destabilization of the chelate phosphine, preventing the catalyst deactivation.

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Palladium and Iridium Complexes based on new lutidine-derived NHC/phosphine mixed ligands

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Metal complexes containing lutidine-derived PNP ligands have gained considerable attention due to their applications in both organometallic chemistry and catalysis (Figure 1).[1] In these complexes, the methylene arms of the ligand are prone to deprotonation, offering an opportunity for metal-ligand cooperation in the activation of different types of H-X (X = H, C, N, O) bonds. Similarly, although less studied than their phosphine counterparts, CNC ligands in which the phosphorus donors are replaced by N-heterocyclic carbenes (NHC) have also been reported.[2]

In this contribution, we present the synthesis and structural characterization of iridium and palladium complexes based on new N-heterocyclic carbene/phosphine hybrid CNP ligands (Scheme 1). In comparison with previously reported PNP and CNC ligands, non-symmetric CNP pincers should allow for a larger electronic and steric diversity that may render improved catalysts and novel reactivities. These derivatives exhibit acid-base reactivity at the ligand, generating the pyridine dearomatized complexes M-CNP* upon reaction with a base. Deprotonated Ir-CNP* complexes are capable of performing ligand-assisted heterolytic H_2 activation.

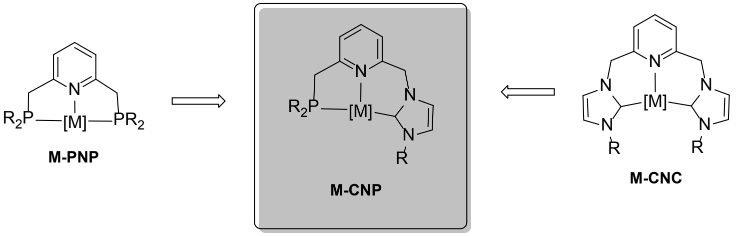
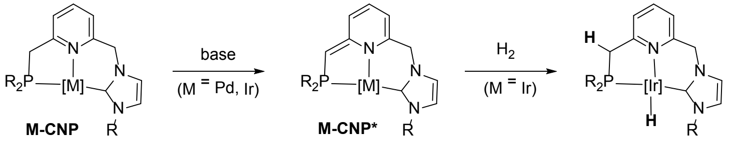


Figure 1



Scheme 1. Reactivity of Pd- and Ir-CNP complexes

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Agostic interactions in a series of rhodium-norbornadiene-phosphine oxide derivatives

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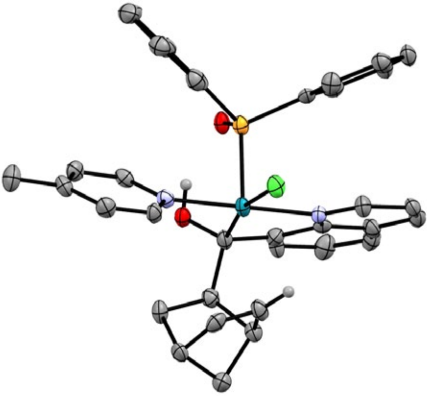
The dimer $[RhCl(Nbd)]_2$ reacts with quinoline-8-carbaldehyde (C_9H_6NCHO) and pyridine type derivatives (L) to give $[Rh(\mu\text{-}Cl)(C_9H_6NCHO)(Nbyl)L]_2$ (**1**) (Nbyl= σ-norbornenyl) (L=pyridine or 4-methylpyridine or isoquinoline). Under CO atmosphere, reductive elimination takes places to give $[RhCl(CO)_2(L)]$ and the hydroacylation product ($C_9H_6NC(O)Nbyl$). The same hydroacylation product is obtained when **1** is reacted with triphenylphosphine.[1] However, when **1** is reacted with diphenylphosphine oxide a new type of compound is created, where the Nbyl fragment has attacked the acyl group to give an alkoxy group. Concomitantly to the attack, a proton is transferred from the diphenylphosphinous acid to the alkoxide, thus yielding a hydroxy group and establishing an intramolecular hydrogen bond with the phosphinito ligand, giving a compound with formula $[RhCl(C_9H_6NC(OH)Nbyl)(L)(PPh_2O)]$. Initially a kinetic compound is formed, supported by theoretical calculations, we believe that this kinetic derivative has a bipyramidal trigonal geometry, and when heated in benzene it evolves to adopt a vacant octahedral geometry, where the vacant site has been filled with an agostic interaction between rhodium and one of the olefinic C-H bond, the 4-methylpyridine derivative of this compound was analysed by single crystal X-ray diffraction.



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P81

Reactivity of irida-β-diketone with furfurylamine

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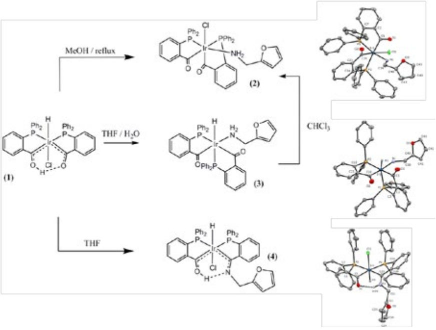
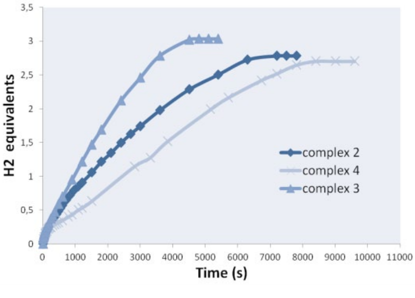
The energy demand of the society has exponentially increased since the beginning of the industrial revolution in the 18th century. A greener energy source, that could substitute fossil fuels, is ammonia-borane (AB)[1]. The hydridoirida-β-diketone [IrHCl{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}] (**1**) is an efficient homogeneous catalyst for hydrogen generation from hydrolysis of AB[2]. In this work the reactivity of complex **(1)** with furfurylamine was analyzed. Three different complexes were obtained and characterized via NMR, IR, conductivity and monocrystal X-ray diffraction.





Furthermore, the catalytical activity of the three complexes **2**-**4** was tested. All complexes showed catalytic activity in the hydrolysis of AB to release hydrogen.

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Carbene insertion to $C_{SP}{}^2$-H bonds catalyzed by a non-heme iron complex

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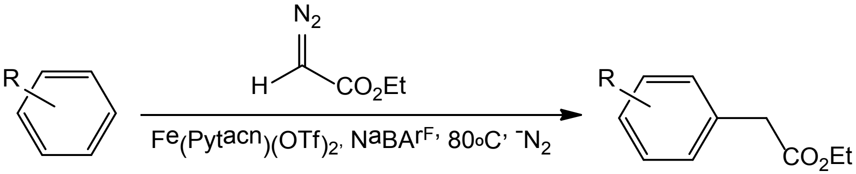
The functionalization of non-activated C-H bonds is a reaction of high interest since it becomes a starting point for the synthesis of value-added compounds. Among all transformations, metal-catalyzed carbene transfer reaction from diazocompounds to inert C-H bonds is a promising methodology to generate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

Although benzene is an important structure present in most of the pharmaceuticals, the use of carbene insertion reaction to functionalize benzene has not been extensively explored due to the existence of a competing reaction, called Buchner reaction, that consists in the addition of the carbene into the C=C bond, yielding a norcaradiene that rapidly opens producing a cycloheptatriene [3].

Herein, we present the functionalization of different arenes catalyzed by Fe^{II} complexes bearing tetradentate aminopyridine-based ligands, through the insertion of ethyl diazoacetate into C-H bonds. The selectivity towards $C_{sp}{}^2$-H bonds and the absence of neither cycloheptatriene product nor carbene dimers provides an efficient transformation catalyzed by a non-precious metal complex.



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Cytotoxic activities in breast cancer cell line of organometallic compounds

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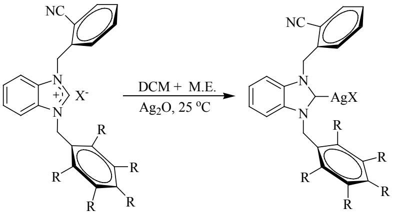
The use of *N*-heterocyclic carbenes (NHCs) as ligands was started by Wanzlick [1] and Öfele [2] almost fifty years ago. Since then, there have been major advances in the design and synthesis of metal complexes containing *N*-heterocyclic carbene ligands in the last two decades and they have had a wide range of applications in different fields, particularly in homogeneous/heterogeneous catalysis [3-5] and bioorganometallic chemistry [6]. This is because NHC complexes are obtained easily by the deprotonation of imidazolium or benzimidazolium salts and most are relatively stable in air and moisture. They are also weak π-acceptors and strong σ-donors and can form strong M-C bonds with transition metal ions compared to trivalent phosphine ligands [7].



Scheme 1: Synthesis of benzimidazolium salts and their Ag-NHC complexes.

We prepared and characterized six compounds as new cancer drug candidates and investigated their anticancer properties. The structures of all compounds were confirmed by various spectroscopic methods and elemental analysis. The *in vitro* cytotoxicity of compounds was determined against human breast cell line by MTT assay.

The silver complexes showed increased potency to inhibit cancer cell growth compared to benzimidazolium salts against MDA-MB-231 cancer cell line.

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P84

Insight into the mechanism of a trifluoromethylation of a well-defined aryl-Ni(II) species via putative Ni(IV) or Ni(III) intermediatestitile

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Trifluoromethyl functional group can modulate several properties in organic compounds, thus its role is well known when it comes to the production of pharmaceutical, agrochemical and specialized materials. [1][2] While the vast majority of these transformations use palladium based catalysts, [2][3] the development of nickel cross-coupling reactions have surge during the last decade [4] motivated by the envision of Nickel catalysts as a low-cost/ less-toxic alternative. Mechanistic studies have shown that Ni-catalyzed reactions can occur via organometallic Ni(0), Ni(I), Ni(II), Ni(III) and, as reported very recently, Ni(IV) intermediates. [5][6] Here density functional theory (DFT) is employed to describe the mechanism of a well-defined aryl-Ni(II) complex (1), which undergoes an aryl-CF3 bond forming cross-coupling-like reactions in the presence of the widely used oxidant agent S-(trifluoromethyl) dibenzothiophenium triflate (TDTT). From the three proposed mechanisms (Figure 1) the most favorable is (C), which occurs via single electron transfer (Trifluoromethyl Radical activation), followed by a CF3-radical addition to Ni(III) to form a Ni(IV)-CF3 intermediate and finally a reductive elimination to the aryl-CF3 product.

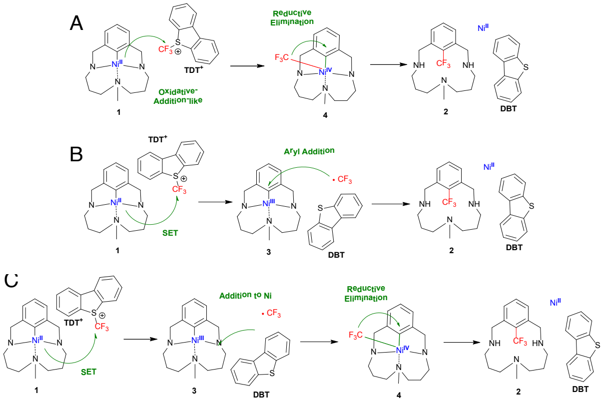

Figure 1: Proposed mechanisms for the reaction of S-(trifluoromethyl) dibenzothiophenium triflate (TDTT) with the Nickel complex **1**.

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P85

Characterization and reactivity studies of a terminal copper-nitrene species

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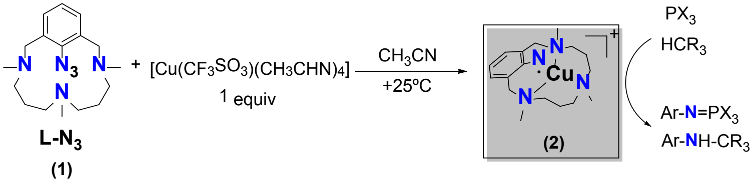
High-valent copper-nitrene species have been postulated as key intermediates in several copper-catalyzed reaction such as aziridination and amination reactions.[1] However, due to their high reactivity, terminal copper-nitrene species have not been either isolated or spectroscopic characterized. However, seminal works have evidenced their formation. For instance, Warren *et al.* could crystallize a dicopper(II)-nitrene complex as a precursor of a terminal copper(III)-nitrene species[2]. Moreover, Ray *et al.* reported the spectroscopic and theoretical characterization of a copper(II)-nitrene radical stabilized by scandium(III)[3,4] and very recently, Bertrand *et al.* could crystallize a copper(II)-bis-nitrene complex without reactivity studies[5].

Herein, we describe the preparation and characterization of a well-defined terminal copper(II)-nitrene radical species (**2**), which is stable at room temperature, formed by reaction of L-N_3 (**1**) with [Cu(I)(CF_3SO_3)(CH_3CN)$_4$] in acetonitrile (Scheme 1). The nature of compound **2** has been established by spectroscopic and spectrometric technics together with theoretical methods. Moreover, compound **2** is able to perform nitrene-transfer reactions and H-atom abstraction reactions of phosphines and weak C-H bonds respectively in modest yields.



Scheme 1: Schematic representation of the mechanism of the reaction of **1** with copper(I) in CH_3CN at +25ºC.

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P86

Dendronized mono and bis-NHC Pd(II) complexes as catalysts for the mizoroki-heck reaction

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Heterogeneous catalysis has the advantages of high catalyst stability and facile separation from the reaction mixture, whereas homogeneous catalysis benefits of higher activity and superior selectivity. Consequently, a significant advance would be the development of catalysts that are able to combine such features of both types of catalysis in the same process [1]. In recent years, the application of nanofiltration techniques for the recovery and reutilization of homogeneous catalyst, using MWE—molecular-weight enlarged—catalysts based on metal complexes, has received widespread attention [2]. Obviously, the task requires enduring active species, and due to the stero-electronic properties of N-heterocyclic carbenes (NHCs), this type of ligands results suitable to strongly bound to metals, giving complexes that are generally stable and resistant to decomposition under the catalytic reaction conditions [3].

We have synthesized new bis [4] and mono-NHC-palladium(II) complexes enlarged with Fréchet type dendrons (Fig. 1) and tested their behavior and durability in model the Mizoroki-Heck reaction. Several conditions have been optimized, including the addition of a reducing agent to promote the reaction, or the use of slight excess of haloarene to maintain the catalytic activity of the complexes in successive runs. In none of the experiments decomposition of the catalyst was observed and all the complexes maintained their catalytic activity for, at least, four runs.

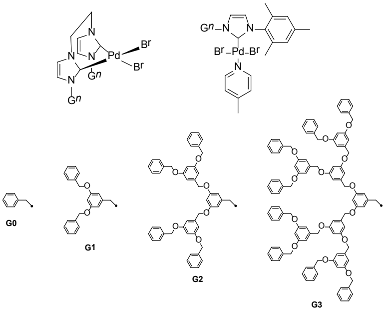

Fig 1

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Enantioselective Rh(I)-carbenoid mediated cascade

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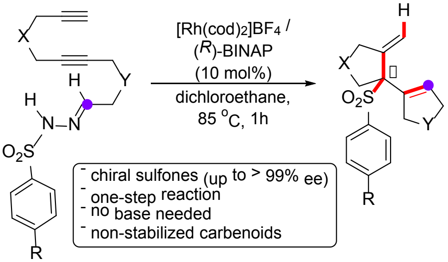
Metal carbenoids are important reaction intermediates capable of mediating in numerous reactions.[1] Rh(II) carbenoids, formed by the decomposition of diazo compounds with Rh(II) dimers, have shown great potential in stereoselective transformations. On the other hand, Rh(I) complexes that are known to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

We present herein a cascade reaction of dynearylsulfonylhydrazones under rhodium(I)/BINAP catalysis, that gives access to sulfonated azacyclic frameworks in a highly enantioselective manner. This new cascade process considerably increases the molecular complexity by generating two C-C, one C-S, and one C-H bond. Theoretical calculations, competitive experiments and deuterium labelling have jointly been used to propose a mechanism that accounts for the reaction. The mechanism involves a two-fold carbene / alkyne metathesis that generates a vinylrhodium carbenoid, hydride migratory insertion, and intermolecular stereoselective nucleophilic attack. The last two steps are the key to the stereoselectivity of the process.[3]



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Rh-catalyzed [2+2+2] cycloadditions of diynes with morita-baylis-hillman adducts: a stereoselective entry to densely functionalized cyclohexadiene scaffolds

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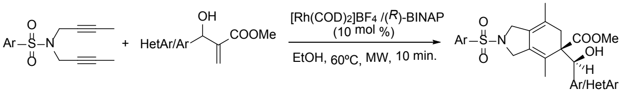
Opposite enantiomers of chiral compounds often display disparate bioactivity profiles. In particular, the introduction of quaternary stereocentres in a molecule constitutes an efficient strategy to complement the chiral three-dimensional space of biological receptors. Nevertheless, the formation of all-carbon quaternary stereocentres represents one of the most difficult contemporary challenges in synthetic organic chemistry since the creation of such centres is hampered by steric repulsion between the carbon substituents [1]. The transition-metal-catalyzed [2+2+2] cycloaddition reaction between diynes and 1,1-disubstituted alkenes provides an approach to the enantioselective synthesis of cyclohexadiene derivatives containing quaternary stereocentres [2].

In this study the synthesis of 5,5-disubstituted cyclohexa-1,3-diene derivatives has been achieved by Rh-catalyzed [2+2+2] cycloaddition reactions between diynes and Morita-Baylis-Hillman adducts as unsaturated substrates. Products containing two adjacent chiral centres (quaternary and tertiary respectively) were obtained with complete diastereoselectivity and high enantioselectivity. Furthermore, these highly substituted cyclohexadienes were reacted with dienophiles to afford the corresponding Diels-Alder cycloadducts in good yields [3,4].



- Diastereoselective process
- Kinetic resolution of the Morita-Baylis-Hillman adduct
- Products with a tertiary/quaternary stereodiad in 84-97% ee

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Approaches for Developing Ligand Scaffolds of Non-Heme Fe and Mn Catalysts

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The selective oxofunctionalization of hydrocarbons is an important goal in synthetic organic chemistry, because of their inert nature.[1] Selective oxidation of C-H and C=C moieties with excellent levels of region and stereocontrol is accomplished in Nature through oxygenase enzymes. Mimicry of structural aspects of enzyme active sites by synthetic transition metal complexes is regarded as a promising strategy to develop C-H and C=C oxidation catalysts.[2]

Non-heme iron and manganese based catalysts have been developed as promising systems for enzymatic oxidation processes; some of them can catalyze oxidative reactions by metal centered mechanisms, avoiding radical pathways. [3] The complexes that use N4-donor aminopyridine ligands are shown as one of the most successful catalysts for chemo-, regio- and enantioselective transformations of organic substrates with peroxide type oxidants.

With this knowledge in mind, we aim at widening the structural versatility of those ligands. So, in this work, we focus on the elaboration of various chiral diamines employed as backbones for these N4-donor ligands, being different from the usual used ones (**Figure 1**).

To understand their reactivity there were tested in some basic C-H and C=C oxidative catalysis. We hope that this structural versatility will allow us to extend the reactivity, the substrate scope and, in some cases, to modify the selectivity of these catalysts.

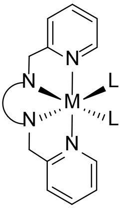

Figure 1: Schematic representation of metal complexes with N4 ligands.

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P90

Efficient transfer hydrogenation of aldehydes in water and deuterium labelling of the resulting alcohols by umpolung

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Reduction of aldehydes by transfer hydrogenation (TH) is not always a trivial item for the conventional TH active catalysts and the control of the chemoselectivity continues being a challenge [1,2].On the other hand, the use of water as a solvent for organic reactions has emerged as one of the most active and interesting fields both from an academic point of view and also considering industrial applications. Recently, we reported [3] the easy TH of several ketones and the deuterium labelling of the resulting alcohols using [Ru(p-cymene)Cl(Me_2-bpy)]BF_4 (**1**) as catalyst precursor and H_2O or D_2O as solvents and the sole deuterium source.

In this communication we focus on the TH process of arylaldehydes in water. The mixture sodium formate/formic acid has been used as hydrogen source and compound **1** as precatalyst. Information concerning the different reactivity of the studied aryl functionalized aldehydes and the tests of recyclability will be provided.

Excellent yields and labelling selectivities have been achieved in D_2O media. In this case, it is not necessary the incorporation of deuterium in the mixture used as hydrogen source since the incorporation of this isotope on the substrate comes from D_2O, as a result of a H/D exchange in the Ru-H moiety of the catalyst (hydrogen umpolung) (Figure 1).

Information concerning the mechanism of this TH and the labelling process will be provided.

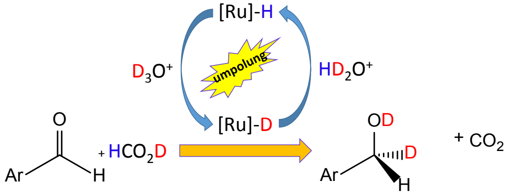

Figure 1

Acknowledgements

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P91

Synthesis and catalytic applications of ruthenium(II)-phosphino-oxime complexes

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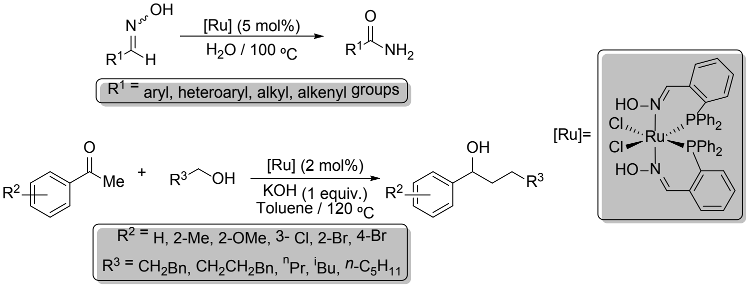
Hybrid ligands with hard nitrogen and soft phosphorus donor sites are highly valuable in coordination chemistry and homogeneous catalysis [1]. In this field, uncommon examples in the literature are the phosphine ligands containing an oxime functionality as the second donor group. Recently, our research group has described the preparation of a series palladium(II) complexes containing a phosphino-oxime ligand (*i.e.* 2-$Ph_2PC_6H_4CH=NOH$), which proved to be very efficient catalysts for the rearrangement of aldoximes to primary amides in water [2].

Herein, we give more evidences of the enormous synthetic potential of the phosphino-oxime 2- $Ph_2PC_6H_4CH=NOH$. In particular, we describe the preparation of the first ruthenium complexes containing this ligand, and their catalytic activity in the rearrangement of aldoximes to amides [3], as well as in the α-alkylation/reduction of acetophenones with primary alcohols [4].



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P92

Hydration of alkynes catalyzed by gold subnanoclusters and the importance of the Au···C-H interactions

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The use of gold in catalysis has experienced a huge development in the last 25 years, mainly due to its great catalytic performance under milder conditions and its high selectivity in organic functional groups transformations.[1-3] Depending on the gold oxidation and aggregation states, different types of reactions have been developed, which include heterogeneous catalysis with Au(0) for the activation of C-X bonds[4] and homogeneous catalysis with Au(I) and Au(III) for the activation of alkenes and alkynes.[5]

Recently Corma and co-workers have reported on a new type of efficient gold catalysts consisting on ultra-small naked Au_n clusters (n = 3-10 atoms) called gold subnanoclusters.[6] The stabilization of such nanocatalysts to prevent self-aggregation represents a true challenge which has been partially remediated, for instance, by the use of polymer matrices.

In this work we describe the transient stabilization of very small gold subnanoclusters (Au_n, n<5) by alkyl chains. A cooperative network of dispersive Au···C-H interactions, is proposed to be the origin of this stabilization. The better results in the case of the hydration of medium to long alkyl chain alkynes with respect to phenylacetylene is demonstrated experimentally and investigated computationally through DFT calculations (Figure 1).

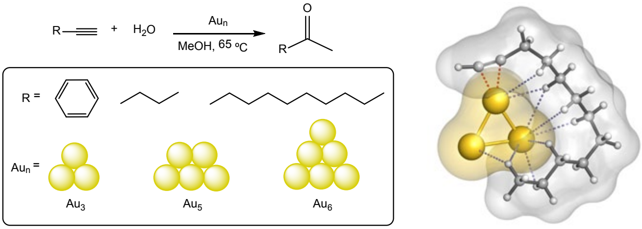

Figure 1. Reaction of hydration of different alkynes with gold subnanoclusters (left), and example of the different Au···C-H interactions in the case of the 1-dodecyne and the Au_3 cluster (right).

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Au(I)-Catalysed Cycloisomerisation of *N*-Tosylalkynyl Amides: Deep Eutectic Solvents *vs.* Water.

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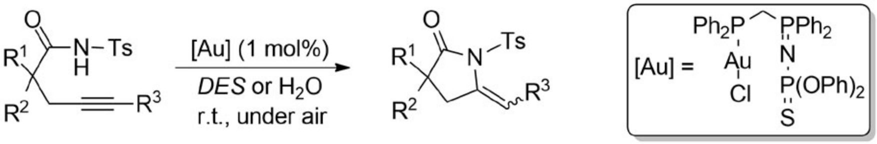
Benefits that *Chemistry* provides to our lives cannot occur at expenses of the environment. Chemist main job should be to design and develop more sustainable and efficient processes trying to fulfil the twelve principles of *Green Chemistry* [1]. In this context, solvents occupy a strategic position as they constitute one of the largest areas of consumption of petroleum-based chemicals in a conventional chemical transformation. To be considered as environmentally-friendly reaction media, these solvents must meet certain criteria related with its non-toxicity, biodegradability, recyclability and non-flammability [2]. This is the case of *Deep Eutectic Solvents* (*DESs*), that could be easily prepared using inexpensive and biorenewable raw materials [mixture of a hydrogen bond donor (*i.e.*, glycerol (*Gly*) or urea) with a simple halide salt (choline chloride, *ChCl*)] [3]. On the other hand, water can also be considered as an ideal *Green Solvent* taking into account its low price, non-flammability and non-toxicity. Taking advantage of these benefits, we have previously used these solvents in cycloisomerisation reactions of different unsaturated organic substrates [4].

Now, in this communication, we present a comparative study about the use of *DESs* or water as *green* and biorenewable solvents for the Au(I)-catalysed cycloisomerisation of *N*-tosylalkynyl amides into alkylidene lactams proceeding: *i*) with efficiency, selectivity and full atom economy, *ii*) at room temperature, *iii*) without protecting atmosphere and *iv*) in short reactions times.



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Double/Mono Suzuki-Miyaura and Hydrodehalogenation Reactions of 1-Benzyl(or methyl)-4,5-dichloro-1*H*-imidazoles in Water Catalyzed by NHC-Pd(II) Complexes.

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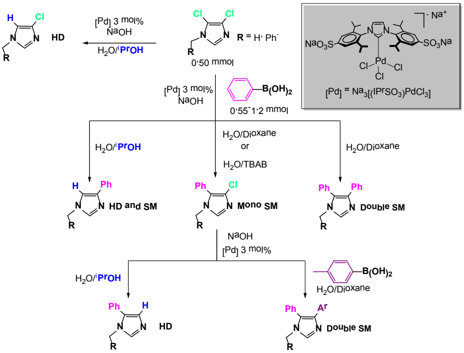
The water-soluble complex $Na_3[(IPrSO_3)PdCl_3]$ prepared in our group[1] showed excellent catalytic behaviour in Suzuki-Miyaura (SM) and hydrodehalogenation (HD) reactions carried out in aqueous media. This complex catalyzes the coupling C-C of inactivated and sterically hindered aryl chlorides with boronic acids under mild conditions.

Modifications of the imidazole backbone has gained increasing attention for the versatility of this heterocyclic moiety within medical chemistry, in natural products synthesis and as precursors for NHC ligands in transition metal- and organocatalysis.[2] For this reason, we decided to design regioselective protocols to synthetize different imidazole derivatives.

In this communication, we will show the results obtained in the SM and HD reactions of 1-benzyl(or methyl)-4,5-dichloro-1*H*-imidazoles carried out in aqueous media. Notably, most substrates afforded the desired product using $Na_3[(IPrSO_3)PdCl_3]$ as catalyst and NaOH as promoter (scheme.1). An appropriate combination of imidazole, boronic acids, solvent, Pd loading and temperature allows reactions with high selectivity and moderate to good yields.



Scheme 1: Selective synthesis of imidazoles employing SM and HD reactions.

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First examples of osmium(II) complexes with phosphinous acid ligands: catalytic behaviour in nitrile hydration reactions

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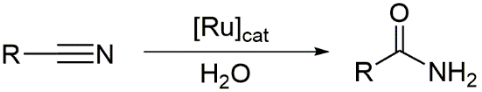
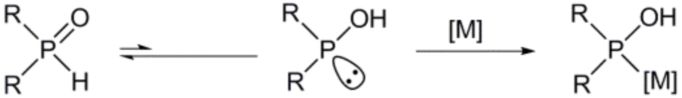
Phosphinous acids R_2POH represent a versatile family of *P*-donor ligands, which have recently found a large number of applications in homogeneous catalysis [1]. In this context, our group has described the preparation of different series of Ru(II) and Ru(IV) complexes with this type of ligands, and demonstrated their catalytic potential for the selective hydration of organonitriles in aqueous media [2].



The method most commonly employed in the literature to synthesize transition metal complexes with phosphinous acid ligands involves the reaction of the corresponding metallic precursor with a secondary phosphine oxide $R_2P(=O)H$. In solution, the secondary phosphine oxides exist as a tautomeric mixture of penta-, *i.e.* $R_2P(=O)H$, and trivalent, *i.e.* PR_2OH, isomers, with the pentavalent one predominating under ambient conditions. In the presence of a metal this equilibrium is driven towards the PR_2OH tautomer *via* coordination.



By following this route, we have been able to synthesize the first examples of osmium(II) complexes containing phosphinous acid ligands, *i.e.* the half-sandwich derivatives $[OsCl_2(\eta^6\text{-}p\text{-cymene})(PR_2OH)]$ (R = Me, Ph). The catalytic behaviour of these complexes in nitrile hydration reactions was also evaluated and compared to that of their ruthenium(II) counterparts $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PR_2OH)]$ (R = Me, Ph) previously described by our group. To our delight and surprise, we found that, in most cases, faster transformations take place using osmium. In this communication we will present a summary of these studies.

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P96

Reactivity relative scale of different C-H bonds of alkanes

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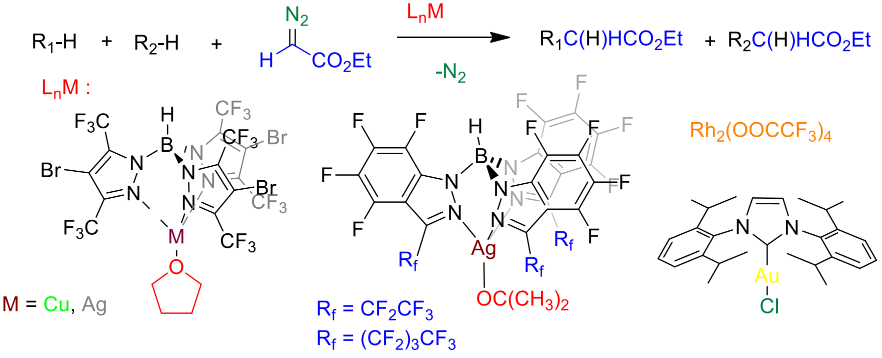
The chemistry of alkanes is still reason to study due to the few examples described so far. There are several reasons for which this chemical is poorly developed up to now, such as the low reactivity due to the high dissociation energy of C-H bonds of molecules and also to the fact that depending on the chain length of these substances may find in the form of gas (C1-C4), liquid or solid at atmospheric pressure. These are the main reasons which make it difficult a comparison of reactivity relative to each other. We recently discovered that complexes of organometallic metal transition can functionalize C-H bonds of alkanes by carbene transfer using EDA (ethyl diazoacetate). We decided to perform a study to describe a reactivity relative scale of different C-H bonds of different alkanes by a catalytic reaction of carbene transfer. The competition experiments were carried out in supercritical CO2 as the reaction medium for the gaseous alkanes.[1] The relative reactivity scale was developed with metal complexes of Ag, Cu, Au and Rh.



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P97

Bipyridine dearomatization *vs.* formation of imidazolyl ligands: dramatic effect of bipy substituents

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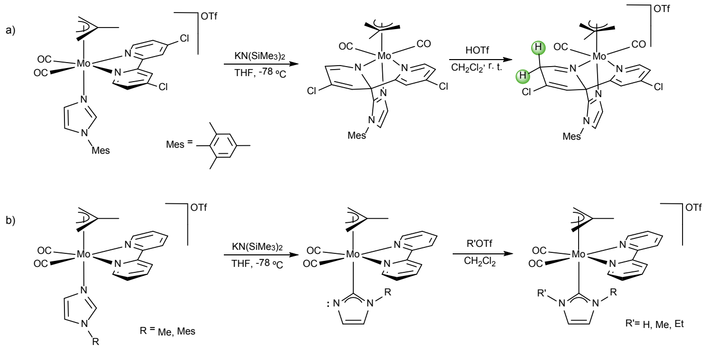
New N-alkylimidazole (N-RIm; R= Me, Mes; Mes= mesityl, mesityl= 2,4,6-trimethylphenyl) complexes of the {Mo(η^3-methallyl)$(CO)_2$(4,4’-X_2-bipy)} (h^3-methallyl= h^3-(2-methylallyl), 4,4’-X_2-bipy= 4,4’-X_2-2,2’-bipyridine) fragment have been prepared, in which the substituents of bipyridine are halogens (X= Cl, Br). The addition of a strong base to the new compounds deprotonates the central CH group of the imidazole ligand and subsequently an intramolecular nucleophilic attack affords a C-C coupling product with the bipy ligand in *cis* disposition (Scheme 1a). This reactivity contrasts with that previously found for the analogous non-substituted bipy, which afforded imidazol-2-yl complexes upon deprotonation (Scheme 1b).[1] Therefore, this is the first report of bipy dearomatization in molybdenum complexes. The reaction of the dearomatized complexes with HOTf afforded immediately cationic species in which a CH group of the dearomatized pyridyl ring has been protonated generating a CH_2 moiety. These new compounds have been characterized by infrared spectroscopy, nuclear magnetic resonance, elemental analysis and in some cases by X-ray diffraction. Furthermore, Density Functional Theory (DFT) computations have been carried out to understand the mechanism of the process.



Scheme 1. Reactivity of [Mo(η^3-methallyl)$(CO)_2$(bipy)(N-RIm)][OTf] compounds.

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Tetrabenzoimidazolium-resorcinarene cavitands for the selective recognition of anions via hydrogen bonding *and/or* hydrophobicity

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The study of the recognition of anions is currently a pillar of supramolecular chemistry with aplications in many areas.[1-4] In this contribution, two tetrabenzoimidazolium-resorcinarene cavitands were prepared and used for the recognition of chloride, bromide, iodide, cyanide, nitrate, perchlorate, hexanoate, phenylsulfonate and *p*-tolylsulfonate. One of the cavitands contains four C2-H benzoimidazolium arms, wile the other is funtionalised with four C2-Me benzoimidazoliums. In the case of the C2-H tetrabenzoimidazolium-resorcinarene, the recognition region of the inorganic anions and hexanoate was located at the rim of the cavitand, although chloride and bromide also interacted with the aromatic C-H bonds placed between adjacent arms of the cavitand (Figure 1). For the C2-Me tetrabenzoimizazolium-resorcinarene receptor, the ability of the molecule to bind all inorganic anions was suppressed, but the ability to strongly bind phenylsulfonate and *p*-tolylsulfonate was maintained.

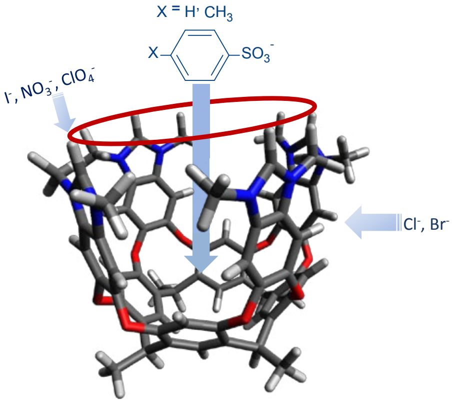

Figure 1

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Synthesis and catalytic activity of new acylrhodium(III) complexes containing pyrazole ligands

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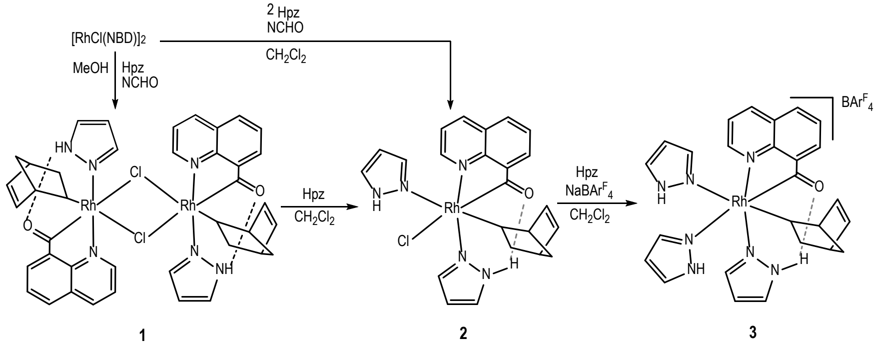
It is known that [RhCl(NBD)]$_2$ (NBD = Norbornadiene) reacts with 8-Quinolinecarbaldehyde (NCHO) in the presence of N-donor ligands to give norbornenylrhodium(III) or nortrycilcylrhodium(III) acyl species.[1] Catalytic activity of acylrhodium(III) complexes in the hydrolysis of $H_3B{\cdot}NH_3$ for the production of hydrogen has been previously reported.[2]

This contribution will deal with the synthesis of acylrhodium(III) complexes with pyrazole (Hpz) ligands. The reaction of [RhCl(NBD)]$_2$ with 8-quinolinecarbaldehyde in the presence of 1 equivalent of pyrazole affords complex [RhCl(Nbyl)(NCO)(Hpz)]$_2$ (Nbyl = Norbornenyl) **(1).** In the presence of pyrazole, this mixture undergoes cleavage of Cl bridges to give complex [RhCl(Nbyl)(NCO)(Hpz)$_2$] **(2)**. This species can also be obtained via reaction of [RhCl(NBD)]$_2$ dimer with 2 equivalents of pyrazole and NCHO. Removal of chlorine from complex **2** by addition of NaBAr$^F_4$ salt in the presence of pyrazole allows the coordination of an additional Hpz molecule, obtaining the cationic complex [Rh(Nbyl)(NCO)(Hpz)$_3$]$^+$ (**3**). Complex **2** has proved to be an efficient precatalyst in the homogeneus reaction of hydrolysis of $H_3B{\cdot}NH_3$ for the production of hydrogen, releasing up to three equivalents per mole of borane adduct under mild temperatures.



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Activación del enlace n-o en el nitrosilo puente del complejo $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$

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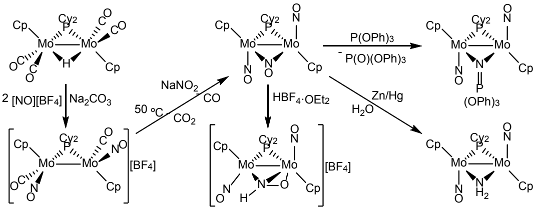
Los procesos de escisión del enlace N-O de ligandos nitrosilo en complejos metálicos resultan de interés para el desarrollo de nuevos catalizadores para la descomposición o reducción de óxidos de nitrógeno. La mayor parte de las rupturas del enlace N-O descritas en compuestos binucleares y polinucleares se producen en sustratos que poseen un ligando NO en posición puente o a través de intermedios de tales características [1, 2]. Hace algún tiempo, nuestro grupo de investigación identificó el complejo $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$ como un subproducto minoritario en la reacción $[Mo_2Cp_2(\mu\text{-}Ph)(\mu\text{-}PCy_2)(CO)_2]$ con NO [3]. Considerando que la reactividad de este subproducto podría ser interesante en el contexto de los procesos de escisión de enlaces N-O, se decidió implementar rutas preparativas eficientes que permitieran explorar con detalle su comportamiento químico. El complejo $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$ se prepara por reacción de $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ con 2 equivalentes de $[NO][BF_4]$ y Na_2CO_3 y posterior tratamiento del producto resultante $[Mo_2Cp_2(\mu\text{-}PCy_2)(CO)_2(NO)_2][BF_4]$ con $NaNO_2$ a 50 ºC. El estudio cristalográfico de este complejo revela que el ligando nitrosilo puente posee una significativa piramilización en el átomo de nitrógeno, lo que podría traducirse en un comportamiento inusual, en lo relativo a la degradación del nitrosilo puente. De hecho, el complejo $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$ reacciona con $HBF_4{\cdot}OEt_2$ para dar el derivado con nitroxilo puente $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}k^1\text{:}h^2\text{-}HNO)(NO)_2]$, se reduce con Zn/Hg en presencia de trazas de H_2O para generar el complejo amiduro $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NH_2)(NO)_2]$, y reacciona con exceso de $P(OPh)_3$ para formar el complejo fosfinoiminato $[Mo_2Cp_2(\mu\text{-}PCy_2)\{\mu\text{-}NP(OPh)_3\}(NO)_2]$ [4].



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Molybdenum-catalyzed sulfur atom transfer reactions: a theoretical study of the key steps in the catalytic synthesis of episulfides and isothiocyanates

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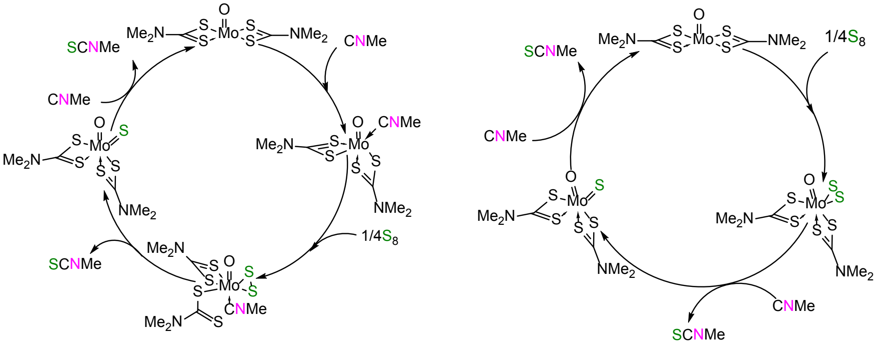
Molybdenum oxo complexes catalyze efficiently the sulfur atom transfer to a series of alkenes and isonitriles, by using different sulfur sources, to afford the corresponding episulfides or isothiocyanates, respectively [1-2]. Following our interest in the theoretical analysis of oxygen atom transfer reactions [3-5], we decide to investigate the related sulfur atom transfer process. Therefore, the two mechanisms proposed in the bibliography for these reactions (see Scheme for the catalytic synthesis of isothiocyanates [2]) were investigated by Density Functional Theory methods. The theoretical characterization of the molybdenum complexes that act as the different intermediates and transition states in the catalytic cycles will be discussed in this communication.



Scheme. Proposed catalytic cycles for the molybdenum-catalyzed synthesis of isothiocyanates from isonitriles.

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Synthesis and characterization of chelating dicarbene iridium complexes

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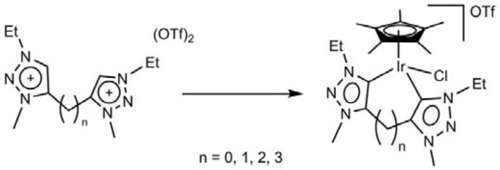
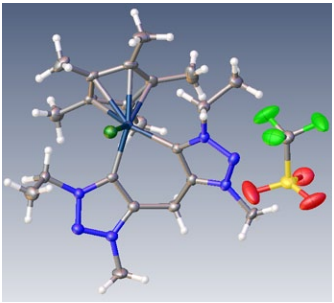
Triazolylidenes are versatile ligands that are readily available through click chemistry. They are a subclass of N-heterocyclic carbenes that impart high electron density at the metal center due to the very strong donor properties, allowing the synthesis of complexes with a broad array of applications such as in catalysis.[1] Despite the kinetic and thermodynamic stability imparted by chelation, chelating ditriazolylidenes are still underexplored. [2]

Here we have synthesized a series of bis(triazolylidene) ligands through [2+3] click reaction of different dialkynes and azides. The corresponding dicarbene iridium (III) complexes, containing flexible alkyl- or ether-linker between the triazolylidine rings, are obtained via formation of the silver carbene complex and subsequent transmetallation.





Depending on the reaction conditions, monocarbene, dicarbene or bimetallic complexes can be obtained. Evaluation of the dicarbene complexes as catalysts in transfer hydrogenation shows a substantial influence of the triazolylidene linker on the catalytic activity.

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P103

Dichloride encapsulation by ellipsoid-shaped vanadium dicarboxylate cage complexes

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The design of polyoxovanadate cluster compounds of specific size has attracted considerable attention for their structure and properties. Basket-, bowl- or ball-type polyoxovanadates have been prepared and some of them encapsulated one halide anion [1-5]. In this communication we describe the synthesis and characterization of two polyoxovanadate clusters with dicarboxylate ligands derived from oxydiacetic and glutaric acids that contain two encapsulated chloride anions. Both compounds have been analytically and structurally characterized. An ORTEP perspective of complex $[NBu_4]_2[V_8O_{16}(oda)_4{\subset}Cl_2]$, oda = oxydiacetate, is shown in figure 1. To our knowledge, ellipsoid-shaped vanadium dicarboxylate cage compounds of the type reported here are completely new. Results of DFT calculations show that the HOMO resembles the antibonding σ 2*p* and the HOMO-6 resembles the bonding σ 2*p* molecular orbitals of Cl_2 molecule (figure 2).

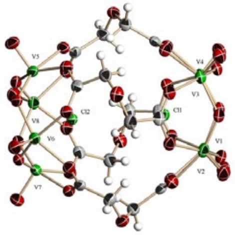

Figure 1. Structure of the $[V_8O_{16}(oda)_4{\subset}Cl_2]^{4-}$ anion.

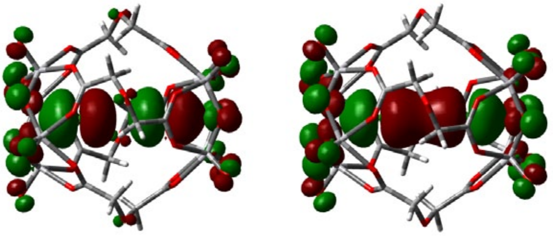

Figure 2. HOMO and HOMO-6 of the $[V_8O_{16}(oda)_4{\subset}Cl_2]^{4-}$ anion.

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P104

Insulation of reactive metallo-complexes guest in a self-assembled metalloporphyrin supramolecular cage

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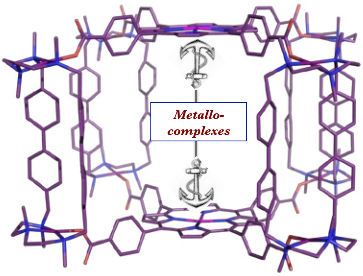
In order to reproduce the efficient chemistry found in Nature, much research is directed to the development of systems that mimic enzyme active sites. Although a myriad of model complexes inspired by the first coordination sphere of metalloenzymes have been reported, systems that also mimic the secondary structure are more rare. However, in the biological world, formation of extremely reactive intermediates is only possible thanks to the insulation provided by enzymatic cavities.

Supramolecular self-assembly is a powerful tool for the development of molecular reaction vessels, which may mimic the cage-like structure of enzymes.[1] The self-assembled metallocage **(Mac_4Por_2)** has a supramolecular nature consisting of four macrocyclic dimetal clips and two tetracarboxylated metalloporphyrin walls. This designed nano-capsule has been reported as an effective tool for anionic π-guests encapsulation,[2] fullerenes purification,[3] and enantioselective induction via indirect through-space control of the chirality around the catalytic centre.[4]

The exceptional behavior of **(Mac_4Por_2)** encouraged us to consider this system toward the confinement of highly reactive complexes similar to that found in metalloenzymes. Using pyridine based anchor, several metallo-complexes have been successfully encapsulated by **(Mac_4Por_2)**. Discussion about the insulation of reactive species inside the **(Mac_4Por_2)** nano-capsule will be the core of this communication, which aims at giving a better understanding of the remarkable properties observed for these supra-structures.



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P105

A General Stereochemical Model to Explain Asymmetric Hydroformylation Catalyzed by Rh-Diphosphane Complexes

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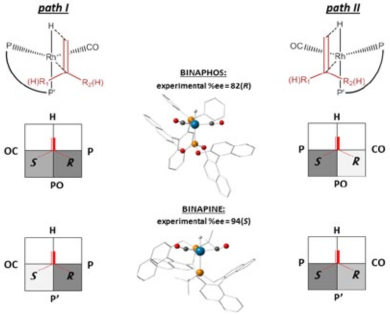
Asymmetric hydroformylation is potentially very useful for the synthesis of chiral aldehydes, which are a valuable tool for the generation of biologically active compounds. Higly successful reactions have been reported with a number of transition metals, but most often with Rh^{I}-diphosphane complexes [1]. The traditional way to rationalize enantioselectivity follows the *quadrant rule* [2], in which the substrate approaches the catalyst minimizing the steric repulsion by placing the larger substituent in the unblocked quadrant. Obeying this premise, our group developed a methodology to generate a quantitative diagram representation of the catalyst (*MolQuo*) that is based on a novel descriptor, the *distance-weight volume* (V_W) [3].

For the Rh^{I}-binaphos and –binapine catalysts the ligand coordinates in an equatorial-axial manner, so there are two possible paths for substrate approach (path I and II) [3,4]. Each path favors the opposite enantiomer but one path is favored over the other leading to highly selectivity route, in which the alkene substituent is placed in an unimpeded quadrant (see Figure). Here we show that this stereochemical model can be generalized for all the privileged ligands of Rh-catalyzed asymmetric hydroformylation found in the literature: binaphos, binapine, diazaphospholane, yanphos, bpe, duphos and bobphos. Thus, our stereochemical model establishes a qualitative relationship between a chemical descriptor and the enantioselectivity of the process, defining rules for the synthesis of novel catalysts.



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P106

Intramolecular apical Metal–H–C_{sp3} interaction in tris[1-diphenylphosphino)-3-methyl-1*H*-indol-2-yl]methane transition metal complexes

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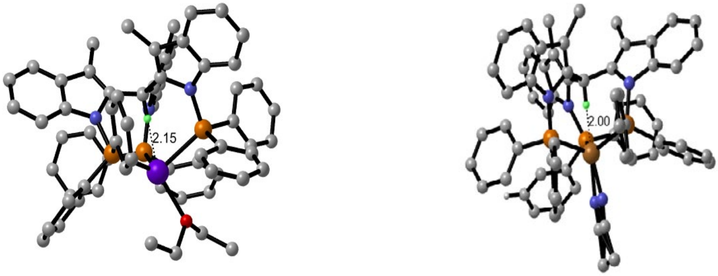
Hydrogen interactions have an extraordinary relevance in inorganic, organometallic, and biological chemistry. Particularly in the analysis, design, and synthesis of (bio) molecular assemblies and in studying enzymatic activities. Among them, M–H–C_{sp3} (M=metal) interactions have been intensively studied for a better understanding of their structural and bonding features [1]. The tris[1-diphenylphosphino)-3-methyl-1*H*-indol-2-yl]methane (HTIMP3) ligand has been successfully applied in the synthesis of C_3-symmetric complexes of Pd(II), which catalytic activity was tested in various Suzuki reactions [2]. In addition, the reactivity of hydride derivatives based on Rh and Ir complexes was studied [3,4]. Interestingly, in the case of silver salts, the reaction with HTIMP3 was found to be sensitive to the choice of solvent, possibly due to non-innocent behaviour of the Ag(I) cation. Formation of the intramolecular apical M–H–C_{sp3} interaction was also investigated in the case of Pt and several first row transition metals (Co, Cu, Ni, Fe).



Complexes with HTIMP3 based on Silver(I) (left) and Copper(I) (right)

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P107

Synthesis and Reactivity of Heterometallic Complexes with Mo–Re Double Bonds

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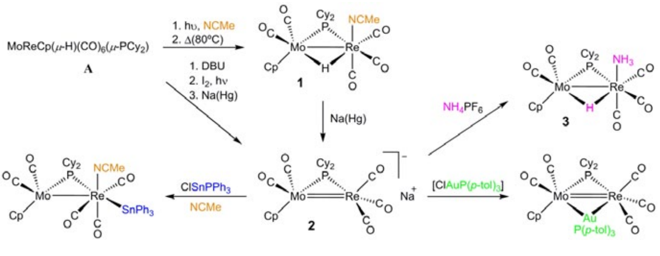
Our research group has developed efficient synthetic routes to the 30-electron complexes $[M_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ and $[M_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2]$ (M = Mo, W).[1] This allowed us to carry out an extensive study on the reactivity of these unsaturated species which revealed that the combined presence of a M≡M bond and a negative charge or an hydride ligand, respectively, provides them with a great chemical versatility, leading to the preparation of new unsaturated compounds with different functionalities (alkyls, carbynes, etc.).[2] Prompted by these interesting results, we aimed to prepare and explore the chemical reactivity of new unsaturated complexes with more polar heterometallic bonds, and herein we report some preliminary results on novel Mo–Re complexes.

Our initial approach to the preparation of unsaturated Mo–Re complexes focused on the reduction of suitable halo complexes. Although this route leads to the unsaturated anion $[MoReCp(\mu\text{-}PCy_2)(CO)_5]^-$ (**2**), it involves a tedious preparation of the corresponding halo derivatives starting from the known hydride $[MoReCp(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_6]$ (**A**).[3] A more convenient route to the anion **2**, involves the reduction of the acetonitrile complex **1**, which is easily accessible from the saturated hydride **A**. As opposed to the chemistry of homometallic complexes, protonation of the anion **2** did not lead to an unsaturated hydride, but to the electron-precise amino complex $[MoReCp(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5(NH_3)]$ (**3**). In contrast the reaction with $[AuCl(PR_3)]$ gives the expected unsaturated MoReAu cluster in a selective way. Other reactions of the anion **2** will be also presented, including those in which the protonation is carried out in the presence of additional ligands such as alkynes this allowing us to trap the putative unsaturated hydride $[MoReCp(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5]$.



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P108

Formate esters as CO sources: synthesis of indoles by palladium-catalyzed reductive cyclization of *ortho*-nitrostyrenes

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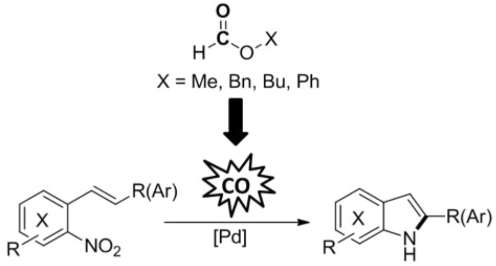
Catalytic reductive cyclization of substituted aromatic nitro compounds represents a valuable approach for the synthesis of N-containing heterocycles. Using gaseous CO as the reductant it is possible to selectively transform the nitro group into much more reactive intermediates (such as nitroso compounds) that can further undergo *inter* or *intra*-molecular amination reactions.[1,2] Nevertheless, CO is a highly toxic molecule whose handling requires the installation of expensive safety measures and high-pressure equipments. In order to overcome this issue, we developed a synthetic protocol in which formate esters (both alkyl and aryl) were employed as CO sources thus avoiding the use of pressurized gas.[3] In particular phenyl formate was found to be an excellent CO surrogates enabling the preparation of various substituted indoles by Pd-catalyzed reductive cyclization of *ortho*-nitrostyrenes with excellent selectivities (up to 98 % isolated yield). Notably, the transformation proceeds more efficiently than the corresponding reaction carried out under gaseous CO conditions.



- CO-gas free , no autoclaves
- Very high selectivities
- Scalable process

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Mechanistic insights into the hydrosilylation of terminal alkynes catalyzed by a ono-pincer iridium(III) hydride compound

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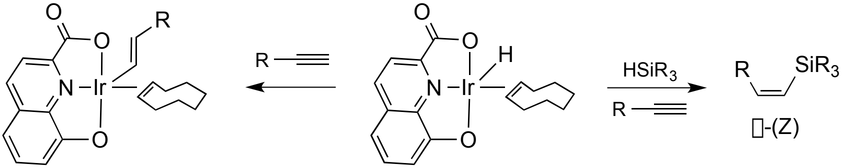
Transition-metal catalyzed hydrosilylation of terminal alkynes is the most straightforward and atom-economical methodology for the preparation of vinylsilanes, which are valuable synthetic intermediates [1]. The control of the regio- and stereoselectivity of the reaction is a key issue and therefore a deeper understanding of the reaction mechanisms is pivotal for the development of more active and selective catalytic systems. On the other hand, pincer ligands are valuable structural motifs for the design of transition-metal complexes for selective stoichiometric and catalytic transformations. In particular, O-based anionic pincer ligands have attracted significant attention for supporting high-oxidation-state metal complexes by modulating the electron density at the metal centre via a hard/hard interaction or π-donating effects. We have recently shown the potential of tridentate dianionic ONO pincer-type ligands for the design of unsaturated iridium(III) compounds which have shown catalytic activity in C–H activation/ functionalization processes. [2]

The unsaturated hydrido iridium(III) compound [IrH(k^3-hqca)(coe)] (hqca = 8-oxidoquinoline-2-carboxylate) is an efficient catalysts precursor for the hydrosilylation of a range of terminal alkynes with excellent yields and an outstanding β-(Z) selectivity for aliphatic alkynes. This species reacts with a range of terminal alkynes to give η^1-alkenyl complexes that are also competent for alkyne hydrosilylation.



The presence of a rigid dianionic ONO pincer-type ligand could facilitate the stabilization of Ir^V intermediates thereby driving the catalytic reaction through a Ir(III/V) mechanism. In view of the lack of mechanistic studies supported by computational studies on rhodium and iridium hydrosilylation catalysts, the operating mechanism has been investigated by theoretical calculations at DFT level. In addition, the mechanism of the competitive dehydrogenative silylation process has also been studied.

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P110

Mechanistic Insights and Kinetic Studies on the Ir-NSiN Catalyzed Hydrosilylation of CO_2 to silyl formates

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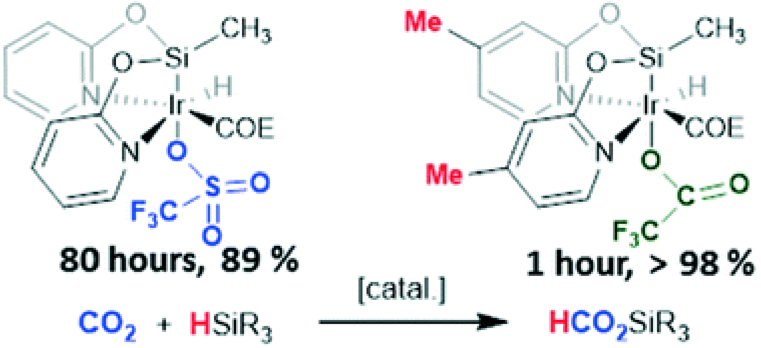
We have recently reported that the catalytic activity of various Ir-NSiN-type species, containing different ancillary ligands and/or modified NSiN-type ligands, as catalyst precursors for CO_2-hydrosilylation depends on the nature of the ancillary ligands as well as on the reaction parameters (temperature and CO_2-pressure).[1,2] The best catalytic performance has been achieved at 328 K and 8 bar of CO_2 using the complex $[Ir(H)(CF_3CO_2)(NSiN^*)(coe)]$ (NSiN* = *fac*-bis-(4-methylpyridine-2-yloxy)methylsilyl) as catalysts precursor.[2] Here we propose a mechanism for this catalytic process based on kinetic and theoretical calculations as well as on stoichiometric experiments.



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Investigation of the organometallic chemistry of cobalt complexes: an attractive alternative to noble metals catalysts

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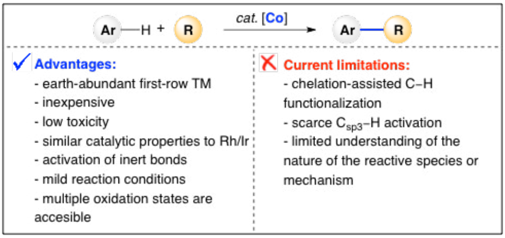
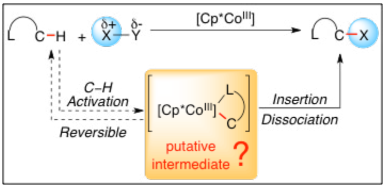
Over the last decades, transition-metal-catalyzed C–H activation has emerged as a powerful tool for the construction of carbon–carbon bonds. Until recently, the majority of these transformations were achieved employing precious second- and third-row transition metals. However, the development of novel methodologies based on more cost-effective first-row transition metal complexes has emerged as a very attractive alternative[1].

Among them, cobalt catalysis has shown its potential to construct C–C bonds via C–H activation using cobalt(III) catalysts [2]. Despite this significant progress, these Co^{III} systems for C–H functionalization are still at their infancy and important, fundamental questions remain unsolved, specially concerning the lack of information on the mechanisms of these transformations[3]. So far, the isolation of any catalytically relevant intermediate, including stable cobaltacycles, is unprecedented.



✓ **Advantages:**
- earth-abundant first-row TM
- inexpensive
- low toxicity
- similar catalytic properties to Rh/Ir
- activation of inert bonds
- mild reaction conditions
- multiple oxidation states are accesible

✗ **Current limitations:**
- chelation-assisted C–H functionalization
- scarce C_{sp3}–H activation
- limited understanding of the nature of the reactive species or mechanism



We have performed a detailed mechanistic investigation of Co^{III}-mediated C–H activation using model substrates with directing groups to explore the role of different additives on this step. During our study we were able to observed Co^{III} dimer species that could be involved in the C–H cleavage.

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P112

Novel platinum compounds with N,N chelating ligands as potential anticancer drugs

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Coordination compounds have been widely used in chemotherapy for cancer treatment. Among them, platinum compounds have achieved great success due to their great cytotoxic properties. The most notable examples are cisplatin, carboplatin and oxaliplatin, which have been used for the treatment of many cancer types for almost 40 years [1]. However, these platinum complexes are inefficient against some certain cancer cell lines or lead to undesirable side effects because of their poor selectivity towards tumour cells. Therefore, efforts must be made to synthetize new platinum compounds with better properties to be used against cancer cell lines resistant to existing drugs or to reduce the side effects.

The most usual mechanism of action of platinum drugs involves an initial aquation process of the platinum complexes, followed afterwards by the coordination to the DNA strand in *cis* position, starting cell apoptosis [2].

In our group, several novel platinum complexes have been synthetized (Fig.1). In order to force the *cis* configuration in the complexes, N,N chelating ligands based on an imidazole skeleton have been used. The aim was that the NN ligands would act as the non-leaving group and the chloride ligands as the leaving groups in the biological medium. It has been verified that all compounds suffer solvolysis when dissolved in DMSO and this is expected that the DMSO molecules will be replaced by H_2O molecules in the cells. These may favour the desired covalent coordination to DNA. It has to be considered that the chloride concentration is lower in cytoplasm.

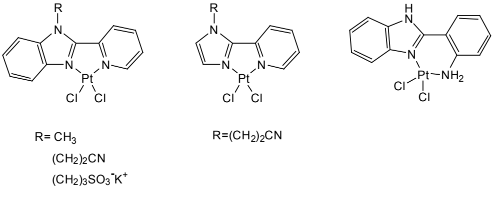

Figure 1: Structure of platinum compounds synthetized in this work.

Acknowledgements

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Very Small Gold Au_4, Au_8, and Bimetallic Au_4Ag Clusters: C-H Functionalization of Carbonyl Compounds and Homogeneous Carbonylation of Amines

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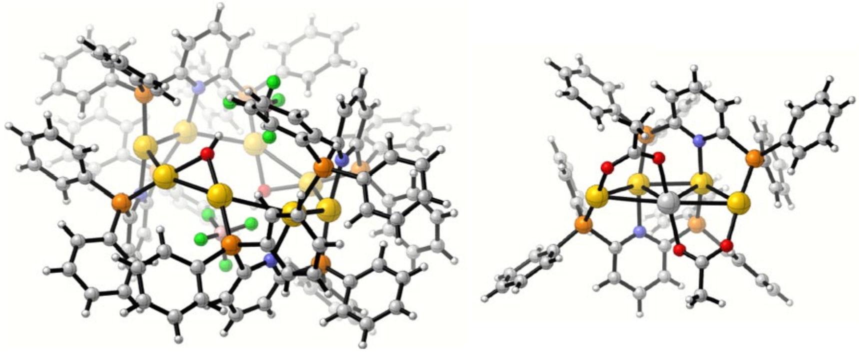
Very recently, small gold clusters have been found to catalyze reactions usually performed by gold nanoparticles or mononuclear gold complexes.[1,2] Herein, we report the synthesis of air- and moisture-stable linear Au_4, octagonal Au_8, and pentagonal Au_4M (M = Cu, Ag) clusters.[3] The linear tetracationic Au_4 complex, prepared in one step from $[Au_2Cl_2\{(Ph_2P)_2Py\}]$, induces C-H functionalization of carbonyl compounds under mild conditions to form square planar clusters. The pentanuclear Au_4Ag complex, readily prepared in one step from Au_4, is highly catalytically active for the oxidative carbonylation of primary amines to form ureas under homogeneous conditions. The efficiencies are comparable with other transition-metal catalyzed processes and higher than those achieved by gold nanoparticles. We have also obtained an octanuclear cluster, which is formally the product of a 4+4 reaction of two Au_4 complexes. X-Ray diffraction revealed an unprecedented planar octagonal structure.



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P114

Influence of N-Heterocyclic Olefins in Catalytic Hydrogen Transfer Reactions. A DFT Theoretical Study.

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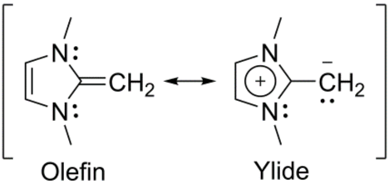
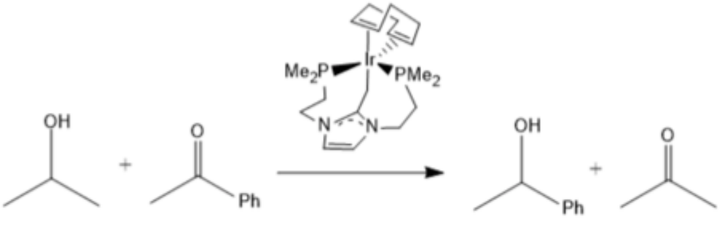
The double bond of N-Heterocyclic olefins (NHOs) is strongly polarized featuring a lone pair of electrons as a consequence of the unique electronic structure of the five-membered heterocycle. That provides it with the ability to react with Lewis acids as boranes and Group 14 adducts. In addition, they can act as ligands for some transition metals, in particular Au, Mo, Rh and Ir.[1] In these complexes, they present a two possible coordination modes from h^1 to h^2 attributed to the dual nature (ylide-olefin) of the NHO scaffold.



In order to get a deeper knowledge on the effect these ligands have on the catalytic activity of Rh and Ir-complexes, a mechanistic study at the DFT level of the hydrogen transfer reaction to hydrogenate ketones was performed using $[\mathrm{Ir(cod)}(\kappa P,C,P'\text{-}\mathrm{NHO}^{P(CH_3)2})]\mathrm{PF}_6$ (cod = 1,5-cyclooctadiene, $\mathrm{NHO}^{P(CH_3)2}$ = 1,3-bis(2-(dimethyllphosphanyl)ethyl)-2 methyleneimidazoline) as catalyst. Theoretical calculations at the B3LYP-D3 def2tzvp//B3LTYP-D3 def2svp have been carried out in order to reveal the mechanistic details and the effect of the NHO ligand on both stepwise and concerted hydrogen transfer.



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P115

New transition metal complexes with N-methylated bis(pyrazolyl)methane ligands

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Since the first reported poly(pyrazolyl)methane ligands [1], a huge amount of work has been carried out in the preparation of these ligands, and their coordination chemistry with different metals has been widely explored. Applications in different fields such as catalysis or bioinorganic chemistry have been reported [2].

N-alkylation of imidazole derivatives leads to precursors of N-Heterocyclic carbenes (NHC) whose use as ligands has been profusely studied. However, the selective N-alkylation of pyrazole rings constitutes another alternative to NHC that has been less explored.

In this work, we report the synthesis of three bis(pyrazolyl)methane ligands, with different substitution at the position 4 of the pyrazole ring. One of the rings of each ligand has been methylated selectively to explore their use as NHC ligands.

When the methylated ligands are made to react with palladium acetate, dinuclear complexes are obtained (Figure 1), as it is deduced from the IR and mass studies. NMR experiments have been carried out to study the cleavage of the dimer to monomers in solution when coordinating solvents (as DMSO) are used.

However, when alternative Pd, Ru or Pt starting compounds are used for the reaction, even in the presence of different bases, the deprotonation required for the NC coordination does not take place and the ligands are only coordinated through the non-methylated pyrazole ring. The X-Ray structure for the platinum derivative [$PtCl_3L$] has been elucidated (Figure 2).

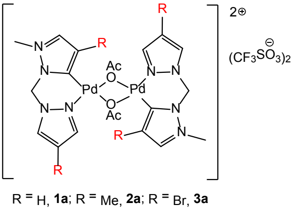

Figure 1. Dimer palladium complexes with a NC coordination of the ligands.

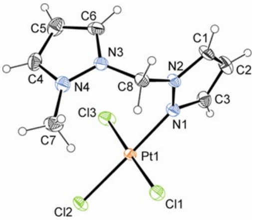

Figure 2. Platinum complex with monodentate coordination of the ligand.

Acknowledgements

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P116

Catalytic nitrene transfer to alkynes: a new route for linear and cyclic imines synthesis

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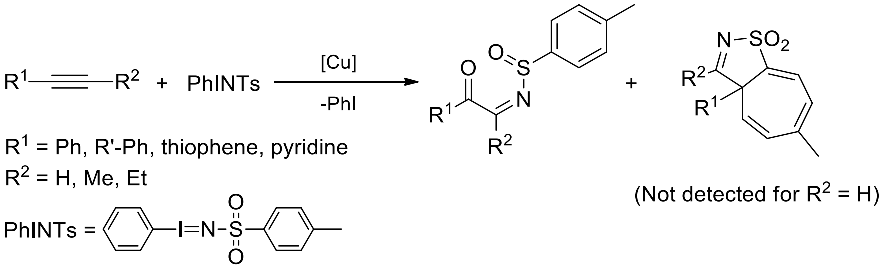
One of the most used strategies in modern chemistry for the formation of new C-N bond is the transfer of a nitrene group onto saturated and unsaturated substrates. Our research group has developed a family of copper complexes bearing hydrotrispyrazolylborate ligands (Tp^x) as efficient catalysts in the nitrene addition and insertion reaction to substrates of different nature such as alkanes, olefins, dienols, furans and aromatic compounds. [1] The reaction between an alkyne and a nitrene fragment could be an alternative transformation to the formation of a new C-N bond, however this reaction has barely been studied. [2]

In this communication, we describe the first example of nitrene transfer to alkynes, terminal and internal, activated and deactivated, catalyzed by Tp^{x}Cu-complexes. This transformation leads to the formation of new linear and cyclic imines.



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P117

Catalytic transfer hydrogenation of 3-pentanone in water with arene ruthenium precursors

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In the second half of the 20th century the interest in homogeneous catalysis has increased substantially parallel to the organometallic chemistry. In the past decade, half-sandwich Ru(II) arene complexes have found a lot of applications as active species in a great number of organic reactions catalytically driven. Our research group is interested in the development of versatile catalysts active in aqueous media for transfer hydrogenation (TH) of organic carbonyl compounds.[1,2] TH is an important alternative to catalytic reduction with molecular hydrogen that precludes the work at high pressure.

In this communication, we describe the use as precatalyst, in the TH of 3-pentanone, of different Ru-arene complexes containing benzoimidazole and benzothiazole ligands (see figure 1) in water with the system HCOONa/HCOOH as hydrogen donor. The effect of the pH has been analyzed. The system allows an easy separation of the organic products.

In order to obtain a detailed microscopic description for all the steps of the catalytic TH cycle we have carried out NMR studies to propose a mechanism.

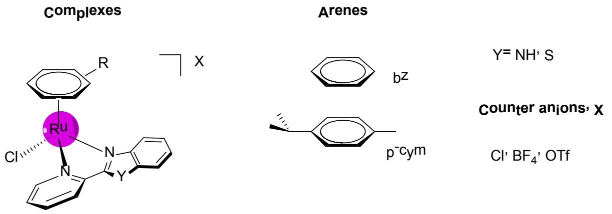

Figure 1. General structure of the Ru(II) arene compounds of formula $[(\eta^6 \text{ - arene})\mathrm{RuCl}(\kappa^2 \text{ -N,N})]\mathrm{X}$.

Acknowledgements

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Synthesis and characterization of ethylene complexes of molybdenum (0) with PNP-type pincer ligand

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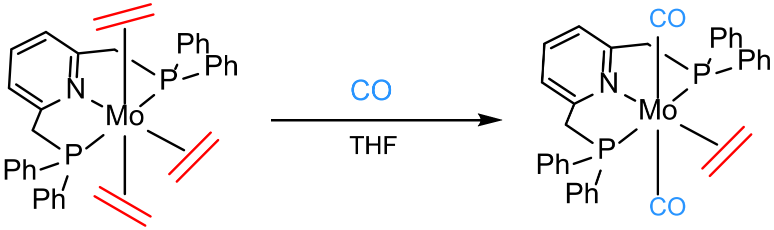
In the last few decades, ethylene complexes of transition metals have become relevant due to their industrial importance as intermediates and catalysts in a wide range of reactions.[1] Several studies have found that molybdenum complexes are active in coupling reactions between ethylene and carbon dioxide, [2] affording high added value products such as acrylates or propionates, both used in industrial applications.



Scheme 1.

In this communication, we present the synthesis and characterization of the first tris(ethylene)molybdenum(0) complex bearing a PNP-type pincer ligand (Scheme 1), as well as its reactivity toward carbon monoxide and carbon dioxide.

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Synthesis of Rhodium(I) Complexes Bearing Coumarin-Substituted N-Heterocyclic Carbene Ligands

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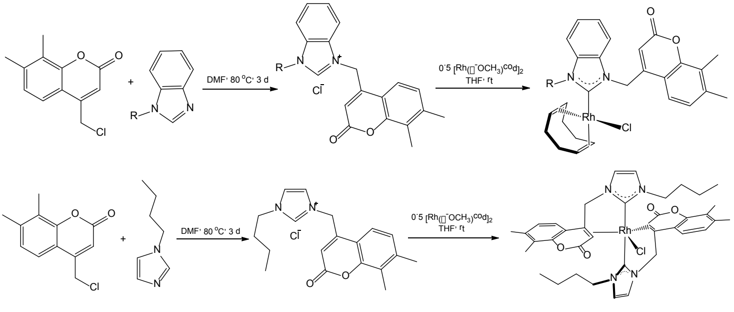
Since the report of first stable *N*-heterocylic carbene (NHC) by Arduengo, metal-NHC complexes have attracted much attention[1]. Particularly, Rhodium-NHC complexes have been revealed as efficient catalysts for X-H addition to unsaturated bonds [2,4]. In other hand, Coumarins are members of a class of compound called benzopyrones and show interesting biological and pharmacological properties[5]. In this study, we present the synthesis of coumarin bearing benzimidazolium and imidazolium chlorides. Rh(I)-NHC complexes of these salts have been prepared by reaction with $[Rh(\mu\text{-}OCH_3)cod]_2$ in THF. Synthesized complexes are fully characterized by X-ray single crystal diffraction, 2D-NMR techniques and elemental analyses. Catalytic activity of the complexes for hydroelementation of unsaturated substrates will be investigated.



Scheme 1. Synthesis of Rh-NHC(coumarin) complexes.

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A practical guide in Ullmann-type C-O and C-N couplings: the quest for orthogonal discrimination among functional groups

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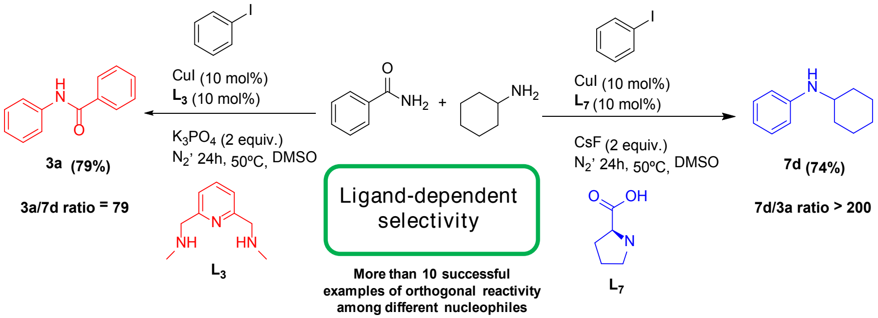

Copper catalysis in organic transformations is one of the most successful and utilized strategies for the formation of C-C and C-heteroatom bonds (Ullmann type couplings), which are present in a large number of natural and pharmaceutical products.[1] Advances during the last two decades, have shown that ligand choice plays a key role in such transformations and can strongly influence the catalytic efficiency as well as the operative mechanism.[2] Although these transformations have found remarkable applications, orthogonal selectivity of different functional groups still constitutes a challenging subject.[3] Herein, we disclose a useful toolkit of Cu-based catalyst systems for highly chemoselective arylation of a wide-range of nucleophiles in competitive reactions using aryl iodides and bromides. The nature of the ligand can determine distinct selectivity, yielding the desired coupling products under mild conditions and high chemoselectivity. The operative catalytic mechanism for such coupling reactions can be favored over other mechanistic pathways depending on multiple factors, with the design of the auxiliary ligand being a crucial one.

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Investigation of the Synergistic Cooperation between Bimetallic Systems

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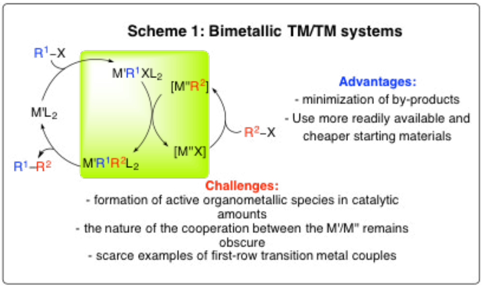
Over the last decade, bimetallic catalysis has emerged as a very attractive approach to promote C–C bond forming reactions[1]. Compared to more traditional Pd-catalyzed cross-coupling methodologies[2], this bimetallic approach offers the benefit of using more ready available and cheaper starting materials. Another advantage is the minimization of by-products formation. The mechanism proposed for these bimetallic systems involves two different catalytic cycles (each with one transition-metal (TM) catalyst) connected by a transmetalation step (Scheme 1). Although the synergism between Pd/Au[3], Pd/Cu[4] and Ni/Cu[5] metal centers to form C–C bonds is well-precedented in organic synthesis, the nature of the cooperation between these TM couples remains unclear. In this context, our goal is to investigate the transmetalation between organopalladium(II) and different well-defined metal transition complexes in order to provide key information about the feasibility of these transformations.



Scheme 1: Bimetallic TM/TM systems

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New Water-Soluble Gold (I) Complexes Containing Guanidiniumphenylphosphine Ligands: Efficient Precursors for the Hydroacyloxylation of Internal Alkynes in Aqueous Media

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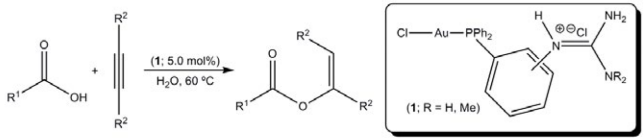
For reasons of cost, safety, and environmental concerns, the development of organic transformations in aqueous media has become one of the major cornerstones in modern chemistry. Following this general trend, the design of transition-metal catalysts for organic reactions in water has arisen a growing interest in recent years.[1] In this sense, introduction of hydrophilic ligands in the coordination sphere of a transition-metal is probably the most popular method for the preparation of water-soluble catalysts.[1,2] Thus, a wide variety of functionalized phosphine ligands containing highly polar sulfonated, hydroxyalkyl, ammonium, phosphonium, carboxylate, carbohydrate or phosphonate groups are actually known and their effectiveness in biphasic catalysis largely demonstrated.[1,2]

Cationic phosphines containing guanidiniumphenyl moieties possess highly polar functions which confer them a pronounced solubility in water. Moreover, the anion binding capacity of the guanidinium groups should exert some precoordination and preorientation of anionic substrates in the periphery of catalyst complexes containing these ligands. Although all these potential advantages, as far as we know there are only few examples of metal complexes containing guanidiniumphenylphosphines in their coordination sphere, as well as their use as catalysts in different organic reactions.[3]

With this situation in mind, we decided to accost the synthesis of various gold(I) complexes (**1**) containing different guanidiniumphenylphosphines as ligands. These complexes were subsequently tested as potential precursors in the hydroacyloxylation of symmetrical internal alkynes employing water as solvent.



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Mechanistic study of C-N bond formation reaction catalyzed by a NHC-nickel(0) complex

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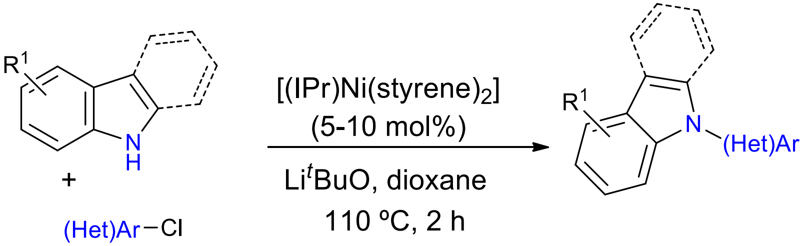
Over the last decade, the number of examples of C-N coupling reactions catalyzed by nickel complexes has increased significantly.[1] Recently, our group initiated a new research line focused on the development of single-component nickel(0) catalysts for C-N bond couplings.[2] In one of these studies, we reported the use of Ni(0) complex [(IPr)Ni(styrene)$_2$] [IPr= 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], **1**, as efficient catalyst in the reaction of aromatic and heteroaromatic chlorides with substituted indoles and carbazoles (Scheme 1).[2b]

Here, we describe a mechanistic study of these reactions, with experimental details about the different intermediates involved in the catalytic cycle.



Scheme 1. Reaction of indoles/carbazoles with (hetero)aromatic chlorides**.**

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Structural analysis, physicochemical properties and application abilities of stable *catena*-poly[[bis(4-(aminomethyl)-5-(hydroxymethyl)-2-methylpyridin-1-ium-3-olato-κ^2*N,O*) copper(II)]-μ-nitrato] nitrate monohydrate

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The syntheses of coordination polymers have received significant attention in the field of chemistry [1,2], not only because of their various structural motifs but also for their potential applications in medicine [3] and molecular sensing [4]. By selecting specific d-block metal ions and organic bio-ligands, coordination polymers with different dimensionalities can be obtained [5].

Generally, the studies on Cu(II) complexes with vitamin B_6 date back to the late seventies of the last century. The mentioned coordination compounds may act as models mirroring the effects of exogenous ligands in biological processes involving vitamin B_6 [6]. However, these reports have mainly focused on X-ray determinations of crystal structures and no detailed characterization of synthetic procedures was given. The same applies to the characterization of the bulk product in the solid state as well as the analyses of such complexes in solution. The present results describe the structural, redox, acid-base and thermal behavior of cationic coordination polymer in distorted tetragonal bipyramide geometry, $\{[Cu(NO_3)(pm)_2]\}_nNO_3\cdot H_2O$ where *pm* denotes pyridoxamine. Our attention was focused on the use during synthesis of specific 1:2 molar ratio of Cu^{2+} to *pm* to prove the complexity of dimensionality due to those described in earlier reports [7,8]. Moreover, only medical possibility of applications Cu(II)-*pm* vitamer coordination compounds have been proposed till now. The applications of resembling complexes to our compound as antimicrobial agents, non-steroidal anti-inflammatory drugs or chelating agents could be found in many scientific research. However, no assay were reported with regard to applications of copper(II)-pyridoxamine complex as acid-base indicator or as sensing material relative to strong acids ($pK_a < 2.5$).

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Amines catalyse diboration reaction

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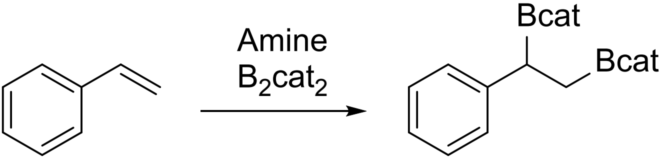
The versatility of carbon-boron bond as a platform for chemical transformations has attracted the attention of many researchers aiming to develop new methodologies to have access to new organoboron compounds. Recently, organocatalytic methodologies[1] have risen as real alternative to the transition metal methodologies. The organoboron catalysis requires a Lewis base for the activation of the diboron compound.

Some amines are able to do the activation as Marder[2] and Ingleson[3] already reported, but they had no a synthethic aplication. During this study a novel methodology for the organocatalytic activation of bis(catecholato)diboron (B_2cat_2) have been used and we have explored their use towards a selective diboration of alkenes.



This new methodology could solve some of the current challenges of the reaction, increasing the substrate scope and funcional group compatibility opening as well new approaches for the enantioselective version of the reaction.

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Donor-adaptive bis-pyridylidene amide ligands for ruthenium-mediated redox catalysis

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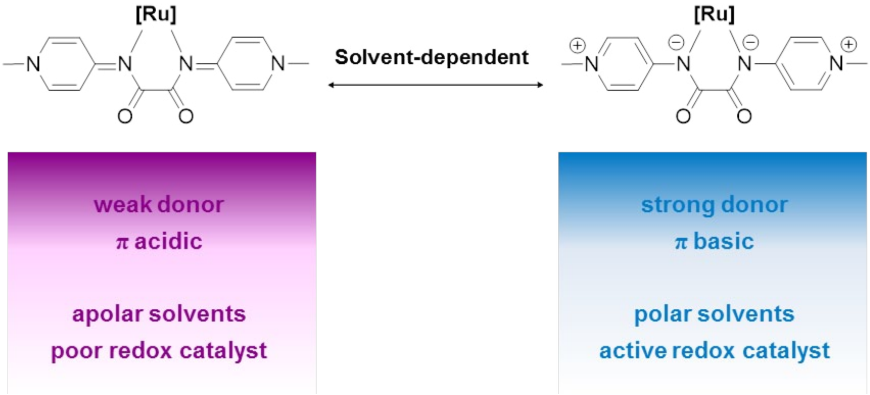
Redox-active ligands are becoming increasingly important for the development of improving the activity of transition metal complexes in their role as homogeneous catalysts.[1] These noninocent ligands, specifically ligands which display varying degrees of donor ability, are very attractive for catalytic applications, as they may stabilize several intermediates of the catalytic cycle. Pyridylideneamides (PYAs) are a new class of flexible ligands that provide access to a neutral and a mesoionic resonance structure, and which are suitable for metal coordination.[2] We have recently demonstrated the adaptiveness of these ligands in response to the external environment, such as the solvent polarity, and have exploited this donor-flexibility to enhance transfer hydrogenation catalysis.[3] Here we introduce novel chelating bis-PYA ligands and their coordination to a ruthenium(II) center. These new complexes benefit from having two mesoionic PYA moieties and their improved donor-flexibility has been explored in redox catalysis.



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Selective separation of fullerenes and endohedral metallofullerenes mediated by copper based supramolecular nanocapsules

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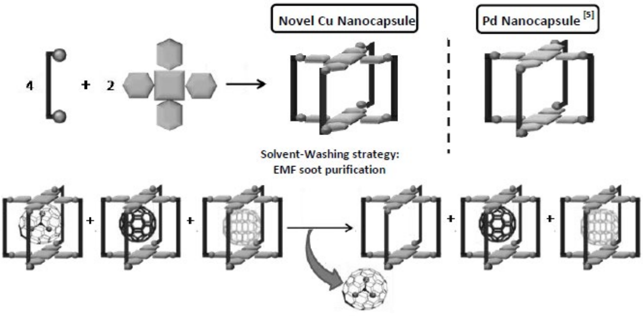
From the early stages of fullerene research, it was shown that fullerenes were able to host atoms and even small molecules in their interior.[1] Generally, fullerenes and endohedral metallofullerenes (EMFs), which are produced as a soot, need to be purified by a multistage high-performance liquid chromatography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



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Molybdenum-catalyzed oxo-transfer reactions: influence of the oxo and peroxo ligands in acylpyrazolonate-molybdenum complexes

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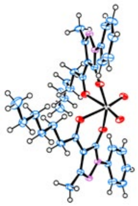
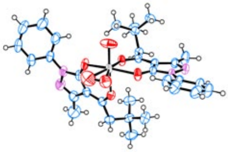
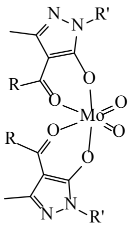
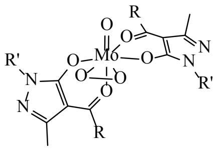
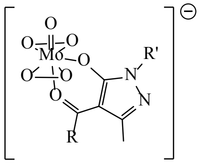
Molybdenum(IV) complexes containing dioxo, oxo-peroxo and oxo-diperoxo moieties have been reported as efficient catalysts in different oxo transfer reactions [1]. Following our interest in this area [2-5], here we describe the synthesis and the spectroscopic and structurally characterization of several dioxo, oxo-peroxo and oxo-diperoxo molybdenum complexes, containing acylpyrazolonate ligands, with the general formula $[Mo(O)_2(Q^R)_2]$, $[Mo(O)(O_2)(Q^R)_2]$ and $[Mo(O)(O_2)_2(Q^R)]^-$, respectively, where HQ^R is the 1phenyl-3-methyl-4-acylpyrazol-5-one ligand. The catalytic behaviour of these acylpyrazolone-molybdenum complexes was investigated in several oxo-transfer reactions, such as epoxidation, sulfoxidation and epoxide deoxygenation. A discussion of the results obtained, along with a comparison of the catalytic activity found for the different dioxo, oxo-peroxo and oxo-diperoxo moieties, will be presented in this communication.











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P129

Ruthenium catalyzed acceptorless dehydrogenation of alcohols in aqueous media: catalysis at the edge of homogeneous and heterogeneous catalysis

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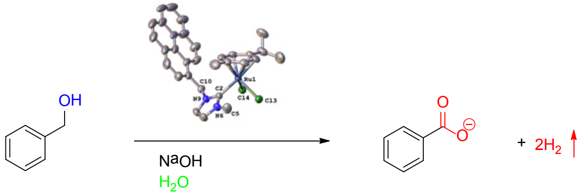
The immobilization of molecular complexes onto solid surfaces is highly desirable because it can facilitate the separation and reutilization of the catalyst. Although several reports regarding the immobilization of molecular catalysts onto silica, alumina and magnetic nanoparticles have been published, in the last years there is a tendency for using chemical derived graphenes as support. In this regard we have recently reported the immobilization of ruthenium and palladium organometallic compounds onto graphene-type materials by π-stacking interactions. [1,2]



Scheme 1

In this work we have synthesized three Ru-NHC complexes bearing different aromatic fragments that allow the immobilization of the complexes onto reduced graphene oxide by non-covalent interactions. The catalytic properties of the molecular complexes and the new hybrid-graphene materials were studied in the oxidative dehydrogenation of primary alcohols in water (Scheme 1). The results showed that the hybrid materials improve the catalytic outcomes of the homogeneous complexes, and that the immobilization of the molecular entities onto reduced graphene oxide allows the recovery and reuse of the catalyst. A plausible mechanism is proposed based on Mass Spectrometry and NMR experiments and DFT calculations.

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Formation and reactivity of a diiron(IV) oxo core

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Nature can reversibly bind and activate O_2, which are key reactions in O_2-transport and oxygenation of various substrates, in a lot of cases performed by non-heme metalloproteins with bimetallic iron centers. Through O_2-activation, these metallic centers are able to form active highly oxidizing species such as oxodiiron(IV), which are responsible of the oxidation of challenging substrates in soft conditions. So mimicking the enzymes with model diiron complexes is of significant importance to understand these mechanisms.

In this context, we target the development of diiron systems with polydentate N-donor ligands (figure 1) with the aim to promote the cleavage of the O-O bond, and to explore the reversibility of the process favored by proximity of the two metallic centers.

The reactivity of the complexes against different oxidants is studied, and high-valent iron species resulting from these reactions are characterized by spectroscopic techniques. The oxidation ability of these species is studied as well as their ability to reverse O-O bond cleavage.

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Alkynyl gold(I) derivatives as selective anticancer drugs

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Despite the effectiveness of platinum based drugs in cancer chemotherapy, the occurrence of some drawbacks such as the development of resistant tumor lines, long term-effects on renal function and lack of specificity [1], have encouraged researches to find alternatives in order to minimize these negative side-effects. In this context, gold-derivate drugs have recently emerged as new chemotherapeutic agents [2]. Two key points make gold compounds an interesting alternative to *cisplatin* and its analogues: their similar chemical behavior (both platinum(II) and gold(III) present electron configuration d^8 and square planar geometry) and its wide coordination chemistry, which allows the synthesis of many different anticancer drugs.

Special attention merits alkynyl gold phosphane complexes due to their stable Au-C bond, which confers high stability under physiological conditions in addition to antiproliferative properties [3].

Flavonoids, natural components of plants, fruits and vegetables exhibit interesting biological properties that include anticancer activity. Alkylation of 3-hydroxyflavonoids with propargyl bromide provides alkyne molecules that easily coordinate gold phosphane units giving rise to the corresponding new alkynyl gold(I) complexes, here described.

Despite all the investigation in gold-based drugs published in the last years, their mechanism of action remains unclear [4]. For this reason, we also include in this report preliminary studies on the mechanism of interaction of one alkynyl gold(I) phosphane complex that comprise the type of cellular death, its implication in cell cycle progression, the role of pro-apoptotic and anti-apoptotic caspases, the interaction with BSA, nucleic acids, their influence in the activity and expression of two important enzymes for redox balance: cytosolic Thioredoxine Reductase (TXNDR1) and Gluthathione Reductase (GR), as well as ROS formation.

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(NHC)Cu(I) Complexes bearing Dipyridylamine ligands: Synthesis, Structural, Photoluminescent Studies and Applications in LEC

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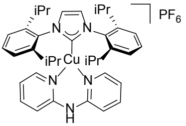
We present in this communication the synthesis of new cationic tricoordinated copper complexes bearing bidentate dipyridylamine (dpa) ligands and NHC as ancillary ligands [Cu(NHC)(HDPA)][X]. [1],[2] These copper complexes have been fully characterized by NMR, X-ray analysis, electrochemistry, and photophysics. TD-DFT calculations were also undergone to rationalize the assignment of the photophysical properties.

Some of these copper complexes exhibit very bright blue emission with high quantum yield at solid state due to TADF participation in the emission mechanism. A variation of the electronic properties on both NHC and dipyridylamine ligands, has been carried out and permitted to establish some structure – properties relationships, also supported by TD-DFT calculations.

Since emissive cationic organometallic complexes can be good candidates for LEC (Light emitting Electrochemical Cells) applications, a selection of copper complexes was achieved for the preparation of those lighting devices. Here is presented the proof of concept that our copper complexes, of general formula [Cu(NHC)(dpa)][X], can be applied for LEC devices. We are pleased to present here a blue emitting LEC device incorporating cationic copper complexes.



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Diastereoselective synthesis of titanium complexes bearing a ligand based on α-pinene as sulfoxidation catalysts

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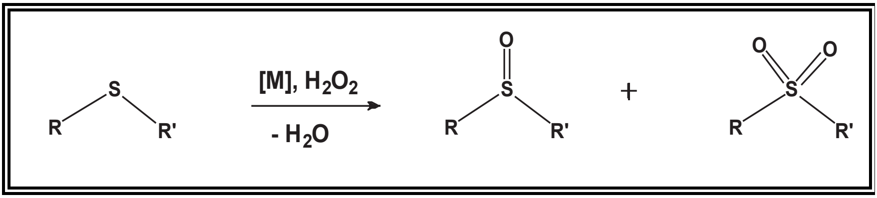
Work hypothesis and objective:

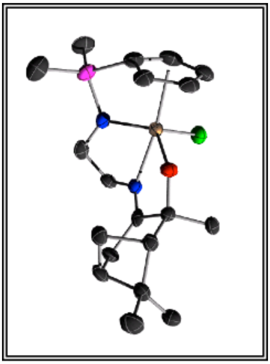
The sulfoxidation of organic sulfides is among the reactions of greater academic and industrial impact, as it is employed in the synthesis of high added value products. In addition, this process is related to the fuel desulfuration and chemical warfare destruction, providing it with vast environmental and social importance.[1,2]



Some of the aspects that are yet to resolve are the control of the process and the nature of the oxidant, which is related to the environmental sustainability.[3] For that purpose we are interested in synthesizing titanium complexes bearing a chiral ligand derived from a natural terpene, to use them as catalysts, which can induce enantioselectivity in the oxidation process.

Results:

In this work we describe the synthesis of an enantiomerically pure polyfuncionalized ligand based on α-pinene, a natural terpene. This tridentate ligand is stereospecifically introduced into the coordination sphere of titanium, rendering only one of the possible diastereoisomers. The resulting complexes have been studied as sulfoxidation catalysts using hydrogen peroxide as primary oxidant. These catalysts show remarkable activity and high selectivity towards the sulfoxide or sulfone, depending on the proportion of oxidant used.



[Ti(η5-C5H4SiMe2-κN(CH2)2-κNpinene-κO}Cl]

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Oxidations catalyzed by an imine-based iron (II) complex: a mechanistic perspective

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Nonheme iron complexes represent promising catalysts to achieve a reliably selective aliphatic C-H bond oxidation. Ligand structure has a deep impact on catalyst's activity and selectivity, with good regioselectivities usually requiring elaborated ligand structures. This feature often leads to expensive and difficult to obtain complexes, which can limit the attractiveness of this synthetic methodology.[1]

In this context we studied a simple nonheme iron complex which can be prepared in situ from cheap and commercially available reagents. This complex is able to catalyse C-H bond oxidation with good TONs (in the order of 40),[2] although the complex is coordinatively saturated. The reaction occurs without involvement of free radical species, and from a mechanistic point of view the active species is proposed to be a pentadentate, metal-based oxidant. The first step of the catalytic cycle is the oxidation of Fe(II) complex 3 into Fe(III). Then, the Fe(III) complex loosens the coordination of a pyridine arm in order to host and activate H2O2 (Fig. 1). Eventually the oxidative degradation pathway of the catalytic species has been studied.[3]

Catalytic activity of this complex in some hydrocarbon oxidations, together with its full characterization and a deep mechanistic investigation of its oxidation reaction, will be here reported.

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Posibilities in the use of primary amines as potential hydrogen storage systems

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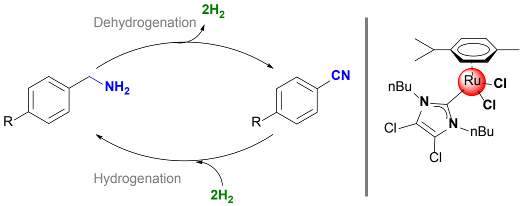
The utility of molecular hydrogen as an alternative energy source requires scientific and technological developments on its industrial production and storage [1]. The sustainable production requires the use of renewable energies to obtain hydrogen from water. This production leads to the development of efficient ways of hydrogen storage. Among others, liquid organic hydrogen carriers (LOHC) show potential applications for hydrogen storage. Recently the amine/nitrile couple has been proposed as a promising system for hydrogen storage [2]. Nitriles are important functional groups with many applications in synthetic chemistry and the reduction process to amines is well defined. Alternatively, amines can be dehydrogenated to nitriles by the use of transition metal catalysis although developments in this field are still scarce.



Scheme 1

In this work we describe the preparation of Ru-NHC (NHC = N-heterocyclic carbene) complexes and the catalytic applications in the dehydrogenation of primary amines. The procedure described allows the formation of nitriles with the concomitant liberation of hydrogen and without any additive (Scheme 1). A plausible mechanism for the acceptorless dehydrogenation of primary amines is proposed based on experimental evidences.

The authors thank the financial support from MINECO (CTQ2015-69153-C2-2-R), Generalitat Valenciana (AICO/2015/039) and Universitat Jaume I (P1.1B2015-09). The authors are very grateful to the 'Serveis Centrals d'Instrumentació Científica (SCIC)' of the Universitat Jaume I.

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Competitive Mechanisms in the Aromatic C-H Bond Functionalisation Mediated by Coinage-Metal Catalysts: A Computational View

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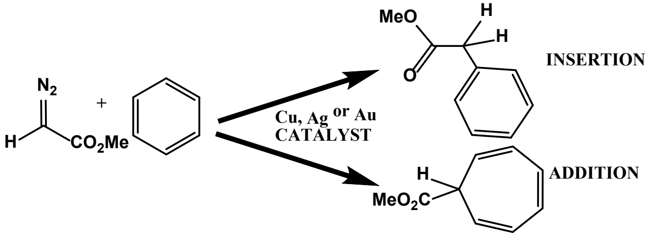
The transfer of carbene units from diazo compounds to different types of nucleophiles has been exploited to generate new value-added products by means of a catalyst. An important contribution in the area has been performed by the group of Pérez that has developed different coinage-metal catalysts with the tris(pyrazolyl) borate or N-heterocyclic carbene based ligands to functionalise a variety of organic compounds.[1,2,3] In our group we have computationally investigated the reaction mechanisms for which a variety of such processes take place, providing information on the nature of the intermediates, the different roles of the catalyst as well as the other species present in the reaction media.[2,4,5]

Recently we have computationally investigated the functionalisation of aromatic C-H bonds by carbene transfer and catalysed by coinage-metal complexes (Cu, Ag and Au) bearing an N-heterocyclic carbene based ligand. Experimentally it has been observed that the catalytic process can follow two different mechanisms: insertion into an aromatic C-H bond or addition to the aromatic six-member ring expanding it to cycloheptatriene. Computational insight on the reaction mechanisms, on the factors affecting the balance between the competitive mechanisms, and the role of the metal will be presented.



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Allyl complexes of Ni(II) and Pd(II) with bulky terphenyl phosphanes: synthesis and catalytic activity

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In recent years, a high degree of interest has been placed on bulky phosphanes as ligands in palladium-catalysed cross-coupling reactions.[1] Recently, in our research group we have prepared a new family of dialkyl terphenyl phosphanes.[2] In this communication we report on the synthesis and structural characterisation of a series of neutral and cationic allyl-nickel(II) and -palladium(II) complexes bearing these phosphane ligands of composition $[MCl(\eta^3\text{-}C_3H_4R)(PR'_2Ar'')]$ or $[M(\eta^3\text{-}C_3H_4R)(PR'_2Ar'')]BAr^F$ (M = Ni, Pd). (Figure 1). The performance of these species in C-C and C-heteroatom bond forming reactions is also accounted.

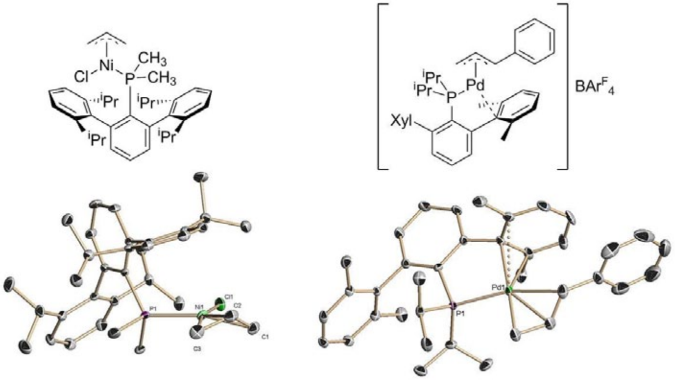

Figure 1. Some complexes prepared in this work.

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Electronic Effects and Mechanistic Insights on Cobalt-Catalyzed C-H Activation: Alkyne Insertion vs Alkoxylation

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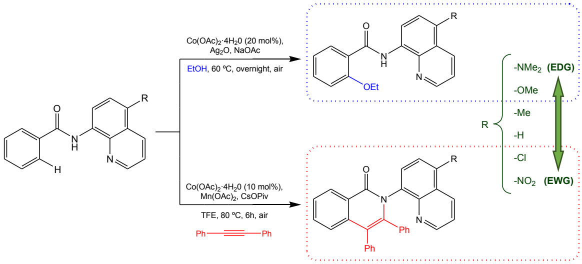
In the last few years, 8-aminoquinoline turned to be an excellent directing/chelating group for C-H bond activation. In addition, its high-potential as building blocks in organic chemistry and pharmaceutical compounds make its derivatization more attracting. On this behalf, Daugulis' [1] and Stahl's [2] published simultaneously in 2013 the first example of Cu-catalyzed C-H activation with this chelating group. In the same year, Chatani and co-workers described the Ni-alkylation of benzamides containing 8-aminoquinoline moieties.[3] Alternatively, the field of Co-catalyzed C-H activation has recently started to receive significant attention, replacing second and third row transition metals with cheaper, more abundant first row transition metals.

The Co-catalyzed alkyne addition reaction on 8-aminoquinoline derivatives has been studied by Daugulis [4], Ribas [5] and others, following a conventional organometallic mechanism (oxidative addition / reductive elimination). Nevertheless, very recent studies from Song [6] and Ribas [7] suggested a Single Electron Transfer (SET) mechanism for the alkoxylation and nitration reactions of this substrate. Herein, we try to obtain some experimental evidence to shed some light on the different proposed mechanisms by the aforementioned authors, tuning the electronics of the substrate by modifications of the backbone of the 8-aminoquiniline moiety.



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P139

Catalizadores de Ir basados en ligandos pincer nhc activos en reacciones de autotransferencia de hidrógeno

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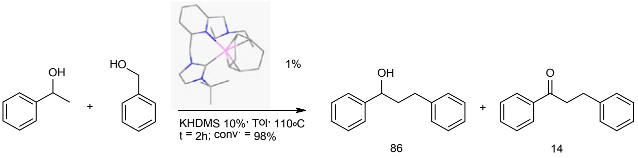
El desarrollo de catalizadores homogéneos posee un papel crucial en química sostenible ya que está asociado al diseño de ligandos con capacidad para influenciar las propiedades del centro metálico y al conocimiento detallado del mecanismo de las reacciones que permiten el rediseño de los mismos, con el objetivo de producir transformaciones más limpias, con elevada economía atómica y altamente selectivas. En este contexto, los ligandos carbeno N-heterocíclicos (NHC) han pasado de ser una curiosidad de laboratorio a constituir la unidad básica para el diseño de nuevos catalizadores homogéneos de metales de transición que han mejorado muchas transformaciones en gran medida y por ello, son la plataforma adecuada para el diseño de catalizadores en procesos químicos sostenibles [1].

El diseño de catalizadores con arquitecturas de tipo pincer basadas en un esqueleto piridina-NHC que incorporan un fragmento básico o de naturaleza hemilábil tienen el potencial de activar procesos de cooperación metal-ligando a través de la aromatización/desaromatización del anillo de piridina. Estos ligandos confieren una gran flexibilidad estructural que permite acomodar diferentes geometrías o requerimientos electrónicos a lo largo del ciclo catalítico, mediante la protección reversible de una posición de coordinación a través de un efecto quelante alternante [2].

La alquilación deshidratante de enlaces C-H y N-H con alcoholes es una aproximación interesante en el desarrollo de protocolos sintéticos para formar nuevos enlaces C-C y C-N ya que muestran una alta eficiencia atómica y un gran potencial sintético. Nuestro grupo de investigación ha descrito complejos de iridio basados en ligandos NHC-con grupos hemilábiles que son muy eficaces en reacciones de transferencia de hidrógeno, en oxidación de alcoholes y en β-alquilación de alcoholes secundarios [3]. En este trabajo, se describe una nueva familia de complejos pincer-py-NHC-grupos hemilábiles con gran actividad en reacciones de autotransferencia de hidrógeno (β-alquilación y N-alquilación) con completa conversión en cortos periodos de reacción y buena selectividad. Estos resultados preliminares justifican el estudio de la reactividad de este tipo de complejos en mayor detalle y profundidad.



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Constrained-hapticity complexes: impact of strong intramolecular coordination

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The mechanism of the $\eta^5\leftrightarrow\eta^3$ ring slippage of indenyl ligand is intensively studied, since the significant role of haptotropic rearrangement on reactivity of molybdenum organometallic compound has been revealed [1]. Understanding of the mechanism is necessary for design lowhapticity complexes which are unique both for chemical reactivity and from structural aspect. As reported recently, hapticity of the indenyl ligand can be easily modified by coordination of the multidentate or bulky ligand [2,3]. Nevertheless, the impact of strong intramolecular coordination has not been described yet. The present work is focused on indenyl complexes of molybdenum and tungsten with intramolecularly coordinated quinoline fragment. Series of newly synthesized complexes exhibit unprecedented structural motif consisting of η^3-bonded indenyl ligand and intramolecularly coordinated nitrogen atom.

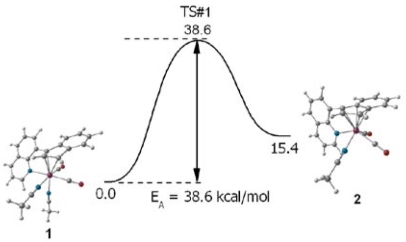

Fig 1. Energy profile of haptotropic rearrangement. Electronic energies (kcal/mol) are related relative to the energy of the complex **1**.

To get an insight into unusual stability of these η^3-indenyl compounds, density functional theory calculations at B3LYP/LANL2TZ level of theory were performed. Theoretical study proved that strong donor-acceptor N®Mo interaction leads to kinetic stabilization of the complexes with η^3-coordinated indenyl ligand (**Fig. 1**). In addition, theoretical survey show that rotation of indenyl ligand is a key step of haptotropic rearrangement.

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P141

Guanidinate-osmium(II) complexes: synthesis and application in the selective dehydration of aldoximes

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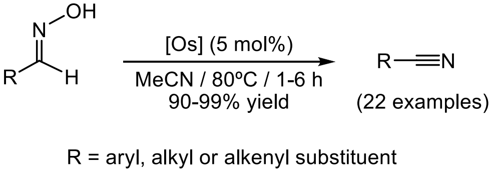
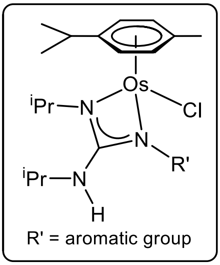
The dehydration of aldoximes represents a convenient and benign method for the synthesis of nitriles, avoiding the use of the toxic cyanide sources commonly employed in the preparation of this important class of compounds. Although the process has been extensively studied and applied in synthetic organic chemistry, the conventional protocols involve stoichiometric amounts of reagents and suffer from substrate scope limitations [1]. More appealing methodologies have emerged in recent years employing metal catalysts, which usually operate under milder reactions conditions and with higher functional group compatibility.





In this context, we describe herein the synthesis of the first arene-osmium(II) derivatives with guanidinate ligands, and their catalytic activity in the dehydration of aldoximes [3]. These complexes turned out to be efficient and selective, allowing the high-yield preparation of a great variety of nitriles.

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Halogen Salt Catalysed Diboration Reaction

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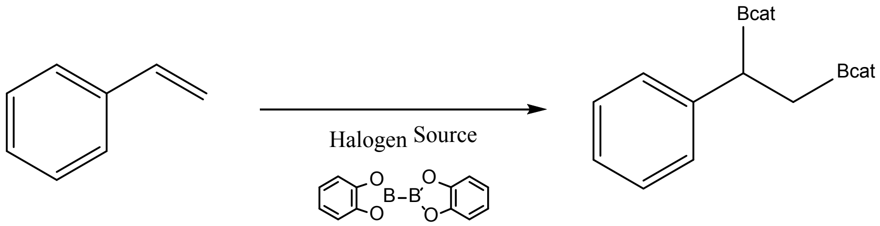
The usefulness of the carbon-boron bond has meant that boron chemistry is an area that has attracted the attention of many researchers all aiming to develop new techniques. Sp^2-sp^3 tetra-alkoxy diboron compounds have attracted considerable attention over the past few years as a source of nucleophilic boryl moieties as they can be prepared through easy to handle diboron reagents using transition metal free catalysis[1].

Transition metal free methodologies requires first the activation of the diboronic ester by a Lewis base which results in the hydridisation state of the diboron reagent becoming an sp^2-sp^3 diboron complex. These sp^2-sp^3 diboron complexes have been applied to different reactions such as β-boration or diboration reactions.

The current methodologies for the activation of the diboron reagent present a few drawbacks for example functional group compatibility or low assymetric approach of the reactions. To solve these problems a new method for the activation of the diboron reagents is required. We have developed a novel transition metal free methodology for the activation of diboron reagents using a halogen salt catalyst. This is a revolutionary new method, it is green and more sustainable than current methods which opens new doors and presents a solution to the current drawbacks of the reaction.



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Síntesis y coordinación de nuevos ligandos aminometilfosfina

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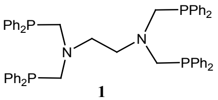
El diseño de ligandos de tipo aminometilfosfina [1] y de sus correspondientes complejos metálicos [2] ha merecido elevado interés por la interesantes aplicaciones que pueden presentar estos sistemas en medicina o en catálisis [2].

La sal de fosfonio $[PPh_2(CH_2OH)_2]Cl$, en presencia de trietilamina, reacciona con diaminas originando la formación de las correspondientes aminometilfosfinas



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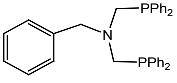

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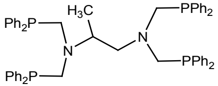
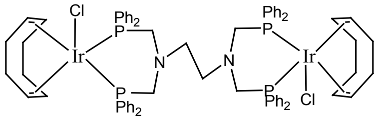


3

Los compuestos **1-3** se coordinan a metales de transición por los átomos de fósforo de manera bidentada quelato. Mientras que **1** y **3** conducen a la formación de complejos dímeros, **2** origina monómeros. Además **3**, que contiene un carbono quiral, podría originar la formación de distintos diasteroisómeros. **1** y **2** reaccionan con $[MCl(diolefina)]_2$ (M = Rh o Ir, diolefina = COD o NBD) originando los correspondientes complejos. Así, con $[IrCl(COD)]_2$ se obtienen **4** y **5** respectivamente.



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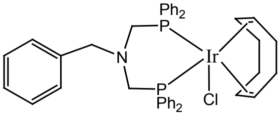
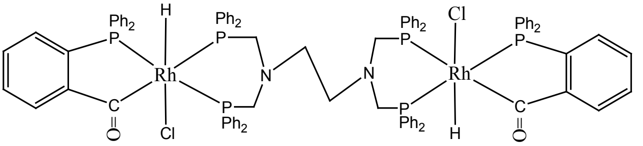


5

Este tipo de complejos puede experimentar adición oxidativa por reacción con *orto*difenilfosfino benzaldehido (PCHO). Así, se ha obtenido el complejo de rodio(III) (**6**)



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Efects of ligands on the reactivity of tantalum organometallic complexes with water: synthesis of organometallic hydroxides

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Hydroxide complexes have been postulated as key intermediates in several catalytic reactions in which water is a substrate as well as in the synthesis of metal oxides through condensation reactions [1]. Moreover, organometallic hydroxides are convenient precursors for the synthesis of heterometallic complexes with M-O-M´ fragments [2].

In this communication, we report the synthesis of tantalum hydroxide complexes stabilized by hard donor polydentate ligands with the aim of understanding their role on the water solubility of the resulting tantalum derivatives.

As an example, the reaction of [TaCp*Me_4] with citric acid and water yields the dimetallic complex [{TaCp*(HCIT)(OH_2)}(μ-O){TaCp*(H_2CIT)(OH)}] (H_4CIT = citric acid). The presence of protonated carboxylate groups as well as that of water molecules and hydroxide ligands play an important role in the formation of the crystal lattice in which two dimetallic molecules are interacting with each other through strong hydrogen bonds (Figure 1).

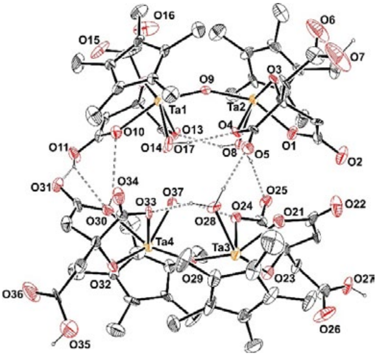

Figure 1

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A Mechanistic DFT Study on the Rh-NSiN Catalyzed Dehydrogenative Silylation of Ketones with Silanes

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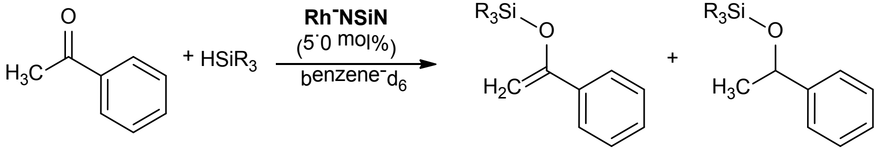
The reaction of acetophenone with $HSiMe(OSiMe_3)_2$ and $HSiEt_3$ in presence of catalytic amounts of the rhodium complex $[Rh(H)(CF_3SO_3)(NSiN)(coe)]$ (coe = cis-cyclooctene; NSiN = bis(pyridine-2-yloxy)methylsilyl fac-coordinated) leads to mixtures of the corresponding silyl enol ether and silyl ether. This complex has proved to catalyze the hydrosilylation of CO_2.[1]

Based on the experimental results found, a detailed study on the reaction mechanism has been carried out DFT calculations obtaining the rate determining step of the process. The reaction mechanism starts when the catalyst precursor is activated by hydrogenation of a cyclooctene following migratory insertion and hydride transfer mechanisms. The active catalyst coordinates a molecule of silane and it may transfer a silyl group to the ketone, assisted by the triflate ligand. The silyl ether can be released by hydride transfer from a silane molecule. Alternatively, C-H β-elimination may occur if there is a vacancy at the metal forming a hydride intermediate and the silyl enol ether. Then, the hydride can release hydrogen gas regenerating the active catalyst.



SiR$_3$ = SiMe(OSiMe$_3$)$_2$

Rh-NSiN = [Rh(H)(CF$_3$SO$_2$)(NSiN)(coe)]

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From trimethyl phosphite to dimethyl phosphonate at iridium(I): the decisive effect of an intramolecular hydrogen bond

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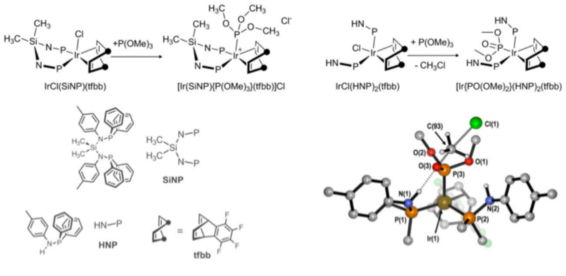
In the last years bifunctional metal-ligand systems – metal-ligand systems containing at least one functional group in the backbone of the ligand – have attracted increasing interest.[1] It has been shown that their ability to provide an extra site for non-covalent interactions of incoming substrates with the metal-ligand platform can be decisive in determining the outcome of both stoichiometric and catalytic reactions. Thus, both the elucidation of the elementary steps of the overall transformation and the detailed description of the interaction(s) of the incoming substrate with the metal-ligand platform have become a major issue in the investigation on bifunctional systems.

On this background and in the framework of our studies on iridium complexes with the amino-phosphano ligands[2a,b] we have synthesized metal complexes containing either SiNP (SiNP = $SiMe_2\{N(4\text{-}C_6H_4CH_3)PPh_2\}_2$) or the parent amino-phosphane HNP (HNP = $NH(4\text{-}C_6H_4CH_3)PPh_2$) and we have investigated the influence of the N-H group on the reactivity of the complexes (Scheme 1). Herein we report novel iridium(I) complexes of formula IrCl(SiNP)(tfbb) and $IrCl(HNP)_2(tfbb)$ (tfbb = tetrafluorobenzobarrelene) and the study of their reactivity with trimethyl phosphite showing the decisive role of the N-H group in the formation of the phosphonato group in $Ir\{PO(OMe)_2\}(HNP)_2(tfbb)$ (Scheme 1).

The thermodynamic and kinetic effects of the N-H group in the formation of the phosphonato ligand has been established by IR and NMR spectroscopic measurements and elucidated by DFT calculations.[2c]



Scheme 1

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From molecular to hybrid metal oxide nanocatalysts for the oxidation of water to dioxygen

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1. Introduction - Molecular hydrogen is a promising candidate for replacing fossil fuels as energy sources. However, its renewable and clean generation is still a great challenge. A particularly attractive solution is the production of this gas from water splitting (WS) by sunlight (Eq. 1), that is, sunlight is used to promote a thermodynamically uphill reaction where water is transformed into molecular oxygen and hydrogen[1]. Therefore, an enormous progress has been recently made on the development of catalysts to speed up the set of redox half-reactions involved (Eq. (2) and (3)).

$$2H_2O \rightarrow 2\,H_2 + O_2 \quad (1)$$
$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \quad (2)$$
$$2\,H^+ + 2e^- \rightarrow H_2 \quad (3)$$

Water oxidation (Eq. (2)) is still nowadays the bottleneck reaction hampering the development of commercial devices for the photo-production of hydrogen.

2. Results and Discussion – both molecular species and metal oxides are plausible candidates for efficiently catalyze this challenging reaction. In general terms, despite high turnover frequencies (TOFs) are obtained with molecular catalysts, the generation of rugged catalysts achieving large turnover numbers (TONs) with no decomposition is still a challenge. However, if durability is the main challenge for molecular WOCs, slow reaction rates are common when their heterogeneous or colloidal counterparts are employed. The lack of both mechanistic and surface chemistry information prevents the rational development of faster nanomaterials for this transformation. This contribution will deal with the work carried out in our laboratories to unravel the key factors that can change these general trends, finally obtaining fast and robust molecular-based anodes[2,3] and extremely fast metal oxides nanocatalysts[4,5] for the oxidation of water.

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Physicochemical characterization of $\{[Cu(Cl)(pn)_2]\}_nNO_3$ cationic coordination polymer in solid state and solution

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Coordination polymers have a great attention in many area of chemistry due to their interesting topologies and potential applications [1-3]. During synthesis this type of compounds, several factors such as appropriate metal ion and its counter ion, organic ligand, molar ratio of substrates, solvent, temperature and pH values have influence on desirable final structure [4].

The presented project involved the synthesis of $\{[Cu(Cl)(pn)_2]\}_nNO_3$ cationic coordination polymer, physicochemical studies and its possible application as visual acid-base indicator. Structural assay was carried out using X-ray diffraction experiment, which was supported by spectroscopic methods (FT-IR, UV-Vis) and thermogravimetry. The obtained results confirmed distorted tetragonal bipyramide geometry of both copper centers. Taking into account the donor sites of pyridoxine (*pn*), we showed that metal ion was surrounded by two bidentate bio-ligands and one simple monodentate ligand. The deprotonated phenolic oxygen at C^3 position and adjacent phenolate oxygen took part in coordination of central atom. In the thermogravimetric studies of Cu(II)-vitamin B_6 cationic coordination polymer, the compositions and stabilities in narrow temperature ranges were confirmed. After fully physicochemical characterization of obtained compound in solid state, we examined its behavior in solution. We confirmed presence of redox-active metal centre by cycling voltammetry measurement in DMF. The acid-base equilibria of synthesized compound were determined by using two independent methods: potentiometric and spectrophotometric titrations. The change of color after addition strong acid (yellow) and back to the original color after the addition of a strong base (green) demonstrates the reversibility of these equilibria. Furthermore, possible application of copper(II)-vitamin B_6 cationic coordination polymer as visual acid-base indicator was investigated. The obtained results demonstrated that examined compound can be used as sensing material to distinguish strong acid among weak acid.

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P149

Group Six Metal Complexes with 2,6-Diaminopyrimidine-based PCP Pincer Ligands

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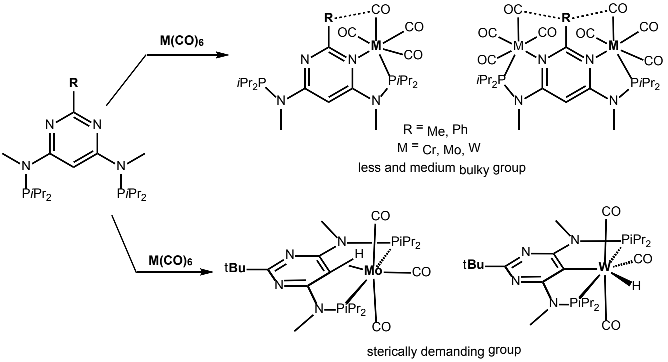
The combination of activity, stability and variability make pincer ligands interesting for many different areas of chemistry including catalysis. A series of pyrimidine-based PCP ligand systems have been successfully introduced for non-precious transition metal complexes. A big advantage of this type of ligands is their modular design by changing the phosphine moiety, the amine linker and the ligand backbone. [1-3]



In this study we report the synthesis of a new series of PCP pincer ligands and complexes based on 2,6-diaminopyrimidine scaffold. The ligands can easily synthesized on a large scale. $M(CO)_6$ (M = Mo, Co, W) was used as metal precursor for the complexation of the new PCP pincer ligands. The goal was to investigate the influence of the para substituent of the pyrimidine moiety on the complexation properties of the PCP ligands. PCP ligands with sterically little demanding substituents coordinate in k^2-P,N fashion, act even as bridging ligand, while bulky groups at the PCP ligand enforce coordination in the typical k^3-P,C,P mode or in a more unusual k^3-P,CH,P fashion with an agostic C-H bond.

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P150

Total Synthesis of the Anti-inflammatory and Pro-resolving Lipid Mediator Maresin n-3 DPA Utilizing an sp3–sp3 Negishi Cross-Coupling Reaction

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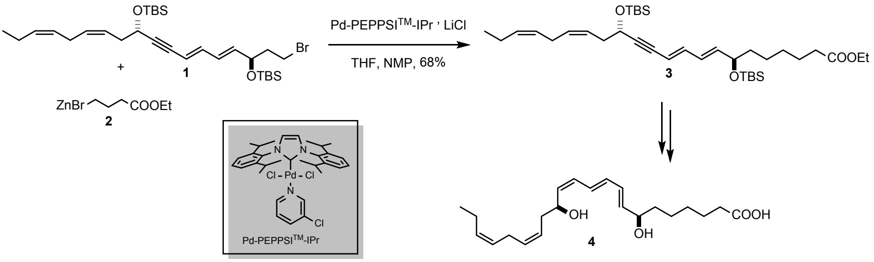
In recent years, important discoveries have been made in the Serhan laboratory regarding the identification, structural elucidation and biological properties of several di- and tri-oxygenated derivatives of eicosapentaenoic acid, docosahexaenoic acid and n-3 docosapentaenoic acid.[1] As a consequence of the protective effects of the oxygenated derivatives during acute inflammation, as well as their ability to assist in the timely termination or resolution of inflammatory processes, this class of compounds is now known as specialized pro-resolving lipid mediators.

The first total synthesis of the lipid mediator MaR1 n-3 DPA has been achieved in 12% overall yield over 11 steps (longest linear sequence).[2] An integral step in the preparation of said natural product involved a Pd-catalyzed sp3–sp3 Negishi cross-coupling reaction between alkyl bromide **1** and 4-ethoxy-4-oxobutylzinc bromide (**2**). Then, following a few additional manipulations, maresin n-3 DPA (**4**) was obtained. Synthetic **4** displayed potent pro-resolving properties stimulating macrophage efferocytosis of apoptotic neutrophils.



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Copper nanoparticles and glycerol for sustainable catalysis

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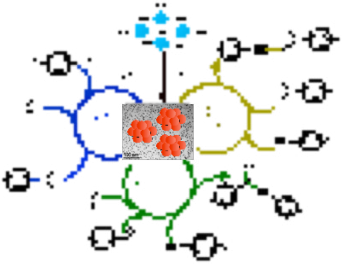
The use of metal nanoparticles (NPs) in catalysis has become more and more attractive for industrial applications [1]. "Nanocatalysis", combining colloidal catalysis and catalysis based on engineered nano-objects, reveals the ability to modify the pathway and selectivity of organic transformations [2]. Concerning solvents, glycerol is considered as an environmentally friendly medium which also permits to immobilise the catalyst, to easily extract the organic products and to recycle the catalytic phase [3]. Based on our previous researches [4], in this communication we report the synthesis of well-defined Cu(0)NPs and their applications in direct C-N bond formation processes, C_{sp3}-H bond alkynylation and three-component A^3 (aldehydes, amines and alkynes) coupling via C-H activation.



CuNPs in neat glycerol and in the presence of poly(vinylpyrrolidone) (PVP) were synthesised under H_2 atmosphere. The effect of the nature of the starting Cu precursors was in particular evaluated. Direct TEM analyses of the resulting colloidal suspensions in glycerol showed the formation of spherical, small (ca. 2 nm) and well-dispersed nanoparticles starting from $[Cu(\kappa^2\text{-}N,N\text{-}TMEDA)(\mu\text{-}OH)]_2Cl_2$, Cu^I/mesityl or CuOAc, but only agglomerates were observed using $Cu(OAc)_2$. The as-prepared copper materials were fully characterised both in colloidal and solid state, by UV-Vis, XRD, HR-TEM, XPS and cyclic voltammetry analyses.

These nanocatalysts were successfully applied in C-N bond formation reactions between aryl halides and amines (including aqueous ammonia), leading to the expected products in high isolated yields. In addition, propargylamines have been selectively synthesised by two different ways: i) oxidative C-C cross coupling of tertiary amines with terminal alkynes using t-BuOOH as oxidant; and ii) a one-pot three-component A^3 process using aldehydes, amines and alkynes. Furthermore, CuNPs-based catalysts in glycerol permit an easy catalyst preparation and handling, together with a convenient recycling.

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Slurry-phase hydrocracking of heavy oil in the presence of organometallic precursors

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Due to the growing demand of transportation fuels and worsening quality of supplied crude, heavy oil upgrading (HOU) has attracted much attention from oil refinery industries[1]. Among HOU technologies, slurry-phase hydrocracking (SHC) allows the total conversion of the bottom of the barrel while the other technologies are suffering from low yield of valuable distillate, catalyst deactivation, limited feedstock flexibility, significant amount of coke formation, and consequent process instability[2]. To make SHC processes commercially viable, efficient design of hydrocracking catalysts is essential. Oil-dispersed catalysts containing Mo, Ni, Co, Fe are used for SHC and should be prepared to meet the following criteria; efficient control of product distribution, low hydrogen consumption, high dispersion in heavy oil feedstock, minimization of expensive metals and deep conversion of residue molecules. In this presentation, the hydrocracking performance, H2 consumption and reaction conditions of several new dispersed catalysts including organometallic precursors will be discussed.

Table. Hydrocracking of vacuum residue over various organometallic precursors

catalysts	products					
	gas	naphtha	middle distillate	gas oil	residue	Coke
VR itself	-	-	-	18.0	82.0	-
thermal cracking	11.9	16.8	25.3	16.0	8.5	21.6
Mo-octoate	12.5	15.9	31.1	27.3	10.3	2.9
Ferrocene	17.1	20.2	28.3	18.3	8.7	7.4
Mo-KRICT-1	15.4	13.1	32.6	28.0	9.0	1.9
Mo-KRICT-2	14.3	12.5	34.2	26.3	10.3	2.4

Thermal and catalytic hydrocracking of vacuum residue (VR) were carried out. In a typical experiment, the batch type autoclave was charged with 40g of VR, pressurized with 80bar of H2 and heated to 430oC for 4 hours in the presence of 250-400ppm of metal (Mo or Fe). At the end of the run, the autoclave was rapidly quenched and the gas was collected into a sampling bag for GC analysis. The liquid and solid products were recovered with toluene. Liquid fraction was analysed by GC simulated distillation analysis (SIMDIS). Chemical properties of raw material, VR are as follows: Saturates 4.0%, Aromatics 61%, Resins 18%, Asphaltene 17%, S 5.5%, N 0.4%, Ni 36ppm, V 151ppm, MCR(micro carbon residue) 20.5%.

The goal of hydroconversion is to maximize liquid yield and minimize coke and gas at high residue conversion. As shown in Table, it is clear that in the presence of H2 and metal precursors, comparing with thermal cracking, coke formation decreases from 21.6% upto 1.9% and liquid (middle distillate, gas oil) yield increases. Mo-based oil-dispersed precursors seem to be better than Fe-based precursors. Although VR conversion is thermally controlled, the addition of organometallic catalyst significantly affects the product selectivity and quality.

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Manganese-catalyzed C-H oxidation by molecular oxygen

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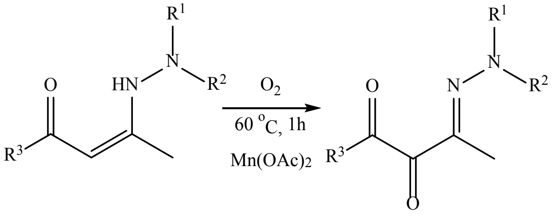
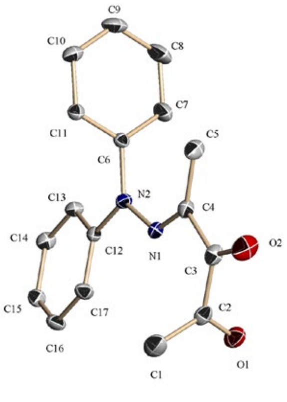
The activation of molecular oxygen for selective oxidation of organic substrates is an essential transformation in organic chemistry at both a laboratorial and industrial level [1]. Molecular oxygen is kinetically quite stable towards reaction at room temperature, but its thermodynamic tendency for reactions with organic substrates is combustion. Consequently, hydrocarbons usually react with O_2 via a complex free-radical pathway called autooxidation. These reactions are typically not selective and offer little synthetic utility. Therefore, developing new selective procedures to oxidize C-H bonds under an aerobic atmosphere are particularly intriguing and desirable [2]. Following our interest in this area [3-4], here we describe a mild and practical protocol for manganese-catalyzed aerobic oxidation of C-H bonds in β-keto-enehydrazines compounds to afford novel a,β-dioxo-hydrazones.





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Study of the electronic effects in the water/proton reduction process catalyzed by pyridilamino cobalt complexes

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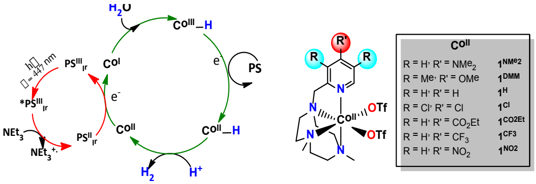
Hydrogen is one of the best candidates as a renewable fuel for future applications. Therefore, efficient H_2 production has become a new challenge in chemistry and the light-driven water reduction (WR) seems to be the better way to obtain H_2. Thus, it results essential to develop new stable catalysts in aqueous solution and atmospheric oxygen, which could work at low overpotentials.[1]

In our group we have synthesised and characterised a set of seven Co(II) complexes derived from the tetradentate ligand Py(tacn) where the pyridine ring has been modified with electron-donating (EDG) or electron-withdrawing groups (EWG). Their catalytic activity in the water reduction process has been evaluated under photochemical conditions (using $[Ir(ppy)_2(bpy)]PF_6$ as the photosensitizer and NEt_3 as the electron donor).[2]



Co^{II}

R = H, R' = NMe_2	1^{NMe2}
R = Me, R' = OMe	1^{DMM}
R = H, R' = H	1^{H}
R = Cl, R' = Cl	1^{Cl}
R = H, R' = CO_2Et	1^{CO2Et}
R = H, R' = CF_3	1^{CF3}
R = H, R' = NO_2	1^{NO2}

Figure 1. Mechanism of the photocatalytic WR process and structure of the Co(II) catalysts studied.

In order to characterise the electronic structure of the active species in the catalytic cycle, DFT calculations have been performed. An analysis of the spin density of the formal Co(I) species has revealed remarkable differences in the electronic structures of the catalysts substituted with EDG in comparison to the catalysts substituted with EWG. The theoretical E° (V) and pK_a have been calculated and they have been compared with the experimental E° (V) values and the Hammett constants.[3] Finally, two different plausible mechanisms have been evaluated in order to elucidate the role of the pyridine ring and the metal centre on the proton reduction process.

The combination of computational and experimental tools will allow us to unravel which are the active species in solution and how to modify our catalytic system in order to obtain more efficient catalysts for the water/proton reduction process.

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New catalytic activation of n-h bond by substituted vinylsilanes

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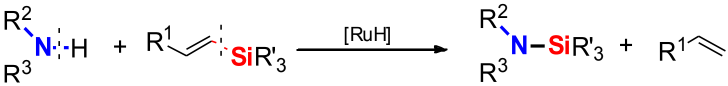
Silylamines have a variety of application such as silylating and coupling agents, ligands for organometallic compounds and precursors for ceramic materials [1]. Main way for preparation of silylamines involves reaction of chlorosilanes with amines proceeding with elimination of stoichiometric amounts of HCl [2]. Catalytic dehydrocoupling of amines with hydrosilanes leads also to Si-N bond formation.

The research on catalytic activation of N-H bonds is an extension of the successful activation of O-H bonds in silanols and boronic acids by vinylsilanes, vinylgermanes and vinylboranes reported by our group in the last decade [3].

In the communication, we present new catalytic coupling reaction that involves activation of the N-H bond in primary and secondary amines by substituted vinylsilanes and divinylsilanes to yield silylamines. The reaction proceeds in the presence of ruthenium-hydride catalyst with the formation of the olefin as a single by-product [4].



Mechanistic studies including catalytic and deuterium labeling experiments using NMR and GC-MS analyses will be also discussed.

Acknowledgment

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Cyclopalladation reactions of 3-substituted benzofuran and benzothiophene nuclei

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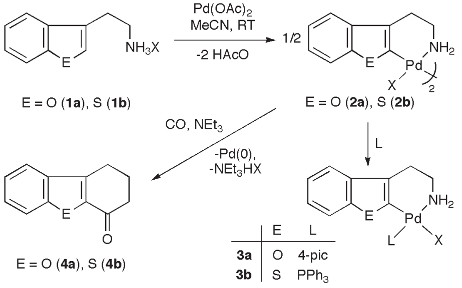
The field of transition-metal mediated or catalysed C–H activation followed by further functionalization has undergone an exponential growth in the last decade, in particular those processes involving cyclopalladation reactions of aromatic substrates containing a suitable directing group.[1] These synthetic methodologies have been applied to the functionalization of heterocycles such as indoles,[2] a topic of tremendous importance since such heterocycles have a widespread presence in pharmaceutical products and natural cores. Nevertheless, only in a few cases the metalated intermediates have been isolated and characterized.[3] Our group has been interested in the study of cyclopalladation reactions of unprotected primary amines for long time.[4] In this work, we have studied the cyclopalladation reactions of the benzofuran and benzothiophene nuclei **1** bearing a primary amine moiety as directing group in the 3-position. The cyclopalladated complexes **2** can react with neutral ligands such as PPh_3 or 4-picoline to give the mononuclear derivatives **3**. The Pd–C bond present in palladacycles **2** are reactive towards unsaturated species like CO, producing the lactams **4** upon decomposition of the acyl intermediates. The development of palladium-catalysed functionalization of these heteroaromatic nuclei is currently underway in our laboratories.



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Synthetic and Predictive Approach to Unsymmetrical Biphenols by Iron-Catalyzed Chelated Radical–Anion Oxidative Coupling

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An iron-catalyzed oxidative cross-coupling of phenols with arenes in 1,1,1,3,3,3-hexafluoropropan-2-ol [1] was exploited to develop oxidative unsymmetrical biphenol coupling that proceeds via a chelated radical–anion coupling mechanism. Based on mechanistic studies, electrochemical methods, and density functional theory calculations, we suggest a general model that enables prediction of the feasibility of cross-coupling for a given pair of phenols[2].

References

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A Suitable Strategy to Prepare N-Substituted Niobium Complexes

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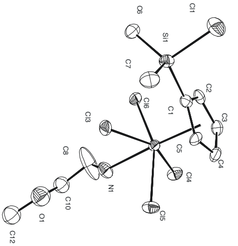
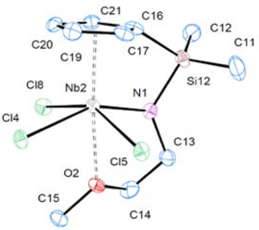
Transition-metal complexes containing nitrogen based ligands, such as amido and imido, acting as a reactive site continue to generate a great deal of interest on account of their crucial role in many stoichiometric and catalytic reactions, such as in olefin metathesis, Ziegler-Natta polymerization, hydroamination reaction, and ring-opening metathesis polymerization [1,2].

One of our ongoing research lines is focused on developing a versatile synthetic strategy for transition metal complexes bearing a polydendate ligand based on protonolysis reactions of Si-Cl and M-Cl bonds from chlorosilyl-substituted cyclopentadienyl compounds, $[M(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_n]$ (M = group 4, n = 3; M = group 5, n = 4) [3].

In this work we describe the reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_4]$ with primary amines bearing an additional donor ending group. Such an approach allows selectively synthesising a wide range of complexes containing nitrogen based ligands, by controlling the nature of this pendant group and the length of the spacer chain, aside from the working conditions. Thus, amino adducts $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)\{NH_2(CH_2)_nOMe\}Cl_4]$ (n = 2, **2**; 3, **3**) and $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)(NH_2CH_2CH{=}CH_2)Cl_4]$ (**4**); amido-amino compounds $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)(NHC_6H_4\text{-}2\text{-}\mathit{k}NH_2)Cl_3]$ (**5**); cyclopentadienyl-silyl-amido complexes $[Nb\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\mathit{k}\text{-}N(CH_2)_2\text{-}\mathit{k}OMe\}Cl_3]$ (**6**) and $[Nb(h^5\text{-}C_5H_4SiMe_2\text{-}\mathit{k}\text{-}NC_6H_4\text{-}2\text{-}\mathit{k}NH_2)Cl_3]$ (**7**); and imido derivatives $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)\{N(CH_2)_3OMe\}Cl_2]$ (**8**) and $[Nb(\eta^5\text{-}C_5H_4SiMe_2Cl)(NCH_2CH{=}CH_2)Cl_2]$ (**9**) have been prepared. Molecular structures of **2** (left) and **6** (right) are depicted in the figure bellow.





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