

MWS2015

Book of Abstracts

A graphic with a textured, orange-to-red gradient background. The text "Workshop Metals, water and Sun 2015" is written in a blue, serif font, centered on the graphic.

Workshop Metals, water and Sun 2015

Almería, 21st to 22nd May, 2015



UNIVERSIDAD DE ALMERÍA



Book of Abstracts

Workshop “Metal, water and Sun 2015”

Almeria from 21st to 22nd May, 2015

La reunión “Metal, Agua y Sol” (MWS-2015) se celebrará en Almería los días 21 y 22 de mayo de 2015, organizada por el Prof. Antonio Manuel Romerosa Nievas, el Dr. Cristóbal Saraiba Bello y los miembros del grupo investigación “Química de Coordinación, Organometálica y Fotoquímica” (FQM-317) de la U. de Almería. Junto a ellos han estado miembros destacados del Centro de Estudios Energéticos Solares (CIESOL), la Plataforma Solar de Almería y el DLR (PSA- DLR) y la U. de Zaragoza.

El congreso representa una gran ocasión para que científicos con inquietudes en el ámbito de la química de coordinación/organometálica en agua tanto en condiciones térmicas como solares provenientes de las universidades y centros de investigación españoles así como de otros países, intercambien sus últimos resultados y compartan experiencias en un ambiente positivo y enriquecedor. El alentar nuevas colaboraciones e intensificar las ya existentes es uno de los objetivos de este congreso.

El congreso está organizado en conferencias plenarias, invitadas y orales impartidas por significativos investigadores nacionales e internacionales así como de una sesión de póster en donde sea posible intercambiar ideas y discutir los resultados presentados.

El grupo de investigación organizador del MWS-2015 desea atender a los participantes y ayudarles en todo aquello que sea necesario. El peso de la organización recaerá sobre la Dr. Sonia Mañas Carpio, Franco Scalambra, Zenaida Medoza y Samira Naim, que estarán alternativamente a cargo de atender a los participantes (móvil: 638140121), sin olvidar que es posible contactar con Antonio Romerosa siempre que se considere necesario (móvil: 638140119).

Nosotros queremos darte la más calurosa bienvenida a Almería y esperamos que sea muy provechosa tanto desde un punto de vista científico como personal, de forma que esta sea una de muchas otras visitas a nuestra ciudad.

Antonio M. Romerosa Nievas
Responsable Organización MWS2015

Mariano Laguna
Corresponsable Organización MWS2015

Cristóbal Saraiba Bello
Secretario Organización MWS215

The meeting "Metal, Water and Sun" (MWS-2015) will be held in Almeria on 21th and 22th May 2015, organized by Prof. Antonio Manuel Romerosa Nieves, Dr. Cristóbal Saraiba Bello and members of the research group "Coordination-Organometallic Chemistry and Photochemistry" (FQM-317) from the University of Almería and members of Solar Energy Research Centre (CIESOL), the Plataforma Solar de Almeria-DLR (PSA-DLR) and the University of Zaragoza.

The conference represents a great opportunity for scientists with interests in the field of coordination/organometallic chemistry in water under thermal and solar and thermal conditions, universities and research centres in Spain and other countries, to exchange and share their latest results experiences in a positive and nurturing environment. Encouraging new partnerships and strengthen existing ones is one of the objectives of this congress.

The conference is organized in plenary, invited and oral lectures, which will be give by significant national and international researchers as well as a poster session will be held, where will be possible to exchange ideas and discuss the results presented.

The organizer of the MWS-2015 want to attend and help in whatever it takes. The weight of the organization lies on Dr. Sonia Mañas Carpio, Franco Scalambra, Zenaída Medoza and Samira Naim, who will meet alternately by the (mobile: 638 140 121) participants, not to mention you may contact Antonio Romerosa provided deemed necessary (mobile: 638 140 119).

We want to give you the warmest welcome to Almeria and expect it to be very rewarding both from a scientific point of view and personal.

Antonio M. Romerosa Nieves
Chair Organization MWS2015

Mariano Laguna
Cochair Organization MWS2015

Cristóbal Saraiba Bello
Secretary Organization MWS215

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Micróteles	Jueves 20 de mayo	Jueves 21 de mayo	Viermes 22 de mayo
8:45-9:00			8:45-9:00
9:00-9:15			P.3 Dr. Maurizio Peruzzini ICCOM CNR, Italia
9:15-9:30			
9:30-9:45			
9:45-10:00		Apertura	9:45-10:00
10:00-10:15	Chair: V. Pascali	P.3 Prof. Dra. Anne Marie Cammado Laboratoire de Chimie de Coordination du CNRS, Francia	10:00-10:15
10:15-10:30			German Aerospace Center, Instituto de Investigación Solar, Tabernas, Almería, España
10:30-10:45			10:30-10:45
10:45-11:00		Coffee break	10:45-11:00
11:00-11:15		Café	11:00-11:15
11:15-11:30			11:15-11:30
11:30-11:45			P.4 Prof. Dr. Armando Pombeiro Universidade Técnica de Lisboa, Portugal
11:45-12:00		P.3 Prof. Dr. Ferran Joró Universidad de Debrevecn, Hungría	11:45-12:00
12:00-12:15			12:00-12:15
12:15-12:30	Chair: E. de Jesus		12:15-12:30
12:30-12:45			12:30-12:45
12:45-13:00			12:45-13:00
13:00-13:15		Departamento de Química, Universidad de Nevada, Estados Unidos	13:00-13:15
13:15-13:30		I.1 Prof. Dr. Brian J Frost	13:15-13:30
13:30-13:45			I.8 L. Bernasconi
13:45-14:00		Lunch	13:45-14:00
14:00-14:15		Almuerzo	14:00-14:15
14:15-14:30			14:15-14:30
14:30-14:45			14:30-14:45
14:45-15:00		I.2 Prof. Dr. Mariano Laguna Universidad de Zaragoza, España	14:45-15:00
15:00-15:15			15:00-15:15
15:15-15:30	Chair: B. Froel		15:15-15:30
15:30-15:45			15:30-15:45
15:45-16:00		I.3 Prof. Dr. Victoria Cadenaro Meréndez Universidad de Oviedo, España	15:45-16:00
16:00-16:15			16:00-16:15
16:15-16:30		Café	16:15-16:30
16:30-16:45			16:30-16:45
16:45-17:00		O.1 Franco Scalamandra Area de Química Inorgánica-CIESOL, Universidad de Almería	16:45-17:00
17:00-17:15	Chair: A. Kholo	X.XXXXX	17:00-17:15
17:15-17:30			17:15-17:30
17:30-17:45			17:30-17:45
17:45-18:00	Registration	I.4 Prof. Dr. Antonio M. Romeroa Nieves Universidad de Almería, España	17:45-18:00
18:00-18:15	Entrega de documentación		18:00-18:15
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19:30-19:45			19:30-19:45
19:45-20:00	Women's reception	Posters Session / Snacks and drinks Sesión de Pósters / Aperitivos y bebidas	19:45-20:00
20:00-21:00			20:00-21:00
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22:00-.....			22:00-.....
			Congress dinner Cena de cierre
			Chair: Prof. Dra. Anna Maria Cammado France

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PLENARY LECTURES

Metal complexes of water-soluble dendrimers for catalysis and biology

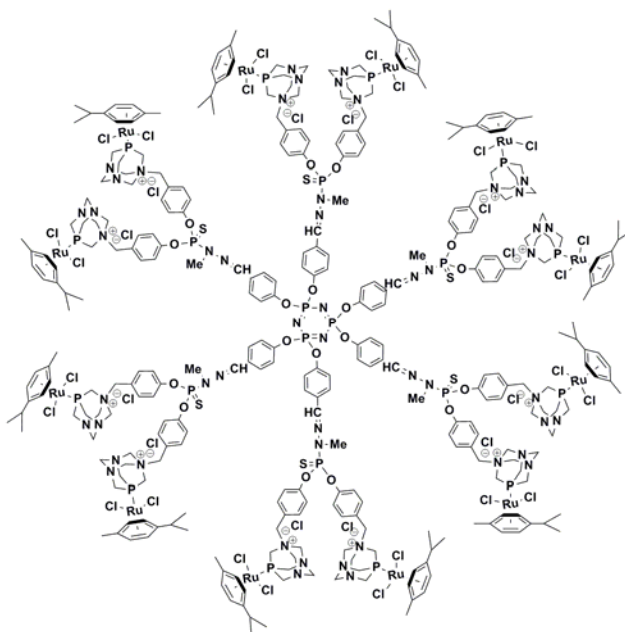
A.-M. Caminade^{1,2}, R. Laurent^{1,2}, A. Ouali^{1,2}, A. Hameau^{1,2}, J.-P. Majoral^{1,2}.

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Dendrimers are hyperbranched macromolecules constituted of repetitive units emanating from a central core [1]. Most of their properties, including the solubility, depend mainly on the type of their terminal groups, and to a lesser extent on the chemical nature of their internal structure. We are specialized since a long time in the synthesis and study of properties of phosphorus-containing dendrimers [2], which have numerous properties, in particular for catalysis, materials, and biology/nanomedicine.

Among the hundreds of dendrimers that we have synthesized, those having metal complexes in their structure (most generally as terminal groups), while being soluble in water (or in mixtures water/organic solvent) plays a particular role, that will be emphasized in the lecture. Most of such dendrimers are used as catalysts [3,4,5] (an example of this type of compounds is illustrated in the Figure on the right [6,7]). Recent examples concern the biological properties of such complexes, in particular for oncology [8,9].



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Complexes of Phosphines, *N*-Heterocyclic Carbenes and Salans and their Applications in Aqueous Organometallic Catalysis

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Organometallic catalysis in aqueous solutions and in aqueous-organic biphasic systems [1] requires strongly hydrophilic (water-soluble) transition metal complex catalysts. Long time ago we introduced the use of monosulfonated triphenylphosphine as stabilizing ligand for metal complex catalysts in aqueous solutions and since then the field of catalysis by water-soluble tertiary phosphine complexes expanded enormously. However, as complexes of *N*-heterocyclic carbenes were more and more intensively investigated (as much as to rival the importance of tertiary phosphine-containing catalysts) the need of water-soluble variants of NHC-complexes became apparent [2]. We have synthesized a series of water-soluble 1,3-disubstituted imidazolium salts and used them to obtain NHC-complexes of Au(I), Ru(II), Rh(I), and Ir(I). More recently several sulfonated analogs of salen (*N,N*-bis(salicylidene)ethylenediamine) and its hydrogenated derivative (salan) have been prepared and used for the synthesis of various transition metal compounds, of which the Pd(II)-complexes showed outstanding catalytic activities.

The catalytic properties of the various phosphine-, NHC- and sulfosalan-containing metal complexes were studied in reactions such as hydration of alkynes and nitriles [3,4], hydrogenation and transfer hydrogenation of alkenes and aldehydes [5], redox isomerization of allylic alcohols [6] and for various C-C coupling processes [7]. In some cases irradiation with visible light led to photochemical reactions of the catalyst complexes, and influenced the reaction rate [8]. An important part of our studies is devoted to the homogeneous catalytic hydrogenation of CO₂/HCO₃⁻ and the construction of hydrogen storage/delivery cycles on the basis of the bicarbonate/formate equilibrium [5,9].

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Recent advancements on the chemistry of phosphorus with water: an eccentric marriage often officiated by transition metals

Maurizio Peruzzini

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In this communication the most recent achievements in the area of elemental phosphorus' reactivity deriving from the author's own research in Florence (Italy), will be presented and discussed.

These will include: i) the activation of white phosphorus mediated by late-transition metal complexes with particular emphasis to the unusual hydrolytic behaviour of the P₄ molecule following its η^1 -coordination to a metal centre (Fe, Ru, Os, Re) [1]; ii) the high pressure reactivity of red phosphorus towards water and other small molecules [2] and, iii) our preliminary results in exploring the chemistry of the less reactive allotrope of the element, i.e. black phosphorus.[3]

Highlights deriving from this work include:

- the presentation of the stepwise demolition by water of both mono- and bidentatetetraphosphorus ligands in ruthenium complexes, which result in a variety of P_x fragments ($x \leq 4$) like P-oxyacids, phosphanes and hydroxyphosphanes stabilised by metal-coordination at ruthenium,
- the electrochemical generation of the so far elusive oxide of phosphine, H₃P=O from white phosphorus,
- the light induced dissociation of water at high pressure using near-UV photons in the presence of red phosphorus which results in the formation of H₂ together with PH₃, H₃PO₂, H₃PO₃, and H₃PO₄,
- the easy access to two dimensional flakes of phosphorene (the all-P analogue of graphene) via a solution synthesis which avoids the use of the boring and scarcely productive scotch-tape exfoliation actions.

References:

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Acknowledgements:

MP thanks all the coworkers listed in the references. Thanks are expressed to EC for funding this research through the *SUSPHOS* project, grant RFP7-PEOPLE-2012-ITN – 317404 and the *PHOSFUN* project, proposal n° 670173 ERC-ADG-2014.

Dedication:

This plenary lecture is dedicated to my Colleagues and Friends Piero Stoppioni (1944 – 2014), Massimo Di Vaira (1940 – 2012) and Stefano Midollini (1938 – 2012) who firstly explored in Florence the funny and puzzling chemistry of white phosphorus mediated by transition metal complexes.

Water as Solvent, Catalyst and Reagent in Selected Coordination Chemistry Systems

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The use of water in synthesis and catalysis can provide important contributions towards the development of environmentally benign and sustainable Chemistry.

Within this general aim, systems that can operate conveniently by using water as an adequate solvent are often searched for. However, water can be applied under different perspectives with advantages relatively to conventional methods.

In this talk, various approaches applied by the author's research Group will be discussed, namely concerning the following types of water applications in Coordination Chemistry and Catalysis:

- As a solvent for synthesis and stabilization of coordination compounds, e.g., of coordination polymers and metal-organic frameworks (MOFs), where a structural function plays a key role;
- As an alternative solvent for catalytic reactions typically performed in organic media (e.g., alkanes functionalization and alcohols oxidation);
- As a reagent, e.g., as a protic nucleophile (e.g. alkane hydrocarboxylation and nitrile hydrolysis);
- As a catalyst or co-catalyst for proton-shift reaction steps.

Further points to be taken into consideration concern the possible role of water as an inhibitor and as an anti-solvent in heterogeneous catalysis (e.g., allowing the performance of catalytic reactions in aqueous medium by using water insoluble heterogeneous catalysts).

The significance of such approaches towards the establishment of green systems will also be discussed.

Acknowledgments

The author is gratefully acknowledged to all the co-authors and Group members. The work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (project UID/QUI/00100/2013).



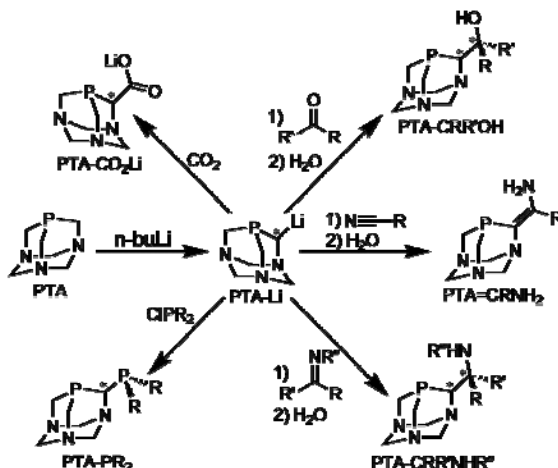
INVITED LECTURES

Advances in the Aqueous Chemistry of PTA: coordination chemistry, derivatization, and catalysis

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Our group is interested in the coordination chemistry and reactivity of metal complexes of the air stable and water soluble heterocyclic phosphine 1,3,5-triaza-7-phosphaadamantane (PTA). The coordination chemistry of PTA including N vs P coordination will be discussed along with recent advances toward the synthesis of “upper” and “lower” rim derivatives. Chiral upper rim derivatives have been synthesized from the convenient synthon 1,3,5-triaza-7-phosphaadamantan-6-yllithium (PTA-Li). Reaction of PTA-Li with a variety of electrophiles including ClPR_2 , CO_2 , ketones, aldehydes, imines, and nitriles has allowed for the isolation of a series of phosphine ligands including diphosphines (PTA- PR_2), β -phosphino alcohols (PTA- $\text{C}(\text{OH})\text{RR}'$), β -amino phosphines (PTA- $\text{C}(\text{NHR}')\text{RR}'$), enamines (PTA- $\text{C}(\text{NH}_2)\text{R}$, and PTA- CO_2Li . Lower rim derivatives, modification of the triazacyclohexane ring, of PTA have been synthesized via condensation of $\text{P}(\text{CH}_2\text{NH}_2)_3$ with a variety of aldehydes. The water solubility of the PTA derivatives synthesized range from ~800 g/L to insoluble with most having a water solubility of ~10-15 g/L (~20–40 mM).



We have utilized PTA as a ligand for a variety of catalytic reactions including hydrogenation, atom transfer radical addition (ATRA), and nitrile hydration. We will discuss our recent work utilizing $[\text{Cp}'\text{Ru}(\text{PTA})(\text{PR}_3)\text{Cl}]$ complexes as ATRA catalysts and $[\text{RuCl}_2(\text{PTA})_4]$ and $[(\eta^6\text{-arene})\text{RuCl}_2(\text{PR}_3)]$ complexes as highly active, air stable, recyclable nitrile hydration catalyst. Near quantitative conversion of aromatic, alkyl, and vinyl nitriles to their corresponding amides was observed at 100° with water as the reaction medium. The reaction tolerated ether, hydroxyl, nitro, bromo, formyl, pyridyl, benzyl, alkyl, and olefinic functional groups. Some amides were isolated by simple decantation from the aqueous phase catalyst. Catalyst loading down to 0.001 mol% was examined with turnover numbers as high as 22000 observed. $[\text{RuCl}_2(\text{PTA})_4]$ is stable for weeks in solution and could be reused more than five times without significant loss of activity. An *in situ* generated catalyst of $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$ and PTA has also been explored with catalytic activity comparable to $[\text{RuCl}_2(\text{PTA})_4]$.

Applications of water soluble phosphanes and their gold complexes: new ceramic pigments and molecular therapy

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The ability of the phosphane 1,3,5-triaza-7-phosphadaamante (PTA) to transmit its water solubility to their gold complexes has permitted the synthesis of complexes that found applications in a wide of different areas. In this communication we present results of our group as new ceramic pigments or as molecular therapy against cancer and alzheimer.

The use of ploter for the new type of ceramics requires the shynthesis of new inks able to develop the colors in the oven at high temperature. The gold complexes are selected for the formation of magenta red color. The new ink should be soluble in water of at least in alcholic media for enviromental aspects.

Regarding their use as new agents of molecular therapy, we present results against different types of cancer cells, both *in vitro* and *in vivo*. Among the new non platinum complexes as potential anticancer drug, gold(I) derivatives have gained increasing attention due to the observation that the action mechanism is different to the *cis*-platinum and non interaction with DNA occurs, and inhibit the enzyme thioredoxin reductasa, (TrxR) [1], making these complexes very appropriate for a second treatment against *cis*-platinum resistance cancer.

The side effects of most of the new anticancerous complexes could be given due to their lipophilicity. For this reason, in the design of new metallic drugs, a balance between hydrophilicity and lipophilicity is required to be water soluble and at the same time be able to pass through the phospholipid cell membrane. Accordingly, water solubility of the drugs could provide such balanced relationship.

The ability of PTA to reduce Cu(II) and stabilize Cu(I) as a tetrahedral coordinated compound has been reported by Pombeiro et al [2]. Bearing this in mind, several experiments have been carried out to show the ability of PTA to reduce Cu(II) to Cu(I) in physiological conditions and its ability to remove copper ions from A β amyloide stoping in ROS production, which is one important aspect in Alzheimer disease [3].

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Catalytic Transformations in Aqueous Media: Some Examples Employing Organometallic Ruthenium and Gold Complexes

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The combination of metal catalysis and water has led in recent years to the development of a huge number of new and greener synthetic methodologies of interest from both academic and industrial points of view [1]. The use of metal catalysts in water or in a two-phase system offers significant advantages versus more classical organic solvents since it simplifies the separation of the products, and that of catalyst, thus favouring the recycling of the catalytic system, a very important aspect for large-scale applications.

In recent years, our research group has been active in this field, developing a number of organometallic complexes, mainly of ruthenium, gold and palladium, capable of promoting the regio- and stereoselective formation of new C-C and C-heteroatom bonds in aqueous media. In this talk, examples of such catalysts, particularly Ru(IV) and Au(I) complexes, and their application in catalytic transformations such as the inter- [2] or intramolecular [3] addition of carboxylic acids to alkynes, or the selective hydration of nitriles to amides will be discussed [4].

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Water soluble Ruthenium complexes containing PTA: a versatile family of complexes with biological, catalytical... to photochemical properties.

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Water-soluble complexes containing the aqua-soluble phosphine ligand 1,3,5-triaza-7-phosphaadamantane (PTA) and their derivatives have shown important properties in large number of research lines [1]. Our team at the university of Almeria has mainly focused its research activity on the synthesis, characterization and study of water-soluble ruthenium complexes. The obtained compounds were shown to be useful as: anticancer active compounds [2], homogeneous catalysis in water and organic solvents [3], active photochemistry compounds [4], new materials such as heterometallic complexes [5], gels in water [6], etc.

Herein a overview of the more important findings in this are will be present, stressing the last obtained results on heterometallic organometallic complexes (figure).

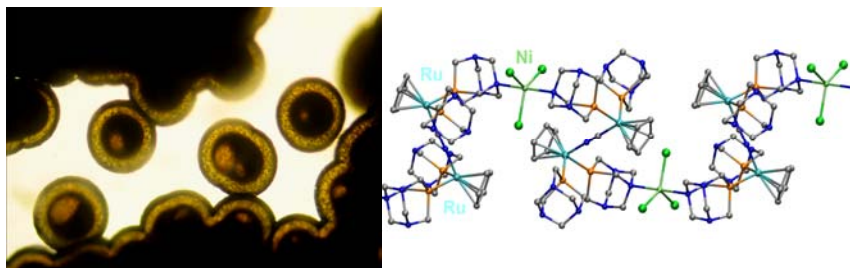


Figure. Optical microscopy picture in aqueous ($6 \cdot 10^{-2}$ M) and crystal structure of $\{[(\text{PTA})_2\text{CpRu}-\mu\text{-CN-RuCp}(\text{PTA})_2-\mu\text{-NiCl}_3]\}_n$.

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Acknowledgement: This work was cofinanced by the European Union (EU FEDER). Thanks are given to Spanish MINECO (CTQ2010-20952) and Junta de Andalucía (Team FQM-317 and project P09-FQM-5402). Manuel Serrano-Ruiz is grateful to Junta de Andalucía for a postdoctoral contract (P09-FQM-5402) and Franco Scalambra to UAL for a PhD grant. Thanks are also given to COST Action CM 1302/WG 1, 2.

High Temperature Solar Energy Applications for Power and Hydrogen Generation

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Concentrating Solar Technologies, usually referred to as CSP, use different mirror configurations for concentration of direct solar radiation to achieve high temperatures approximately in the range from 200 – 2000°C to drive conversion processes for power generation and eventually different industrial high temperature production processes, especially thermochemical cycles. Power generation is currently by far the most important and developed sector with a total global installed capacity of about 100 operating solar thermal power plants in a range of 10 – 280 MW each, totally approaching 4 Gigawatt. A distinctive characteristic of CSP plants is their ability to incorporate high temperature thermal storage to shift the power production to hours without sunshine or help to balance the power supply in electricity grid with growing shares of fluctuating renewable energy especially from wind or photovoltaic power plants.

One important R&D line for mid- to long term applications in Concentrating Solar Technologies is the development of thermochemical cycles to generate hydrogen as an energy vector and basis for future “solar fuels” for the transport sector. This contribution will give an overview about the current state of development in this area.

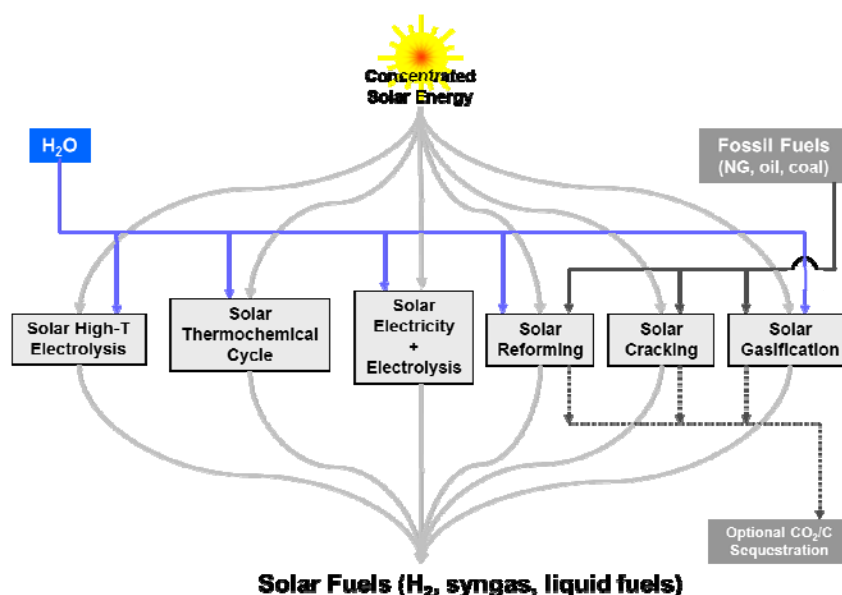


Fig 1: Overview of different pathways to generate Solar Fuels

References:

IEA Technology Roadmap Solar Thermal Electricity

<http://www.iea.org/publications/freepublications/publication/technology-roadmap-solar-thermal-electricity---2014-edition.html>

Multi-probe methods for investigating metal ion hydration

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Techniques developed at large scale facilities such as X-ray synchrotrons and pulsed or reactor based neutron sources have, over the past few decades, played a significant role in unravelling many of the mysteries that underpin the chemical, physical and biochemical properties of metal ions in solutions. In this presentation we will illustrate how the combination of X-ray diffraction, neutron diffraction and X-ray absorption spectroscopy can be applied to the investigation of the structure of ion hydration shells. Examples of hydration of di- and tri-valent ions will be shown [1-4].

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Effect of UV-light on solar photo-Fenton when removing contaminants at $\mu\text{g/L}$ scale

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There is an increasing environmental concern due to the presence of low concentrations of persistent pollutants in waters ($\mu\text{g/L}$ or ng/L), also called micropollutants. Advanced oxidation treatments have been proposed as efficient system for their removal. The successful application of solar-driven photo-Fenton to treat highly polluted wastewaters (g/L and mg/L of pollutants) has prompted its application to lowly polluted effluents. However, the decrease in contaminant concentration involves an alteration in the intrinsic process phenomenon, which until now has only been widely studied at the milligram-per-litre level or higher with this process. First we present a study on the combined influence of the operating variable (iron concentration) and the environmental variable (irradiance) and its application on the photo-Fenton process at pH 2.8 when removing micropollutants. For this purpose, results obtained at laboratory and pilot plant scales with the biocide acetamiprid (ACTM) at $100 \mu\text{g/L}$ concentration are presented using ACTM the model pollutant. Results indicate that above $15 \text{ W}_{\text{UV}}/\text{m}^2$ and a light path length of 5 cm (the most commonly used path for this type of application) iron concentration limited the process and there is irradiance excess under these conditions. On the other hand, and given the circumstances of irradiance excess, a higher light path length (10 cm) was assessed, showing that wider path lengths than 5 cm are recommended since more wastewater volume could be treated with a higher process rate per surface unit. To this aim, raceway ponds reactors (RPRs) are proposed as new reactor configuration to carry out the photo-Fenton process as an alternative to the commonly used tubular reactors with compound parabolic collectors (CPC). RPRs are extensive non-concentrating photoreactors, which allow large volumes of water to be treated. They consist of channels where water is set in motion by a paddlewheel system. Therefore, in the second stage of this research, we present the effect of solar irradiance on RPR operation to remove micropollutants by solar photo-Fenton. A RPR was used at pilot plant scale (up to 360 L) and the pesticide acetamiprid was used as a model pollutant ($100 \mu\text{g/L}$) in synthetic WWTP effluent. Averaged UV irradiances ranged from 10 to $30 \text{ W}/\text{m}^2$ and three values of iron concentration (1, 5.5 and 10 mg/L) were used. Different liquid depths were also used to evaluate the relationship between the rate of photon absorption and pollutant removal. We propose a model to predict degradation rate and treatment capacity as a function of the volumetric rate of photon absorption (VRPA). Treatment capacity values of $133 \text{ mg}/\text{h}\cdot\text{m}^2$ can be reached under these conditions.

This research was supported by the Ministerio de Economía y Competitividad (Spanish Government) CTQ2013-46398-R; and the European Regional Development Fund (ERDF).

***Ab initio* modelling of chemical reactivity in solution**

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I will address the application of electronic structure theory and *ab initio* molecular dynamics (AIMD) to the study of chemical reactivity and catalytic processes in solution. I will focus on the use of AIMD as a tool to investigate mechanistic details of complex chemical reactions at a quantum mechanical level and to study the influence of the solvent structure and dynamics on the chemical reactivity. I will examine in particular the catalytic properties of high-valent Fe(IV)oxo complexes in the oxidation of poorly reactive hydrocarbons for fuel production in water solution. [1-3] I will show how AIMD and free-energy calculation methods can be used to make quantitative predictions on thermodynamic and kinetic properties, as well as to identify optimal catalyst structures and working conditions. [4] I will also briefly outline how AIMD methods can be extended to study photo-induced chemical reactivity in condensed phase environments. [5-7]

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Eliminación de contaminantes de agua y otras aplicaciones de los procesos avanzados de oxidación mediante energía solar

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Los procesos avanzados de oxidación, más conocidos por sus siglas inglesas AOP (Advanced Oxidation Processes) se basan principalmente en la generación de radicales hidroxilo ($\text{HO}\cdot$) con un alto potencial oxidativo y baja especificidad, capaces de mineralizar y degradar una gran variedad de compuestos orgánicos. El especial interés en los AOP recae en aquellos procesos capaces de utilizar la radiación solar y permitir el desarrollo de tecnologías con bajo impacto medioambiental como es la fotocatalisis heterogénea basada en semiconductores y el proceso de foto-Fenton, basado en la fotoquímica del hierro [1]. Su aplicación potencial se centra fundamentalmente en la eliminación de compuestos tóxicos y persistentes, no degradados mediante tecnologías convencionales [2]. En el ámbito del tratamiento de aguas, las principales áreas objeto de estudio son:

- Tratamiento de efluentes industriales procedentes de actividades agrícolas, agroquímicas, destilerías, textiles, papeleras, petroleras, metalúrgicas, hospitales y lixiviados de vertedero.
- Eliminación micro-contaminantes persistentes (fármacos, disruptores del sistema endocrino, etc.) en efluentes de depuradora y aguas naturales.
- Eliminación de patógenos tanto para aplicaciones en agua potable como para irrigación.

Además de estas aplicaciones, recientemente se ha retomado con creciente interés el uso de la fotocatalisis para la producción de hidrógeno [3]. Este trabajo revisará todos estos aspectos en los que se centra la labor de la Unidad de Tratamientos solares de la Plataforma Solar de Almería, una Instalación Científico Técnica Singular del Gobierno de España (www.psa.es). Se dará especial énfasis a



mostrar el desarrollo tecnológico que en este campo ha supuesto los captadores solares específicos para estas aplicaciones, como el mostrado en la figura.

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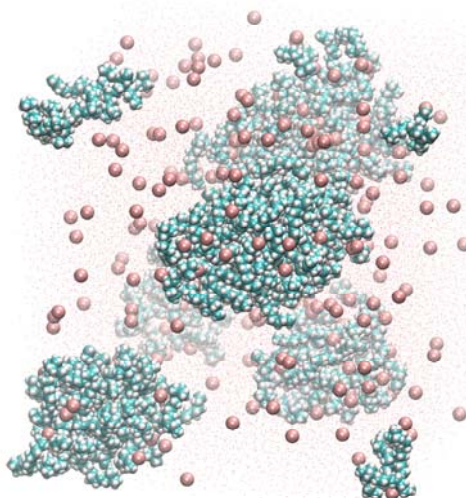
Characterizing the structure of liquids and solutions using neutron scattering methods

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Wide Q-range neutron scattering is a powerful technique for investigating the atomic, molecular and nano-scale structure of liquids and complex systems. In combination with hydrogen-deuterium isotopic substitution methods, it is possible to comprehensively characterise the key intermolecular correlations that underpin the physical and chemical properties of multicomponent liquid mixtures. In this presentation I will give an introduction to the wide Q-range neutron scattering method as implemented at the ISIS pulsed neutron and muon source in the UK. To illustrate the current capabilities of these methods, I will then demonstrate how this technique has been used, in combination with atomistic structure refinement methods, to characterise multi-component molecular liquids [1], self-assembling systems [2], and chemical reaction processes in confined fluids [3].

Figure 1 shows an atomistic model of a 0.04M solution of C₁₀TAB (decyltrimethylammonium bromide) micelles in aqueous solution at 25°C. The model was refined against wide Q-range neutron scattering data on a series of solutions making use of H/D isotopic enhancement of structural contributions. This model consists of 105216 atoms in a cubic simulation box of side length 101.7Å.



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ORAL COMMUNICATIONS

Snorkelling in the flask: a spot about the isomerization of allylic alcohols in water catalysed by $[\text{CpRu}(\text{PTA})_2(\text{H}_2\text{O})]\text{CF}_3\text{SO}_3$

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In recent years much effort has been devoted to developing an efficient and general process to isomerise allyl alcohols in water, following early evidences provided by McGrath and Grubbs [1]. Some years ago, we synthesized the water soluble ruthenium complex $[\text{RuCp}(\text{PTA})_2\text{Cl}]$ which has been found to be an excellent and versatile catalyst for many catalytic synthetic processes, such as the isomerization of the allylic alcohols from 1-penten to 1-octen-3-ol. The catalytic reaction was studied by NMR and IR spectroscopy, which provided valuable information to propose its mechanism. Nevertheless, some aspects of the mechanism, such as the role of the water in the reaction, are not clear and there is necessary more experiments and theoretical studies. It is becoming more and more evident that the complete reaction mechanism cannot be understood without first answering the following question: where and how are the water molecules positioned around the catalyst? Do the water molecules form a bond with catalyst and substrate? and what is the nature of the interaction of the water molecules with the catalyst? This questions remain common to all homogenous catalysed by metal complexes reactions in water. Actually only by the synergic combination of traditional experimental techniques, neutron scattering, EPSR simulations and theoretical calculations is possible to obtain an unprecedented level of insight into the reaction mechanism and the structure of the catalytic reaction intermediates in aqueous media. Not only can the results from these experiments be potentially ground breaking in the field of aqueous homogeneous catalysis but, in turn they may also highlight new opportunities offered by neutron scattering techniques to researchers in this field.

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Photo-Fenton modelling including VRPA as photo-reactor design tool

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Industrial wastewater is often toxic and non-biodegradable so that conventional biological treatments are not adequate processes to achieve decontamination. In this respect, photo-Fenton treatment, based on hydroxyl radical generation, evolved as an economical and technical alternative [1] as it can be powered by solar light irradiation. Nowadays, many aspects of this process have been thoroughly studied, nevertheless, some key fields needed to introduce this technology as a normalized treatment –as modelling, process control or economical assessment- are still under development.

Despite this extensive body of knowledge on the photo-Fenton process, the mathematical modelling of the treatment process is still underdevelopment, probably due to the large number of reactions involved (some of them nowadays even under discussion) which makes modelling a complex task. First principle models are limited to approximations in which no more than one or two pollutants are considered. In contrast, although more simple, mathematical models are limited to process optimization under narrow operational conditions. In the middle of both options, semi-empirical models based on lumped simple reactions have been developed [2].

The aim of this work was to develop a semi-empirical photo-Fenton model including the effects of liquid depth, illuminated to total volume ratio and catalyst-UV radiation interaction. This analysis requires the use of detailed expressions regarding the relationship between reactor geometry and UV radiation distribution and the calculation of the local (LVRPA) and the volumetric rate of photon absorption (VRPA) [3]. The prediction capability of the model was evaluated in terms of total organic carbon (TOC) mineralization, hydrogen peroxide consumption and dissolved oxygen evolution. The system was run under different photo-reactor configurations (optical path and illuminated to total volume ratio) and operational conditions (catalyst and hydrogen peroxide concentrations). The satisfactory results found demonstrated that the model, which can be easily extended to model other water contaminants, provides a robust method for process design, process control and optimization.

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POSTERS

Catalytic rearrangement and dehydration of aldoximes promoted by palladium(II) complexes containing phosphino-oxime ligand

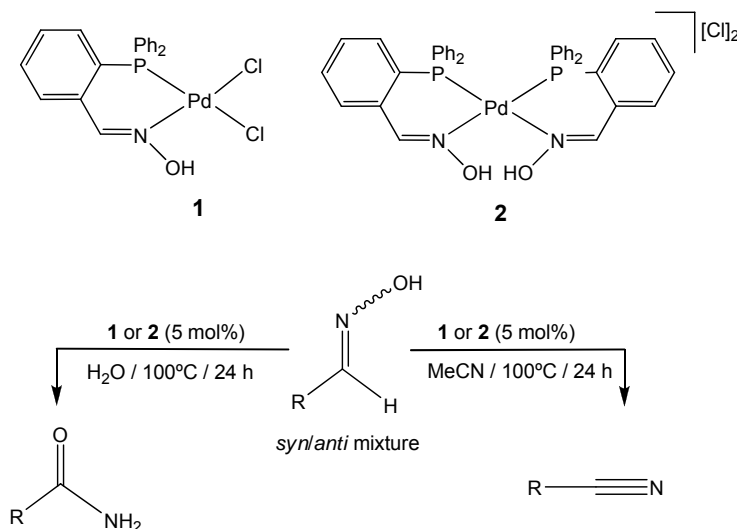
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Coordination of heteroditopic ligands featuring mixed *P,N*-donor sets, such as phosphines with amino, imino, pyridyl, iminophosphorane or oxazoline groups, has been extensively studied and their resulting complexes have found application in a wide range of catalytic synthetic processes [1]. In contrast, bidentate phosphine ligands containing an oxime functionality still remain uncommon in the literature [2].

In the present communication, we report the synthesis of the first phosphino-oxime palladium(II) complexes (**1** and **2** in Scheme) easily obtained from the $[\text{PdCl}_2(\eta^4\text{-cod})]$ precursor. These derivatives, and especially complex **1**, turned out to be active in the catalytic transformation of oximes, the outcome of the reaction being dependant of the solvent used. Thus, catalytic experiments performed in water gave rise to the rearrangement of the oxime, providing the selective formation of the corresponding amide [3]. In contrast, the reactions made in MeCN conducted to high yields of the organonitriles, through dehydration processes (see Scheme).



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Efficient and selective hydration of nitriles to amides in aqueous systems with Ru(II)-phosphatriazaadamantane catalysts.

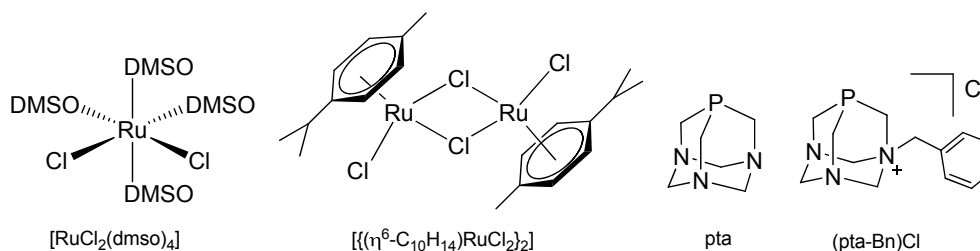
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Selective hydration of nitriles to amides is an important reaction applied for -among others- synthesis of pharmaceuticals, detergents, polymers and rubber products. Water is a straightforward choice as solvent for hydration reactions, and several water-soluble ruthenium-based catalysts[1] are known for such transformations, for example $[\text{RuCl}_2(\text{pta})_4]$ [2] and related catalysts [3] having the general formula of $[(\eta^6\text{-arene})\text{RuCl}_2(\text{L})]$ ($\text{L} = 1,3,5\text{-triaza-7-phosphaadamantane}$, pta; N-benzylated pta = $(\text{pta-Bn})\text{Cl}$).

We have developed a simple and efficient catalytic method for selective hydration of aliphatic and aromatic nitriles to the corresponding amides. The catalysts are prepared „in situ” from the mentioned ligands and easily available Ru-precursors such as $[\text{RuCl}_2(\text{dmsO})_4]$ and $\{[(\eta^6\text{-cymene})\text{RuCl}_2]\}_2$.



The most active catalyst is obtained from $[\text{RuCl}_2(\text{dmsO})_4]$ and $(\text{pta-Bn})\text{Cl}$. The reactions take place in aqueous reaction mixtures on air at reflux temperatures in short reaction times and are characterized with excellent conversions and isolated yields. The catalyst can be efficiently recovered in the aqueous phase, shows high stability, and retains its activity through several repeated cycles.

Of 16 substrates examined, 92-99% conversions of 14 nitriles was achieved in one hour at reflux temperature. In several cases the product amides precipitate or crystallize from the aqueous mixture upon cooling and can be isolated by filtration and aqueous washing in high purity. This latter feature makes the procedure operationally simple and largely eliminates contamination of the environment.

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Transfer Hydrogenation Process of Aldehydes and Ketones in water with Highly Active Ruthenium Precursors. Selective Catalytic Deuterium Labelling.

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In the past decade, Half-sandwich Ru(II) arene complexes have found most applications as active species in homogeneous catalysis of a great number of organic reactions. Our research group is interested in the development of versatile catalysts in aqueous media for transfer hydrogenation of organic carbonyl compounds.[1,2] Transfer hydrogenation is an important alternative of catalytic reduction involving the transfer of H₂, from a donor molecule to a substrate.

We describe in this communication the synthesis of Ru-arene complexes containing substituted bipyridine ligands and their use as catalysts for transfer hydrogenation of ketones and aldehydes in water with HCOONa/HCOOH at pH = 4,4. The use of simple hydrogen source, such as HCOOH and HCOONa, has evident benefits from an environmental point of view, and for the separation of the organic products.

In addition, when the reaction was carried out in D₂O, selective deuteration was observed in the C_α of the obtained alcohols due to a quickly Ru-H/D exchange in a side catalytic cycle coupled to the hydrogenation. Labeling with deuterium is a useful procedure to obtain molecules and biomolecules with a wide range of applications.

Although a detailed microscopic description and Gibbs energy landscape of the catalytic cycle will be exposed, in Figure 1 a proposed mechanism for the hydrogenation of aldehydes and deuterium labelling of the alcohols is included.

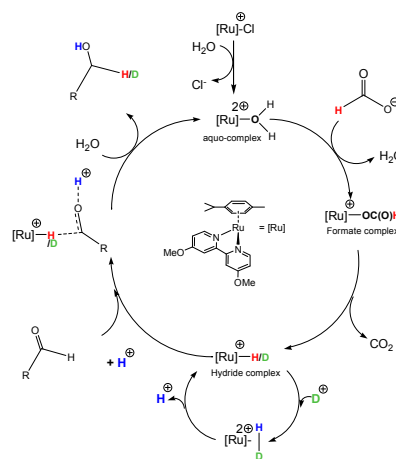


Fig. 1. Proposed mechanism for the Coupled TH/Deuteration Catalytic Cycle.

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A new family of cumulene complexes containing monodentate NHC ligand 1,3-Diisopropylimidazolilidene

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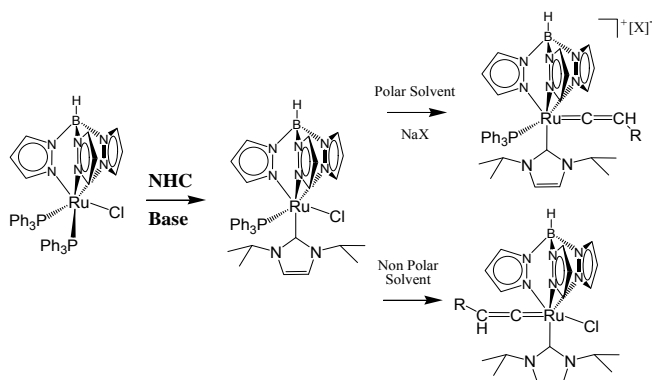
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N-heterocyclic carbene ligands (NHC) are widely employed as auxiliary ligands in the synthesis of new transition metals organometallic complexes and in their application in catalysis. Originally described as substitutes of the phosphines, the NHC ligands have displayed a more versatile and rich coordination chemistry due to the synthetically easier tuning of their electronic and steric properties.[1]

Hydrotris(pyrazolyl)borate (Tp) ruthenium complexes have been studied over the past two decades.[2] In 2001, Grubbs *et al* described the reaction of the bis-pyridine complex $\text{RuCl}_2(=\text{CHPh})(\text{H}_2\text{IMes})(\text{C}_5\text{H}_5\text{N})_2$ with KTp to produce $\text{TpRuCl}(=\text{CHPh})(\text{H}_2\text{IMes})$ (H_2IMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene), which is to the best of our knowledge, the first example of a compound combining the TpRu fragment with a NHC ligand.[3]

Our group has recently studied the synthesis and reactivity of the complexes $[(\kappa^3\text{-Tp})\text{Ru}(\text{L})(\text{Cl})]$ (L = picolylimidazol-2-ylidene ligands)ⁱ. They are the first Tp-ruthenium complexes containing functionalized N-heterocyclic carbene ligands.[4]

In this communication, we report now a new access to a family of ruthenium complexes in which Tp and monodentate NHC ligands are employed jointly. A series of neutral vinylidene, cationic vinylidene and cationic allenylidene complexes have been obtained and characterized.



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PREPARATION OF EXFOLIATED BLACK PHOSPHORUS AND ITS GAS ADSORPTION PROPERTIES

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2D materials are very promising in nanodevice applications due to their surprising properties such as high electric mobility, outstanding structural properties and large specific surface area. [1] Recently, phosphorene (Figure 1), the all-P counterpart of graphene, has been prepared starting from black phosphorus (BP). Small amounts of single and few layers sheets of the new material have been obtained by either micromechanical cleavage (Scotch tape method) or liquid exfoliation.[2]

Almost nothing is known about the reactivity and the physico-chemical properties of this new fascinating material and only sparse theoretical [3] and experimental [4] studies have been reported so far. The former include computational analysis addressing the reactivity of phosphorene towards small molecules such as O₂, H₂O, CO₂, CO, NO_x, etc.

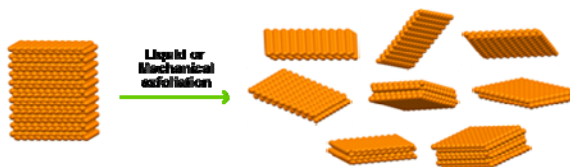


Figure 1. Exfoliation of black phosphorus

In this communication, we present our first results on this subject and firstly describe the adsorption properties towards different gaseous molecules, such as CO₂, CO, O₂ and H₂ by BP and few layers phosphorene.

Acknowledgement: Thanks are expressed to EC for funding the project PHOSFUN “Phosphorene functionalization: a new platform for advanced multifunctional materials” (ERC ADVANCED GRANT 2015 - 2019)

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SYNTHESIS AND CHARACTERIZATION OF [RuCp(dmoPTA)(PPh₃)₂] AND THE BIMETALLIC COMPLEX [RuCp(PPh₃)₂-μ-dmoPTA- 1κP:2κ²N,N'-PdCl₂].

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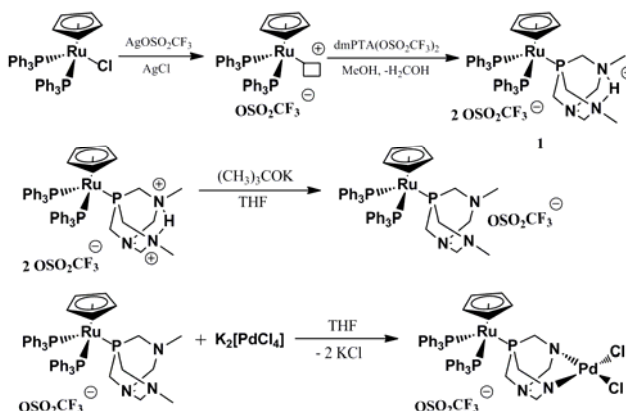
Tertiary water-soluble phosphines have always been widely used because of their capacity to stabilize metallic centers and confer them particular properties

As part of our investigation on the water soluble complexes our research has been focused on the synthesis of ruthenium complexes containing PTA (1,3,5-triaza-7-phosphaadamantane) and its methylated derivatives mPTA (*N*-methyl) and dmPTA (*N,N'*-dimethyl).

Particularly interesting is the ligand dmPTA shows particular coordinative properties by having a soft coordination position, the phosphorus atom, and two hard coordination positions with the ability to form chelate rings.

To increase the solubility of metal complexes containing the ligand dmoPTA, the complex [RuCp(dmoPTA)(PPh₃)₂] (**1**), in which there are two PPh₃ ligands, was synthesized (Scheme 1). This new complex shown to be very soluble also in a non polar solvent like THF. Reaction of this complex with K₂[PdCl₄] in THF gave rise to the new dimeric complex [RuCp(PPh₃)₂-μ-dmoPTA-1κP:2κ²N,N'-PdCl₂],

which was fully characterized by NMR, IR and elemental analysis.



Scheme 1

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Water soluble bis(2,2'-bipyridine)ruthenium(II) dyes: pH-dependent optical properties.

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The increasing demand of energy is worldwide pushing a huge slice of the chemical research in the design of new and possibly eco-friendly materials to transform the sunlight into directly expendable sources as hydrogen or electric energy. During the last decades the attempts of the man to emulate photosynthesis poured in the scientific panorama a wide variety of molecules useful for water splitting under sunlight and/or for sunlight conversion into electricity. These processes need a catalyst and Ruthenium poly-bipyridyl complexes are among the most useful due to their quantum yields, suitable redox potentials and tunability [1].

Recently we synthesized two highly soluble in water ruthenium bis-bipyridyl isomers bearing 1,3,5-triaza-7-phosphaadamantane (PTA). The PTA ligand revealed to be useful not only to provide a large solubility in water (which reaches 1M for both of them) but also to easily tune their luminescence (Figure). Herein we present a pH-dependent study of the fluorescence properties of both ruthenium complexes as well as the description by TD-DFT calculations of their electronic transitions.

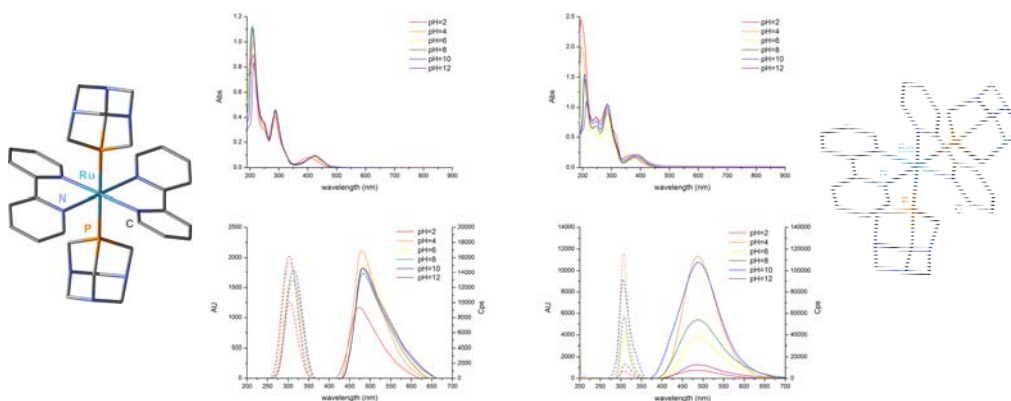


Figure 1. Left: x-ray crystal structure of trans-[Ru(bipy)₂(PTA)₂](OTf)₂. Right: Left: x-ray crystal structure of cis-[Ru(bipy)₂(PTA)₂]Cl₂. Centre: experimental absorptions and emission of the presented complexes.

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Heterometallic polymers containing PTA as new dye-sensitizer for solar cells (PTA = 1,3,5-Triaza-7-phosphaadamantane)

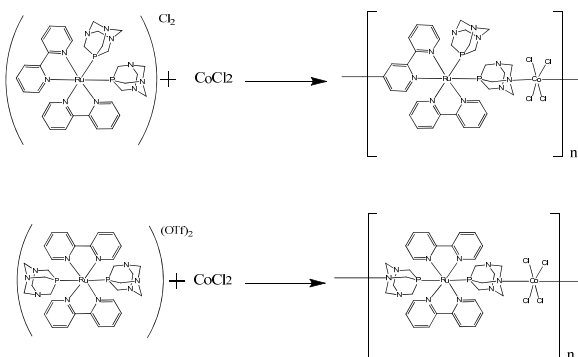
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The society demands more and more energy and there are not too many alternatives. The solar light provides the energetic for all process on the Earth from the life to the rain. Unfortunately the capacity of the human being for obtaining electricity from the light of the Sun is very limited but it was increased the last years by several important finding such as the dye-sensitized solar cell (DSCs). This solar cell variety has emerged as a promising alternative to conventional Si-based and thin-film photovoltaic technologies because of their low cost and high efficiency. DSCs are constituted by three crucial components: porous nanocrystalline TiO₂ film, photosensitizers and electrolyte. [1]

In recent years, a large amount of dyes have been intensively investigated, and in particular much attention was paid to polymers due to their tailored design of the molecular structures, their high molar extinction coefficients, their environmental friendliness and low cost. However, most polymers suffer from poor solubility. [2,3]

Heterometallic polymers containing ruthenium, which constitutes most of the most useful and studied dye-sensitizer, should be interesting compound to be synthesized as the can be helpful compounds for obtaining new materials with possible useful properties. Herein we present the synthesis and characterization of the two air-stable water soluble heterometallic polymers based of two new fluorescent ruthenium complexes, the isomers *cis*-[Ru(bpy)₂(PTA)₂]Cl₂ and *trans*-[Ru(bpy)₂(PTA)₂](OTf)₂, and the Ru-Co heterometallic polymer obtained by the reactions of this isomers with CoCl₂.



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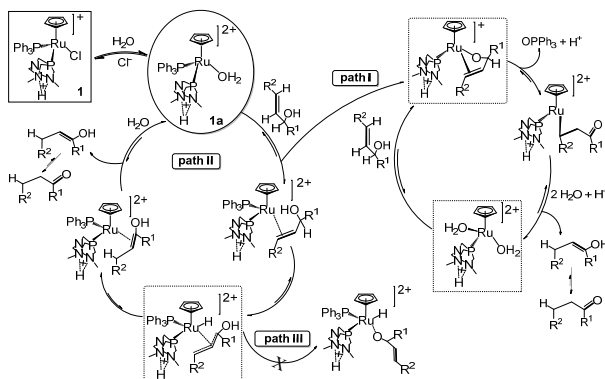
COMPARATIVE STUDY OF THE CATALYTIC ACTIVITY OF [RuClCp(HdmoPTA)(PPh₃)](OSO₂CF₃) AND THE BIS-HETEROMETALLIC COMPLEXES [RuClCp(PPh₃)-μ-dmoPTA-1-κP:2κ²N,N'-MCl₂] FOR THE ISOMERIZATION OF ALLYLIC ALCOHOLS IN WATER

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Our research group has paid special attention during the last few years to the air stable and cheap ligands (PTA, mPTA and dmPTA) and their ruthenium complexes. The wide coordination possibilities and interesting properties of these ligands has incited us to synthesize new PTA derivatives (HdmoPTA and dmoPTA). We have synthesized ruthenium complexes containing these ligands and assessed their catalytic properties. The obtained ruthenium complex [RuClCp(HdmoPTA)(PPh₃)](OSO₂CF₃) (**1**) showed to have interesting catalytic activity for the isomerization of allylic alcohols. Additionally, this complex is able to bond a hetero-metal on its dmoPTA-N-atoms. The obtained bis-heterometallic complexes displayed different catalytic properties than **1**, suggesting that the hetero-metal is able to synergized the catalyst properties of the {Ru}-unit for the isomerization process [1-4]. The complex **1** is more active for the isomerization of allylic alcohols in water than the complexes 2-4 under air and argon atmosphere. In contrast with the behaviour previously observed for [RuClCp(mPTA)₂](OSO₂CF₃)₂, [RuCp(mPTA)₂(OH₂-κO)](OSO₂CF₃)₃ and [RuClCp(PTA)₂], complex **1** display a better catalytic activity for the isomerization of 1-octen-3-ol in phosphate buffer than in water. A proposed mechanism for the isomerization of 1-octen-3-ol catalysed by **1** in water is shown in the Scheme.



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Investigation of the solvent's effect in tautomeric equilibrium of triazino benzimidazoles and a series of meta, para and ortho substituted acetophenones

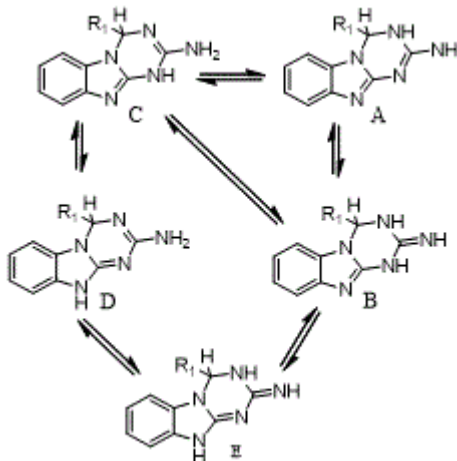
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Several 4-substituted 1,3,5-triazino[1,2-a] benzimidazole-2-amine were synthesised via cyclization of 2-guanidinobenzimidazole with a series of metasubstituted benzaldehydes[1]. The triazinobenzimidazoles obtained can exist in five tautomers forms. To confirm the most stable structure, an investigation of tautomerism and transition states in the gas phase and different solvents (ethanol, THF, hexane, chloroform and water) was performed by calculation at the DFT-B3LYP/6-311+g(d,p) level of theory [2]. The solvent was taken into account with CPCM model [3].

In addition to the tautomeric equilibrium, the reactivity of a series of meta, para and ortho substituted acetophenones has been studied in several solvents (water, heptane, toluene, acetonitrile and THF) using Fukui Function (FF) and the frontier molecular orbital theory, in order to predict the best experimental conditions to obtain good yields.



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Water soluble ruthenium complexes containing PTA and mPTA against natural purine bases: novel purine coordination sites to ruthenium.

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Water is the main component of animals and plants on Earth. Water soluble metal complexes, therefore, could have a important influence on the biological processes and for this reason these compounds should be studied deeply. In particular, water soluble metal complexes are excellent candidates to be active drugs against diseases such as cancer, malaria, etc. We have shown that organometallic water soluble ruthenium complexes containing the moiety $\{\text{CpRuLL}'\}^+$ ($\text{L}, \text{L}' = \text{PPh}_3, \text{PTA}, \text{mPTA}$; $\text{PTA} = 1,3,5\text{-triaz-7-phosphatricycle}[3.3.1.13,7]$ decane; $\text{mPTA} = \text{N-methyl-1,3,5-triaz-7-phosphaadamantane}$) display valuable anti-cancer activity depending on the ligand bonded to the metal.¹ The study of the interaction between obtained water-soluble ruthenium complexes and natural purines is the first step to understand how them interact with DNA. Reaction of $[\text{RuCpCILL}']$ ($\text{L} = \text{PPh}_3, \text{PTA}, \text{mPTA}$; $\text{L}' = \text{PTA}, \text{mPTA}$) with adenine, guanine and thymine led to the synthesis of new water soluble ruthenium complexes in which the purine is bonded to the metal by new coordinative modes, such as that shows in the figure, that is the first example of an adenine molecule bonded to the metal only by N9. Additionally, it is important to point out that in solid state this compound is constituted by two metal complexes linked by two hydrogen bonds ($\text{dN1-NH2} = 3.074 \text{ \AA}$), like those in the DNA molecule, giving rise to a dimer-ruthenium-complex unit. This complex showed a anticancer activity larger than *cisplatin* against resistant *cisplatin*-cancer cells SKOV3 but similar to non-resistant cell.

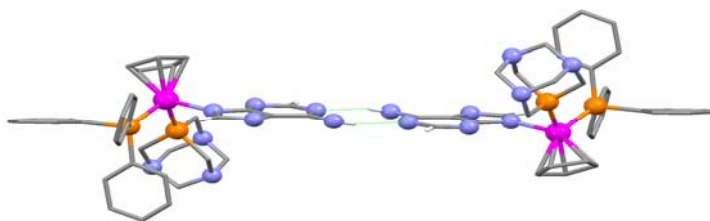


Figure. Figure. X-ray crystal structure for $[\text{RuCp}(\text{adeninate-}\kappa\text{N9})(\text{PPh}_3)(\text{PTA})]$

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Acknowledgement: This work was cofinanced by the European Union (EU FEDER). Thanks are given to Spanish MINECO (CTQ2010-20952) and Junta de Andalucía (Team FQM-317 and project P09-FQM-5402). Manuel Serrano-Ruiz is grateful to Junta de Andalucía for a postdoctoral contract (P09-FQM-5402) and Franco Scalambra to UAL for a PhD grant. Thanks are also given to COST Action CM 1302/WG 1, 2.

Synthesis, NMR elucidation and assignments of a series of bioactive Phthalonitriles, metal-free, zinc, copper, cobalt and nickel phthalocyanines bearing coumarin derivatives

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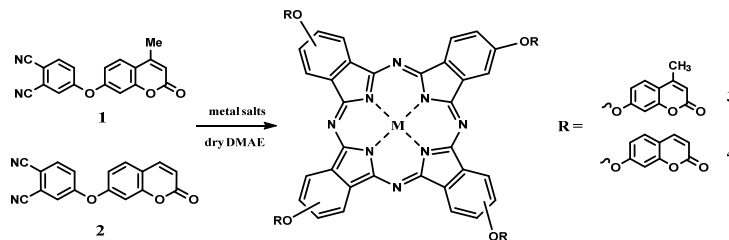
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Abstract

Phthalocyanines have been shown to have very interesting properties coupled with excellent stability to heat, light, and harsh chemical environments. Phthalocyanines can also be used for the production of solar energy conversions, corrosion inhibitors, the prevention and treatment of infectious diseases and in the last few years, substituted phthalocyanine derivatives have also been used in photodynamic cancer therapy (PDT) [1,2]. Also, metallophthalocyanines and its derivatives represent one of the most active classes of compound possessing a wide spectrum of biological activity [3].

In continuation of the search for such potent molecules and as a part of our ongoing research, we plan to synthesize novel phthalonitrile derivatives **1-2** that were synthesized by the reaction between 4-Nitrophthalonitrile with 7-hydroxy-4-methylcoumarin and 7-hydroxycoumarin respectively. New phthalocyanines and metallo-phthalocyanine complexes (Zn, Cu, Co and Ni) were synthesized using the phthalonitrile derivatives **1-2**. The complete IR, UV, ¹H and ¹³C signal assignment of a series of metallophthalocyanines bearing coumarin derivatives are presented. The structures and NMR signal assignment were established by the combined use of 1D and 2D homo- and heteronuclear NMR experiments supported by mass spectrometry and CHN analysis. To elucidate their biological activity, those compounds were screened for their antibacterial activity, which was evaluated against a panel of nine bacterial strains using broth microdilution method.

Keywords: metallophthalocyanines derivatives; antibacterial activity; ¹H NMR; ¹³C NMR; HMQC; HMBC



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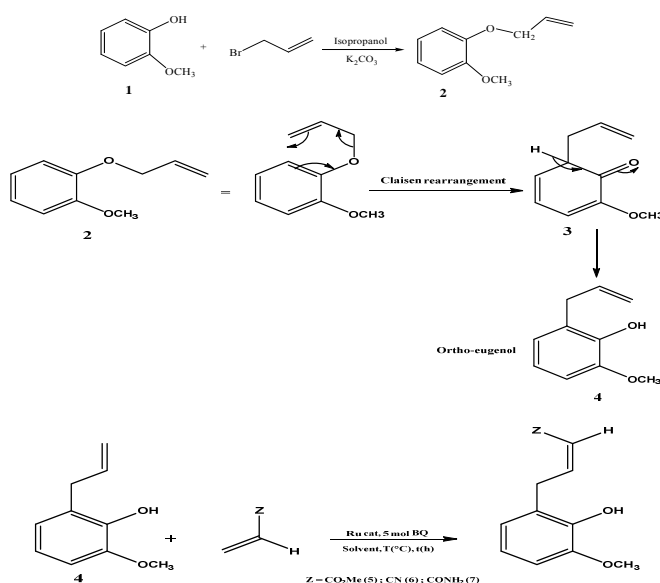
Orthoeugenol a versatile molecule for the production of polyfunctional alkenes via organometallic catalysis

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Abstract

In this study synthesis of ortho-eugenol has been investigated. Synthesis was conducted through two stages of reaction. The first step in the synthetic procedure was to obtain the intermediate **2**. Then the heating of the intermediate **2** will initiate a [3,3] sigmatropic rearrangement to give the orthoeugenol with a good yield. The ruthenium-catalyzed cross-metathesis of ortho-eugenol derivatives with electron deficient olefins including methyl acrylate, acrylonitrile and acrylamides was also reported. **Scheme 1**



Scheme 1: cross metathesis of ortho eugenol with methyl acrylate, acrylonitrile and acrylamide

Keywords: Claisen rearrangement; orthoeugenol; isomerization; O-allylation

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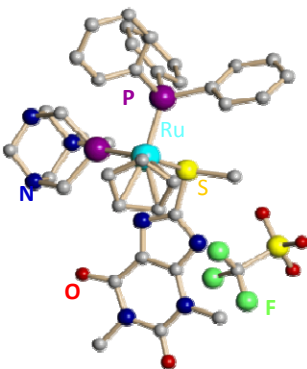
Synthesis, anticancer activity and DFT study of complexes [RuCp(X)LL'] (Cp= cyclopentadienyl; X = 8-thio-theophyllinate (8TTH), 8-methylthio-theophyllinate (8MTT), 8-benzylthio-theophyllinate (8BTT); L=L' = mPTA; L = mPTA, L'= PPh₃; mPTA=N-methyl-1,3,5-triaza-7-phosphaadamantane;PPh₃=triphenylphosphine).

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Water-soluble complexes are excellent candidates to be a new family of active drugs against diseases such as cancer, malaria, etc. Recently, we have shown that organometallic water soluble ruthenium complexes with the moiety {CpRuLL'} display valuable anti-cancer activity.[1] Interestingly interaction of the starting water soluble complex [RuClCpLL'] (L = mTPA; L' =mPTA, PPh₃) with 8-thiotheophyllinate, 8-methyl-S-theophyllinate and 8-benzyl-S-theophyllinate, leads to anticancer active complexes in which the thiopurine is coordinated to the metal by the S atom instead of the N7 imidazolic atom as found until now for thio-purines and lineal-thio-ethers.[2].

An extensive DFT theoretical study was performed in gas phase and aqueous and ethanol solution to elucidate the possible reasons for the new coordination mode of the 8-S-thio, 8-methyl-S-thio and 8-benzyl-S-thiotheophyllinate derivatives (Figures and Table). In gas phase, Gibbs free energies G^0 at 298 K and 1 atm show that S8 coordination is thermodynamically favoured. Their higher dipole moments when compared to N7 coordinated complexes make them even more favoured in polar solvents such as ethanol and water. All calculations were performed at B3LYP/DZVP level of theory and solvents were treated using the continuum CPCM model of Tomasi and coworkers.



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NOTES

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A rectangular graphic with a light orange background. In the center, there is a horizontal brushstroke of red paint. Overlaid on this red stroke is the text 'Workshop Metals, water and Sun 2015' in a blue, serif font. Below the red stroke, the text 'Almería, 21st to 22nd May, 2015' is written in a smaller, blue, italicized serif font.

Workshop Metals, water and Sun 2015

Almería, 21st to 22nd May, 2015



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