Catalysis In Aqueous Media

CIAM Workshop
November 30-December 1, 2007
Laboratoire de Chimie de Coordination du CNRS
205 route de Narbonne,
Toulouse, France

Catalysis In Aqueous Media

Laboratoire de Chimie de Coordination
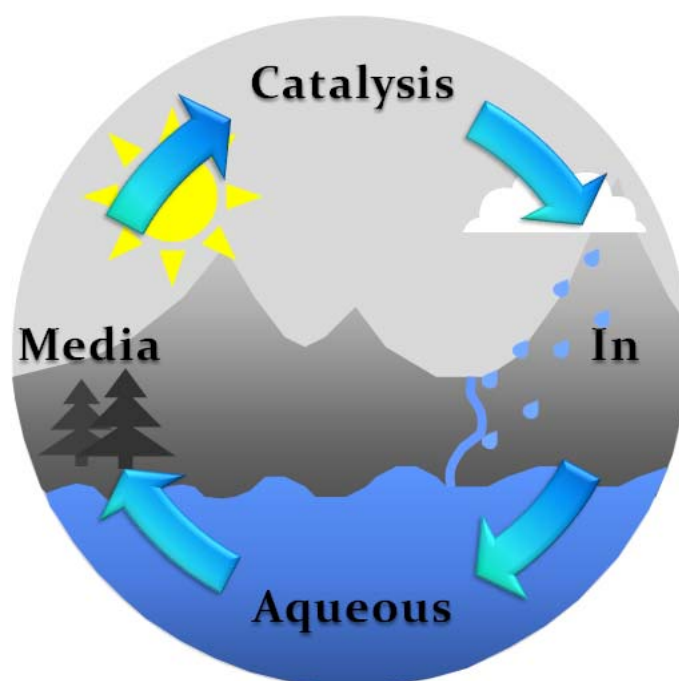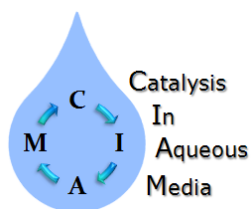
Welcome to CIAM

Catalytic technology is the workhorse of chemical industry and growing concern on the quality of the environment and on sustainable development for society, calls for an increased attention to its improvement. In particular, processes should create less waste (higher selectivity), by-products should be safely removed or transformed into other useful products, new ways to exploit renewable resources and safer operating procedures should be developed. Among various possible approaches, the use of alternative solvents can provide the solution to many of the above problems and the use of water, in particular, presents many attractive features. The use in an industrial process is well exemplified by the Rhône-Poulenc-Ruhrchemie propene hydroformylation to butanal. Although, at the moment, this is probably a unique example of large scale industrial production by aqueous catalysis, it is certain that industry's interest in this technology will keep growing in the years to come. Water has the advantage of being cheap and non toxic while offering the same advantages in terms of phase separation, catalyst confinement and recycling as other less common reaction media such as fluorous solvents and ionic liquids. Much effort is currently undertaken for the development of hydrosoluble ligands and catalysts.

The aim of the meeting is to gather together academic and industrial chemists interested in the state of the art and future perspectives of aqueous catalysis. The topic of this meeting is also of interest to the activities of two European Networks, the AQUACHEM Research Training Network and the IDECAT Network of Excellence. The meeting takes place in conjunction with the Final Meeting of the AQUACHEM Network and is part of the IDECAT conference series. It will represent an occasion to bring together junior and senior researchers from the groups participating in the activities of these European projects, together with outstanding scientists and junior researchers from other European public and private institutions. The workshop will consist of six invited lectures (40 + 5 minutes) and about 14 oral presentations (15 + 5 minutes) selected from the participants, in a warm and informal atmosphere. A poster session will also be organized. Communications by young researchers are particularly welcomed.
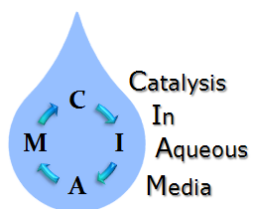
We warmly welcome you to Toulouse and hope this event will be profitable from both scientific and social aspects.

**Anne-Marie Caminade** (co-chair)
Rinaldo Poli (co-chair)
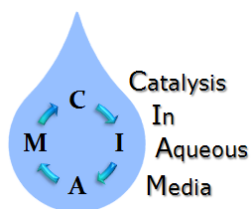**Maurizio Peruzzini** (AQUACHEM coordinator)

Scientific Program

|	Friday, 30th November	Saturday , 1st December
9.00-9.45	PL1: R. Neumann	PL5: D. Cole-Hamilton
9.45-10.05	OC1: L. Ruhlmann	OC10: F. Hapiot
10.05-10.25	OC2 : R. Cibulka	OC11: A. Jentys
10.25-11.05	Coffee break and poster session	Coffee break and poster session
11.05-11.25	OC3 : C. Dinoi	OC12 : N. Legagneux
11.25-11.45	OC4 : S. Otto	OC13: J. Collin
11.45-12.05	OC5 : G.L. Puleo	OC14: V. Landaeta
12.05-12.50	PL2 : J.P. Genet	PL6: F. Joo
13.00	Lunch	Lunch
15.00-15.45	PL3 : A. Lledos	
15.45-16.05	OC6 : O. Filippov	
16.05-16.25	OC7 : K. Vilonen	
16.25-17.00	Coffee break and poster session	
17.00-17.20	OC8 : D. Coquière	
17.20-17.40	OC9 : A. Almassy	
17.40-18.25	PL4 : L. Gonsalvi	
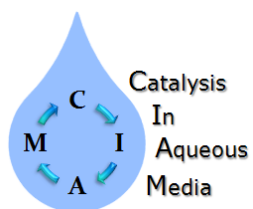
CIAM Invited lectures

PL1 **Organic Chemistry in Water – Polyethylenimine Based Compounds as Facilitators for Catalytic Transformations in Water**

R. Neumann

PL2 **Recollections and New Developments in Transition Metal-Catalyzed Reactions in Aqueous Medium-Synthetic Applications.**

J.P. Genet.

PL3 **Reactions in a reactive medium: Mechanistic features of organometallic hydrogenations in water**

A. Lledos.

PL4 **Aqueous phase catalysis, organometallic reactivity and much more: the renaissance of the water soluble monodentate phosphine PTA**

L. Gonsalvi

PL5 **Tackling a 30 year old problem : Fast reactions of medium chain-length alkenes under aqueous biphasic conditions with rapid phase separation**

D. Cole-Hamilton.

PL6 **Transition Metal-N-Heterocyclic Carbene Complexes as Catalysts of Hydrogenation, Transfer Hydrogenation, Hydration and Redox Isomerization in Homogeneous and Biphasic Media**

F. Joo

CIAM oral communications

OC1 **Photocatalytic reduction and recovery of silver by Dawson-derived sandwhich complex. Mechanistic implications.**
L. Ruhlmann, C. Costa-Coquelard, D. Schaming, S. Sorgues, and I. Lampre.

OC2 **Flavin based oxidation catalysts.**
R. Cibulka, F. Hampl, L. Marková, S. Sayin, E. Svobodová.

OC3 **Efficient oxidation of thiophene derivatives catalyzed by organomolybdenum and -tungsten oxido complexes.**
C. Dinoi, M. Ciclosi, S. Vincendeau, R. Poli, L. Gonsalvi and M. Peruzzini.

OC4 **Catalysts from Dynamic Combinatorial Libraries in Water.**
S. Otto.

OC5 **Influence of water in the aldol reaction promoted by prolinamide derivatives of bile acids as asymmetric organocatalysts.**
G.L.Puleo and A. Iuliano.

OC6 **Solvent Effects in Dihydrogen Bonding: A Computational Analysis.**
O. Filippov, V. Tsupreva, E. Shubina, L. Epstein and A. Lledos.

OC7 **Enzymatic isomerization reactions in aqueous solvent – need of activity coefficients for calculations?**
K. M. Vilonen and A.O.I. Krause.

OC8 **DNA-Based Catalytic Enantioselective C-C Bond Forming in Water.**
D. Coquière, A. J. Boersma, B. L. Feringa, and G. Roelfes.

OC9 **Synthesis and catalytic activity of water-soluble Au(I)-NHC complexes.**
A. Almássy, F. Joó.

OC10 **Biphasic Catalysis Promoted by Modified Cyclodextrins: Current Scope and Future Developments.**
F. Hapiot, A. Ponchel, S. Tilloy and E. Monflier.

OC11 **Hydrogen production by aqueous-phase reforming of Glycerol on supported metal catalysts.**
A. Wawrzetz, A. Jentys, J. A. Lercher.

OC12 **Pd(TPPTS)$_3$ reactions with butenols and butadiene in water.**
N. Legagneux, C. Lucas, E. Kuntz[*].

OC13 **A recyclable multi-substrates catalytic system for enantioselective reduction of ketones in water.**
J. Collin,*[a] J.C. Fiaud, S. Zeror,[a] and L. A. Zouioueche*

OC14 **Synthesis and Characterization of Novel Iridium Complexes with Water-Soluble Phosphine Ligands.**
V. R. Landaeta, M. Erlandsson, M. E. Vásquez-Pérez, C. A. Urbina-Blanco, A. D. Phillips, L. Gonsalvi and M. Peruzzini.
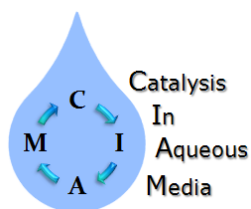
CIAM Posters

P01 **Comparative kinetic and DFT studies on the stabilisation of pyrammidal tautomers of low-valent phosphorus acids**
A. G. Algarra, M. G. Basallote, M. J. Fernández-Trujillo, R. Hernández-Molina, and V. S. Safont.

P02 **Aqueous-biphasic hydroformylation: How to bring higher alkenes into play ?**
S. L. Desset, and D. J. Cole-Hamilton.

P03 **Comparative studies for the catalytic water phase carbon dioxide hydrogenation using iridium and ruthenium PTA complexes (PTA = 1,3,5-triaza-7-phosphaadamantane)**
M. Erlandsson, V. R. Landaeta, S. S. Bosquain, A. Dorcier, A. D. Philips, P. J. Dyson, G. Laurenczy, L. Gonsalvi, and M. Peruzzini.

P04 **Photochemical Behaviour of the Water Soluble Complex [RuCl$_2$(PTA)$_4$]**
A. Romerosa, R. Girotti, S. Mañas and R. N. Perutz.

P05 **Theoretical investigation of the stereoselective reduction of diphenylacetlyene in acidic aqueous solutions catalyzed by water soluble ruthenium(II) phosphine complexes**
G. Kovács, G.Ujaque, A. Lledós, F. Joó.

P06 **Consecutive palladium-catalyzed Hiyama-Heck reactions in aqueous media under ligand-free conditions**
Á. Gordillo, C. López-Mardomingo and E. de Jesús.

P07 **Highly efficient Suzuki-Miyaura cross coupling in aqueous media catalyzed by *trans*-[Pd{NH(CH$_2$CH$_2$OH)$_2$}$_2$(Cl)$_2$][1] complex**
O. Galicia López, D. Morales Morales.

P08 **Catalysis in biphasic (water-CH$_2$Cl$_2$) medium and in water with core/shell bimetallic Rh-Pd nanoparticles.**
C. Bergounhou, C. Blandy, C. Lorber and J.L.Pellegatta.

P09 **Stability of allylphosphonium chloride salt of TPPTS**
C.Lucas, N.Legagneux, E. Kuntz.

P10 **Water soluble metalic compounds**
A. Luquin, S. Schäfer, E. Cerrada, A. Mendía, M. Laguna.

P11 **Preparation and Characterization of Water-Soluble Ruthenium(II) Complexes Containing one Triisopropylphosphine**
M. Martín, E. Sola, H. Horváth, Á. Kathó, F. Joó.

P12 **Deboronation of phosphines containing amine acids. Theoretical and experimental results.**
E. Petersen, G. Kovács , M. Serano, A. Lledós, A. Romerosa, C. Ciardi, G. Reginato and M. Peruzzini.

P13 **PTA ligands as end groups of water-soluble phosphorus dendrimers. Use of their Ru(II) complexes as catalysts**
P. Servin, R. Laurent, L. Gonsalvi, M. Peruzzini, J.P. Majoral, and A.M.Caminade.
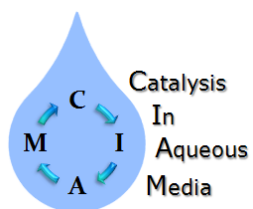
P14 **Synthesis of dendrimers ended by bis(diphenylphosphinomethyl)amino ligands and their use in Palladium catalyzed C-C cross-coupling reactions in the presence of water**
P. Servin, R. Laurent, A. Romerosa, M. Peruzzini, J.P. Majoral, and A.M.Caminade.

P15 **Grafting of scorpionate and other N-ligands to the surface of dendrimers. Preliminary results on the use of their Palladium complexes as catalyts in the presence of water**
P. Servin, R. Laurent, R. Wanke, A. Pombeiro, J.P. Majoral, and A.M.Caminade.

P16 **Towards Janus-type and other types of bifunctional water-soluble dendritic catalysts**
M. Tristany, R. Laurent, J.P. Majoral, and A.M.Caminade.

P17 **Synthesis of new water soluble gold (I) alkynyl complexes**
E. Vergara , E. Cerrada, F. Mohr and M.Laguna.

P18 **Microemulsions for hydroformylation of 1-octene**
K. Voiges, J. Kupka and A. Schumpe.

P19 **Hydrogenation of Carbon Dioxide to Formic Acid Catalyzed by Water-Soluble Rh and Ru Phosphine Complexes**
G. Zhao, F. Joó.

P20 **Application of Dynamic Combinatorial Chemistry in Catalysis**
T. Zieliński, F. Cougnon, E. Bergin, S.Otto.

P21 **Rhenium Complexes as Catalysts for the Baeyer-Villiger Oxidation**
G. Lopes, E.C.B. Alegria, L.M.D.R.S. Martin and A.J.L. Pombeiro

P22 **Catalytic Hydrogenations in Water Phase using Ruthenium(II) Complexes bearing sulfonated phosphines and diamines.**
I. M. M.Ayala, L. Gonsalvi, M. Peruzzini, A. Romerosa and M. S. Ruiz
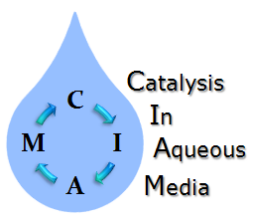
Oral Contributions

Organic Chemistry in Water – Polyethylenimine Based Compounds as Facilitators for Catalytic Transformations in Water

Ronny Neumann

Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel 76100 Fax:+972-89344142;
E-mail: Ronny.Neumnann@weizmann.ac.il

Aqueous biphasic catalysis can be defined as a system wherein an aqueous phase containing a catalyst leads to reaction with an immiscible organic substrate. Importantly, the recovery and recycle of the catalyst containing aqueous phase is by simple phase separation, which also allows separate purification of the organic product. Two factors have considerably limited the application of aqueous biphasic catalysis. The first factor has been the availability of suitable water-soluble catalysts. The second factor and the one principally addressed in this talk is the slow mass transfer of the substrate to the catalytic site. In the past, mass transfer limitations have been tempered by use of surfactants in emulsion, microemulsion and micellular systems. However, these methods suffer severely from difficult separation of the products, very significant difficulty in recovering and recycling the catalytic aqueous phase, and low volume yields of products.

Our foray into the area of aqueous biphasic catalysis began several years ago when we used a water soluble polyoxometalate, $Na_{12}[ZnWZn_2(H_2O)_2(ZnW_9O_{34})_2]$, that could be assembled *in situ* from Na_2WO_4 and $Zn(NO_3)_2$ as catalyst for the selective oxidation of low molecular weight alcohols, vicinal diols and amines with aqueous hydrogen peroxide.[1] These reactions were successful because the more hydrophilic functional groups that were oxidized were available to the catalytic site at the interface of the organic and aqueous phases. Although, the polyoxometalate solubilized into an organic medium was very active for epoxidation of hydrophobic alkenes, this reaction failed completely in the analogous aqueous biphasic reaction. In order to overcome the obstacle of lack of availability of the hydrophobic substrate to the catalytic site and to allow aqueous biphasic oxidation of hydrophobic alkenes with H_2O_2 catalyzed by polyoxometalates, we utilized the idea that alkylated polyethylenimine could be considered a very primitive enzyme or synzyme having a hydrophobic core and a hydrophilic surface. Indeed, alkylation of polyethylenimine led to an amorphous structure, soluble in water that retained hydrophobic cores that intercalated polyoxometalate catalysts and permitted solubilization of the hydrophobic substrates in the alkylated polyethylenimine-catalyst construct.[2] This allowed for the efficient aqueous biphasic oxidation of even very hydrophobic substrates such as methyloleate with hydrogen peroxide. The recovery and recycle of the aqueous catalyst phase was simple and efficient.
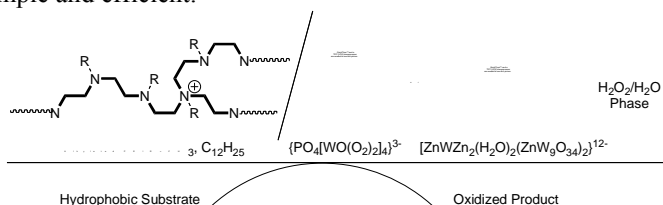
Consequent to this proof of principle, that is use of alkylated polyethylenimine to facilitate aqueous biphasic catalysis, we extended the concept in two directions. First, alkylated polyethylenimine stabilized palladium nanoparticles in water allowing aqueous biphasic catalytic hydrogenation of alkenes. Surprisingly and rather inexplicably the hydrogenation was highly *chemoselective* for hydrogenation of the less hindered alkene; for example 3-methylcyclohexene was reduced selectively in the presence of 1-methylcyclohexene.[3] Furthermore, the preparation of a crosslinked polyethylenimine assembly that encapsulated a polyoxometalate catalyst resulted in the *lipophiloselective* oxidation of secondary alcohols.[4] Thus, even though reactions were carried out in water competitive oxidation of a more hydrophobic alcohol in the presence of a hydrophilic alcohol significantly favored the former. The lipophiloselectivity was proportional to the relative partition coefficient of the substrates. See Figures below.
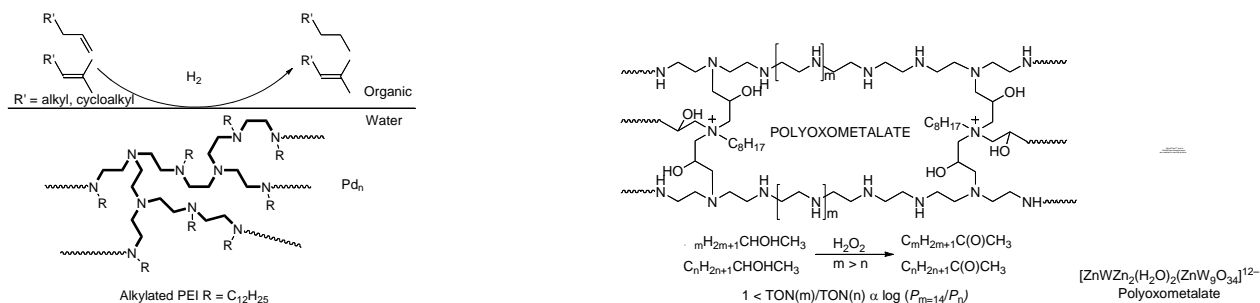
1. (a) Sloboda-Rozner, D.; Alsters, P. L.; Neumann, R. *J. Am. Chem. Soc.* **2003**, *125*, 5280-5281. (b) Sloboda-Rozner, D.; Witte, P.; Alsters, P. L.; Neumann, R. *Adv. Synth. Catal.* **2004**, *346*, 339-345.
2. Haimov, A.; Cohen, H.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 11762-11763.
3. Vasylyev, M. V.; Maayan, G.; Hovav, Y.; Haimov, A.; Neumann, R. *Org. Letters*, **2006**, *8*, 6445-5448.
4. Haimov, A.; Neumann, R. *J. Am. Chem. Soc.* **2006**, *128*, 15697-15700.

Photocatalytic reduction and recovery of silver by Dawson-derived sandwhich complex. Mechanistic implications.

Laurent Ruhlmann, Claire Costa-Coquelard, Delphine Schaming, Sébastien Sorgues, and Isabelle Lampre [a]

Laboratoire de Chimie Physique, UMR 8000 CNRS/Université Paris-Sud 11, Faculté des Sciences d'Orsay, Bâtiment 349, 91405 Orsay Cedex, France.
Fax: +33 1 69 15 43 28; Tel: +33 1 69 15 47 32; E-mail: Laurent.ruhlmann@u-psud.fr

Metal recovery is a topic of great interest concerning metal pollution and resource conservation. Up to now, various methods have been established for the recovery of metals, involving chemical and electrochemical processes. A photocatalytical processes using polyoxometalates (POMs) have appeared as an alternating solution.[1]

Within this context, we present the photocatalytic reduction of $Ag^I_2SO_4$ by Dawson-derived sandwich type polyoxo-metalates $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{12-/16-}$ (M = Fe^{3+}, Co^{2+}, Ni^{2+}, or Zn^{2+}) in aqueous solutions in the presence of an organic substrate (propan-2-ol) as sacrificial electron donor.
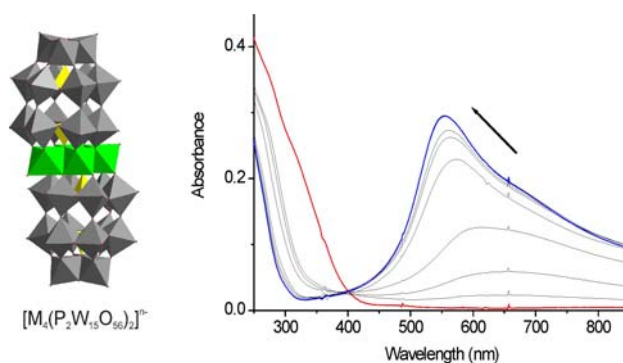

Fig. 1. UV-vis spectra of irradiated solution showing formation of reduced $[Fe_4(H_2O)_2(P_2W_{15}O_{56})_2]^{14-}$.

Direct illumination at the O-M charge transfer band (near visible and UV region) renders POM strong oxidants able to abstract electrons from propan-2-ol which is converted to hydroxy-isopropyl radical and, finally, acetone (Fig. 1). The reduced polyoxotungstate is able, in turn, to transfer one electron to Ag^+ to give Ag^0 which form colloidal metal nanoparticles Ag_n stabilized by POM. The TEM pattern of the Ag_n particles showed lamellar structures suggesting the stabilization of surfaces by surfactant POM molecules (Fig. 2).[2]
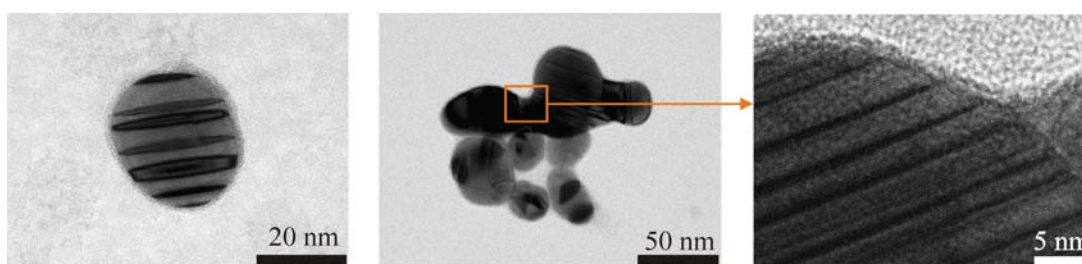

Fig. 2. TEM micrographs of Ag nanoparticles stabilized by $[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$.

Complexes based on the association of POM and tetracationic metalloporphyrins $ZnTMePyP^{4+}$ were also prepared with the aim of obtaining new hybrid organic – inorganic complex which would appear to be quite promising in relation to photocatalytic reactions.

References

1. A.Troupis, A. Hiskia, E. Papaconstantinou, "Synthesis of Metal Nanoparticles by Using Polyoxometalates as Photocatalysts andStabilizers" *Angew. Chem. Int. Ed. Engl.*, **2001**, *41*, 1911-1914. and references therein.
2. L. Ruhlmann, C. Costa-Coquelard, S. Sorgues, and I. Lampre, *Macromolecular Symposia*, **2007**, in press.
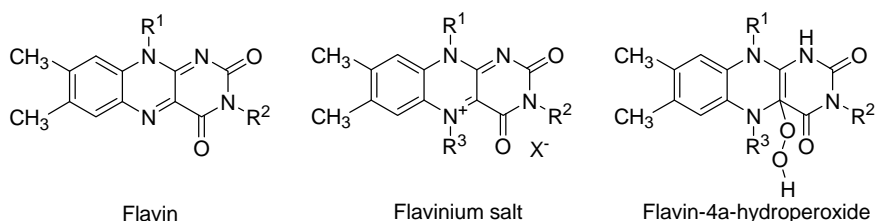
Flavin based oxidation catalysts

**Radek Cibulka, František Hampl, Lenka Marková, Serkan Sayin, Eva Svobodová**

Department of Organic Chemistry, Institute of Chemical Technology, Prague, Technická 5, Prague 6, Czech Republic. Fax: +420 220444288;
Tel: +420 220444279; E-mail: cibulkar@vscht.cz

Flavins represent an important group of natural compounds acting as versatile reducing or oxidizing agents in many types of enzymes[1] (oxidoreductases, monooxygenases, hydroxylases). Considerable versatility of flavins in various redox reactions in natural systems ensues from their ability to participate either in electron or in hydride transfer reactions.[1,2] Besides that, flavins are present in natural photoactive systems utilizing their facile excitability by visible light. Excited flavins can either emit light or oxidize or reduce suitable quenchers by photoinduced electron transfer.[2]

Both "light" and "dark" reactions mediated by flavoenzymes inspired many authors to employ flavin derivatives in oxidation of various organic substrates. Flavin-4a-hydroperoxide generated from flavinium salts was used for Baeyer-Villiger oxidation of cycloalkanones, oxidation of tertiary amines to *N*-oxides, and sulfoxidations.[3,4] A few chiral flavinium salts have been reported to catalyze sulfoxidations or Baeyer-Villiger oxidations with moderate stereoselectivity.[3,4] Flavins were also tested as mediators of photooxidation of benzylalcohols.[4,5] However, in spite of a broad spectrum of reactions provided by flavoenzymes, applications based on artificial flavin organocatalytic systems in organic syntheses are still limited.[4]

Flavin   Flavinium salt   Flavin-4a-hydroperoxide

Our research is aimed at the design of new flavin oxidation catalysts and photocatalysts and investigation of their properties. Special attention will be paid on the efficiency, chemoselectivity and stereoselectivity of the prepared catalysts, and on the possibility to perform the oxidations under enviromentally friendly conditions in water-based media. Here, we report supramolecular systems based on nanoaggregates (anionic, cationic and nonionic micelles) containing 5-alkylflavinium salts which are efficient organocatalysts for the oxidation of thioethers with hydrogen peroxide at room temperature (Scheme 1). We have found that in contrast with the oxidations performed in homogeneous solutions, cationic micelles favour catalyzed reaction in comparison with the non-catalyzed one (relative reaction rate v_{cat}/v_0 is increased).[7] The efficiency of flavinium catalysts in micelles strongly depends on their structure, lipophilicity, and on pH of the reaction medium. Suppression of the non-catalyzed reaction in micellar systems is interesting from the point of view of potential applications in stereoselective oxidations mediated by chiral flavinium salts.
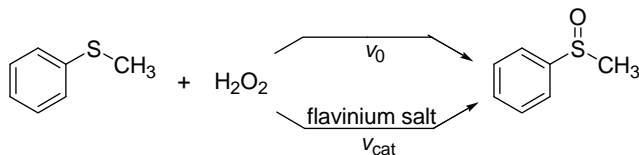
1   B. Palfey, V. Massey, in Comprehensive Biological Catalysis (Sinnott M., Ed.), Vol. 3, , Academic Press, London 1998, pp. 83 – 154.
2   F. Müller (Ed.), Chemistry and Biochemistry of Flavoenzymes, CRC: Boca Raton, Fl, 1991, pp. 171 – 193.
3   J. –E. Bäckvall, in: Modern Oxidation Methods, Wiley-VCH Verlag, Weinheim 2004, pp. 193 – 222.
4   F. G. Gelalcha, *Chem. Rev.* **2007**, *107*, 3338.
5   S. Fukuzumi, K. Yasui, T. Suenobu, K. Ohkubo, M. Fujitsuka and O. Ito, *J. Phys. Chem. A* **2001**, *105*, 10501.
6   R. Cibulka, R. Vasold and B. König, *Chem. Eur. J.* **2004**, *10*, 6223.
7   L. Marková, R. Cibulka, F. Hampl, *J. Mol. Catal. A*, **2007**, *277*, 53.

Efficient oxidation of thiophene derivatives catalyzed by organomolybdenum and -tungsten oxido complexes

Chiara Dinoi[a], Marco Ciclosi[a], Sandrine Vincendeau[a], Rinaldo Poli[a], Luca Gonsalvi[b] and Maurizio Peruzzini[b]

[a] *Laboratoire de Chimie de Coordination, UPR 8241 liée par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 Route de Narbonne, UPR CNRS 8241, 31077 Toulouse Cedex, France, Fax: +33-561553003, chiara.dinoi@libero.it*
[b] *ICCOM CNR, 50019 Sesto Fiorentino FI, Italy, Fax: +39-055-5225203; Tel: +39-055-5225289; E-mail: mperuzzini@iccom.cnr.it*

In order to decrease the formation of sulfur oxides (SO_x), produced during the combustion of sulfur-containing diesel oil contaminants, very stringent environment regulations have been recently imposed. The existing hydrodesulphurisation technology (HDS), however, can hardly decrease the sulphur content to an ultra low level, especially in the case of some specific refractory sulfur-containing organic molecules, such as the thiophene derivatives, benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT).[1]

One of the most promising alternatives to HDS is considered to be the oxidative desulphurisation process (ODS), in which sulphur contaminants are oxidized into the corresponding sulfoxides and sulfones under mild conditions and then removed from the treated fuel by extraction and adsorption techniques.[2]

The $Cp^*_2M_2O_5$ complexes (M = Mo, W), for which an improved synthesis has recently been reported by our group,[3] are now investigated as catalysts for the BT, DBT and DMDBT oxidation reaction in aqueous acetonitrile by using H_2O_2 as oxidant. Both compounds are efficient catalysts, the W compound resulting much more efficient than the Mo analogue. Kinetics studies have also been carried out showing, in the case of DBT and DMDBT, the formation of a considerable amount of sulfoxide as an intermediate product to the final sulfone. The rate constants and activation parameters relative to the oxidation process of the three thiophene substrates will be also presented.
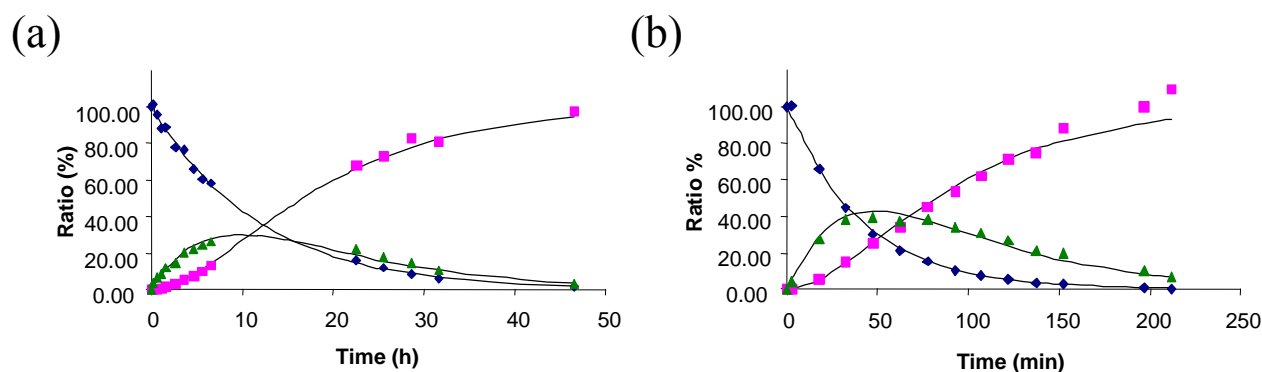
(a)   (b)

Figure I: Evolution *vs.* time of sulfide (diamonds), sulfoxide (triangles) and sulfone (squares) in the $Cp^*_2M_2O_5$-catalysed DBT oxidation (M = Mo, (a), W, (b)).

1   H. Lu, J.Gao, Z. Jiang, Y. Yang, B. Song, C. Li, *Chem. Commun.* **2007**, 150.
2   L. Lu, S. Cheng, J. Gao, G. Gao, M. He, *Energy & Fuels* **2007**, *21*, 383.
3   C. Dinoi, G. Taban, P. Sözen, F. Demirhan, J.-C. Daran, R. Poli, *J. Organomet. Chem.* **2007**, *692*, 3743.

Catalysts from Dynamic Combinatorial Libraries in Water

Sijbren Otto[a]

[a] *University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK. Fax: +44 1223 336017; Tel: +44 1223 336509; E-mail: so230@cam.ac.uk*

Whilst the rational design of catalysts remains a huge challenge, the use of combinatorial methods for catalyst discovery is an attractive alternative. Dynamic combinatorial chemistry[1] has largely unexplored potential in this regard and relies on the use of a reversible reaction to link building blocks together to form an equilibrium mixture of compounds. We have adapted disulfide chemistry for the generation of dynamic combinatorial libraries (DCLs) in water.[2] Screening of our dynamic libraries of macrocyclic disulfides against several guests resulted in the identification of a series of new synthetic receptors.[3]

Exposing a DCL to a compound that resembles the transition state of a reaction (a transition-state analogue or TSA) should result in a shift in the library distribution towards those compounds that bind the TSA. Receptors that have an affinity for the transition state of a reaction should be catalytically active (provided this affinity exceeds that for the initial state).

We have found that macrocycles **1** and **2** are selected and amplified upon exposing a DCL made from two dithiol building blocks to a TSA for the Diels-Alder reaction of diene **3** with cyclopentadiene to give adduct **4** (Figure 1). Indeed receptor **1** was found to have modest catalytic activity.[4,5]

These results constitute the first example of the use of dynamic combinatorial chemistry for identification and synthesis of receptors with catalytic activity; the supramolecular chemists' equivalent of the catalytic antibody approach with important advantages over the latter in terms of controllability (through building block design) and practicality (timescale, expense and ability to scale up).
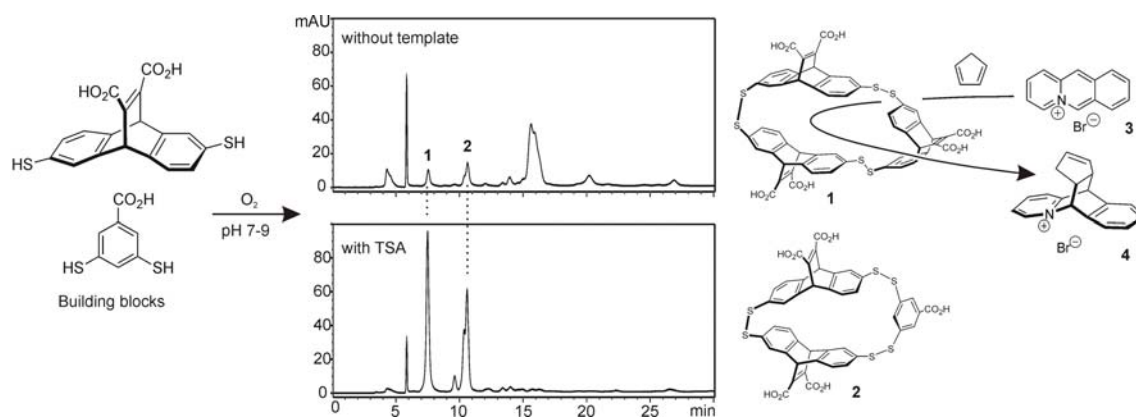
Figure 1. *HPLC analysis of a DCL made from two dithiol building blocks showing amplification of receptors **1** and **2** upon addition of a TSA for the Diels-Alder reaction of **3** to give adduct **4**.*

1   P. T. Corbett, J. Leclaire, L. Vial, K. R. West, J.-L. Wietor, J. K. M. Sanders and S. Otto, *Chem. Rev.*, **2006**, *106*, 3652.
2   S. Otto, R. L. E. Furlan and J. K. M. Sanders, *J. Am. Chem. Soc.*, **2000**, *122*, 12063.
3   S. Otto, R. L. E. Furlan and J. K. M. Sanders, *Science*, **2002**, *297*, 590; P. T. Corbett, L. H. Tong, J. K. M. Sanders and S. Otto, *J. Am. Chem. Soc.*, **2005**, *127*, 8902; L. Vial, R. F. Ludlow, J. Leclaire, R. Perez-Fernandez and S. Otto, *J. Am. Chem. Soc.*, **2006**, *128*, 10253.
4   B. Brisig, J. K. M. Sanders and S. Otto, *Angew. Chem., Int. Ed.*, **2003**, *42*, 1270.
5   L. Vial, J. K. M. Sanders and S. Otto, *New J. Chem.*, **2005**, *29*, 1001.

Influence of water in the aldol reaction promoted by prolinamide derivatives of bile acids as asimmetric organocatlysts

Gian Luigi Puleo,[a] and Anna Iuliano[b]

[a] Scuola Normale Superiore di Pisa,Piazza dei Cavalieri 7, 56126 Pisa, Italy. Fax: +39 050 2219260; Tel: +39 050 2219230; E-mail: g.puleo@sns.it
[b] Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy. Fax: +39 050 2219260; Tel+39 050 2219231; E-mail: iuliano@dcci.unipi.it

Organocatalysis offers the advantage to be environmental friendly, because no metal species are involved, and to perform a lot of reactions without the use of inert atmosphere or absolute solvents.[1] These considerations have prompted scientists to search for organocatalytic systems that can work under very environmentally benign conditions, i.e. low catalyst loading or water as reaction solvent. Many efforts have been addressed toward the synthesis of such appealing organocatalysts that have produced systems able to afford very good stereoselectivities under such a kind of conditions.[2] However, the achievement of a versatile organocatalyst, able to work with low catalyst loading or in water is still challenging. In fact, it often happens that the use of water as solvent requires the presence of acid or salt additives[3] in order to the organocatalyst be efficient, or that a large excess of the donor carbonyl compound is mandatory to perform the reaction.[4] We have recently synthesized a new family of asymmetric organocatalysts, by linking the prolinamide moiety to the different functionalized positions of cholic and deoxycholic acids.[5] The preliminary study aimed at verifying the capability of these systems to work as organocatalysts in the direct asymmetric aldol reaction between acetone and 4-nitrobenzaldehyde showed that the best combination position on the cholestanic backbone-absolute configuration of the prolinamide moiety is obtained when the D-prolinamide unit is linked at the 12-position of the bile acids; in addition, the presence of free hydroxyl groups at 3 and 7 positions guaranteed the achievement of good levels of asymmetric induction (80% of e.e.).[5] In particular organocatalyst **1** is able to catalyze without the presence of any additive also the aldol reaction also between cyclic ketones and electronpoor aromatic aldehydes, affording aldol products in good yield and e.e.s up to 98%, in water as solvent[6]. Interestingly water made easy the recover of the product, produced a great increasing of reaction rate and, in the case of cyclopentanone, led to the presence of the opposite diastereoisomers with respect to the use of organic solvent[6].

structure of the best organocatalyst   n=1, 2.   e.e up to 98%
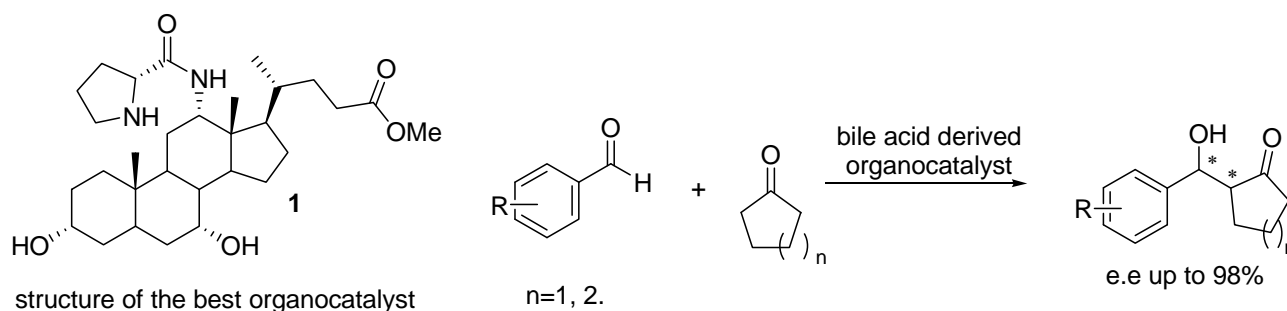
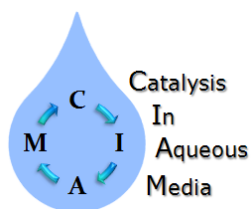1 a) Ley S. *Asymetric Synthesis*, **2007**, 201-206.
2 a)Sathapomvajana S. Vilaivan T., *Tetrahedron* **2007**, *63(41)* 10253-10259; b)Maja V.; Raj, M.; Singh, V.K.; *Org. Lett*. **2007**, *9(13),* 2593-2595;
3 a)Zhang, L.; Gao, Q.; Gao, J.; Xiao, J.; Li, C.; *Journal of Catalysis*, **2007**, *250(2)*, 360-364. b)Guillena, G.; Hita, M. C.; Najera, C.; *Tetrahedron: Asymmetry,* **2007**, *18(11),* 1272-1277; c)Gryko, D.; Saletra W.J.; *Org. Biomol. Chem.,* **2007**, *5(13)*, 2148-2153; d)Zhang L.; Liu, S.; Xu, H.; Chey, J.-P.; *Tetrahedron*, **2007**, *63(9),* 1923-1930; e)Chen, X-H; Luo, S.-W., Tang, Z.; Cun, L.-F., Mi, A.-Q.; Jiang, Y.-Z.; Gong, L.-Z.; *Chem. Eur. J.*; **2007**, *13(2),* 689-701. f) Giacalone, F.;, Guttadamia, M.; Marculescu, A. M., Noto, R.; *Tetrahedron Lett.* **2007**, *48(2),* 255-259;
4 a) Guizzetti S.; Benaglia, M.; Raimondi, L.; Celentano, G.; *Org. Lett.* **2007**, *9(7),* 1247-1250); b)Sakthivel, K.; Notz, W.; Bui, T. Barbas C. F. III, *J. Am. Chem. Soc.* **2001**, *123(22),* 5260-5267.
5 Puleo, G.L., Masi, M.; Iuliano, A.; *Tetrahedron: Asymmetry*, **2007**, *18(11),* 1364-1375.
6 Puleo, G.L., Iuliano A.; *Tetrahedron: Asymmetry*, **2007,** article in press.

Recollections and New Developments in Transition Metal-Catalyzed Reactions in Aqueous Medium-Synthetic Applications.

Jean-Pierre Genet

Ecole Nationale Supérieure de Chimie de Paris
Laboratoire de Synthèse Sélective Organique et Produits Naturels - UMR CNRS 7573
11 rue P. et M. Curie – 75231 PARIS Cedex 05, France
fax 33(0) 1 4407 1062;Tel: 33 (0) 1 4427 6743 jean-pierre-genet@enscp.fr

The use of water in organometallic catalysis for the synthesis of organic compounds is now well-documented [1]. Reactions carried out in aqueous medium may offer some advantages over those occurring in organic solvents.

Recent examples and recollections from our laboratories will highlight the utility of water as solvent or co-solvent in catalysis and synthetic organic chemistry.[2]

1) Reviews: a) C.J. Li, Chem. Rev. **2005**, 105, 3095; b) J.P. Genet, M. Savignac, S. Lemaire-Audoire in *Transition metal catalysed reactions*, Ed. S.I. Murahashi and S. G.Davies, Blackwell Science, **1999**, 55;c) J.P. Genet, M. Savignac *J. Organomet. Chem.,* **1999** 576, 305,

2) R. Amengual, V. Michelet, M. Savignac, J.P. Genet, *Adv. Synth. Catal*. **2002**, 344, 393;R. Amengual, V. Michelet, J.P. Genet, *Synlett* **2002**, 1791;E. Genin, V. Michelet, J.P. Genet, *Tetrahedron Lett*. **2004**, 45, 4157; ibid. *J. Organomet. Chem*. **2004**, 689, 3820;E. Genin, R. Amengual, V. Michelet, M. Savignac, A. Jutand, L. Neuville, J.P. Genet, *Adv. Synth. Catal*. **2004**, 346, 1733. M. Pucheault, S. Darses, J.P. Genet, *Tetrahedron Lett*. **2002**, 43, 6155; ibid. *Eur. J. Org. Chem.* **2002**, 3552; M. Pucheault, S. Darses, J.P. Genet, *Chem. Commun*. **2005**, 4714; E. Genin, L. Leseurre, P. Y. Toullec, J.P. Genêt ,V. Michelet *Synlett* **2007**,11,1780.

Reactions in a reactive medium: Mechanistic features of organometallic hydrogenations in water

Agustí Lledós[a]

[a] Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain. Fax: 34 935812920; Tel: 34 935811716; E-mail: agusti@klingon.uab.es
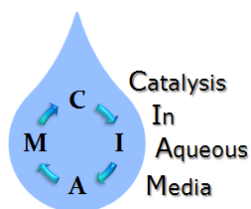
Water is a reactive medium. Water molecules can form hydrogen bonds with different parts of the catalyst or the substrate can take part in proton transfer reactions and can coordinate to the metal centers. Moreover the pH of the solution can alter the presence of the different catalytically active species. Reaction mechanisms in aqueous solution can be very different to those in the conventional organic solvents. A deeper comprehension of the reaction mechanisms of the organometallic transformations in water is required for developing efficient catalytic processes in aqueous media. In close collaboration with experimental studies, computational studies can contribute to this aim giving a microscopic picture of the organometallic reactivity in water. In the framework of the EU funded AQUACHEM network we have been involved in an initiative devoted to this purpose. The research activity of the UAB group in this field will be reviewed in this lecture.

Mechanistic studies of efficient hydrogenation processes which can be performed by water-soluble Ru(II) complexes will be presented. The mechanism of the H-H bond splitting in water will be first analysed.[1] Then the reaction mechanism of the pH selective C=C/C=O reduction of α,β-unsaturated aldehydes[2] and the stereoselective hydrogenation of disubstituted alkynes[3] will be discussed. Overall calculations highlight that water presents a distinct reaction environment for organometallic processes. The solvent molecules and its ions can take part in the reaction and make unconventional pathways possible.

4'
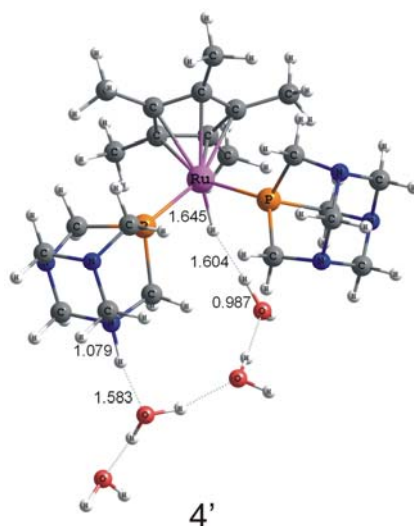
1   A. Rossin, L. Gonsalvi, A. D. Phillips, O. Maresca, A. Lledós and M. Peruzzini, *Organometallics*, **2007**, *26*, 3289.
2   (a) G. Kovács, G. Ujaque, A. Lledós, F. Joó, *Organometallics* **2006**, *25*, 862. (b) A. Rossin, G. Kovács, G. Ujaque, A. Lledós, F. Joó, *Organometallics* **2006**, *25*, 5010.
3   G. Kovács, G. Ujaque, A. Lledós and F. Joó, *Eur. J. Inorg. Chem.* **2007**, 2879.

Solvent Effects in Dihydrogen Bonding: A Computational Analysis

Oleg Filippov,[ab] **Viktoria Tsupreva**[a]**, Elena Shubina,**[a] **Lina Epstein**[a] **and Agusti Lledos**[b]

[a]*A.N. Nesmeyanov Institute of Organoelement Compounds (INEOS), Vavilov str. 28, V-334, 119991 Moscow, Russia. Fax: +7 499 1355085; Tel: +7 499 1356448; E-mail: H-Bond@ineos.ac.ru*

[b]*Departament de Química, Edifici Cn, Universitat Autónoma de Barcelona, 08193 Bellaterra, Catalonia, Spain Fax: 34 93 5812920; Tel: XX 34 93 5811716; E-mail: agusti@klingon.uab.cat*
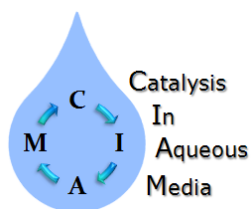
The knowledge of solvent influence on the proton transfer reactions of hydride compounds is very important for the understanding of catalytic and other chemical processes involving proton transfer via dihydrogen bonds steps. The change of acidity and basicity scales on going from the gas phase (or apolar organic solvents) to a protic solvent is well established but is still not completely understood. Moreover, the influence of the solvent properties (polarity and ability to form hydrogen bonds as acid and base) on the stability of hydrogen bonded intermediates has not been previously investigated by quantum chemical approaches. Here we present the results of our computational study addressing these' questions.

Dihydrogen bonded (DHB) complexes of main group anionic hydrides AlH_4^- and $[B_{10}H_{10}]^{2-}$ with alcohols were studied by quantum chemical calculations (DFT/B3LYP and second order Møller–Plesset (MP2)) in gas phase and wide range of solvents of different polarity from hexane to water. Non-specific interactions were taken by PCM calculations and for specific solvatation introducing of solvent molecules were used.

Dependence of geometric and spectral characteristics of DHB complexes from solvent polarity was established. In polar solvents DHB complexes become less stable with elongation of H…H bond and lowering interaction energy. In acidic solvents like $CHCl_3$, H_2O, CH_3OH specific solvatation both of hydride and alcohol significantly changes DHB complex properties.

Several approaches for computation of interaction energy in solution were probed. While enthalpy values are well described by PCM correction for calculation of Gibbs free energy in solution special techniques are needed. An approach which takes into account chemical nature of interaction of solvated molecules is proposed for sufficiently accurate estimation of Gibbs free energy in solution.

Enzymatic isomerization reactions in aqueous solvent – need of activity coefficients for calculations?

Kati M. Vilonen and **A. Outi I. Krause**

Laboratory of Industrial Chemistry Helsinki University of Technology (TKK), Espoo, Finland.
Fax: +358 9 451 2622; Tel: +358 9 451 2627; E-mail: kati.vilonen@tkk.fi

Xylose isomerase enzyme, also known as glucose isomerase, (EC 3.5.1.5), is an effective catalyst for isomerisation of different pentose and hexose sugars. Industrially important reaction is the isomerisation of glucose to fructose, which is the final process step in the production of high fructose corn syrup.

Enzymatic reactions are typically done in pure aqueous phase, because organic solvents deactivate enzymes easily. However, cross-linked enzyme crystals form an exception, having usually good stability in aqueous organic solvents. One example is cross-linked xylose isomerase crystals (CLXIc), which made possible to study isomerisations also in aqueous organic media [1]. This was done because it was found earlier that addition of organic co-solvent to reaction medium affects to reaction equilibrium [2,3]. The organic co-solvents were found out to affect both the conversion and the reaction rate [3]. It is also found out that the sugar concentration in pure aqueous solvent affected reaction equilibrium.

The effect of sugar concentration and organic co-solvent on the equilibrium needs some explanations. The change in the reaction rate could be related to different reaction mechanism because of organic co-solvent, but this can not explain the effect on equilibrium conversion. According to thermodynamics the equilibrium constant of a reaction can be calculated using the Gibbs free energy change for the reaction (eq 1).

$RT \ln K_a = \Delta G_r$ (1)   where R = the gas constant, T = temperature, K_a = equilibrium constant, G_r = Gibbs free energy of reaction

Based on equation one, the sugar concentration or reaction solvent should not change the reaction equilibrium in a way which was experimentally found. An example of measured effect of sugar concentration on the reaction equilibrium between glucose and fructose is shown in figure 1 (K_x). The explanation of changes might be related to non-ideality of the reaction system, because concentrations of sugars were used in calculations instead of activities (eq 2). For the reversible reaction, such isomerisation between compounds A and B, in an ideal system the equilibrium constant is calculated using only concentrations (eq 2), but in a real system concentration should be corrected with activity coefficients (eq 3).

In ideal system $K_a = K_x = c_B / c_A$ c_A = concentration of A (activities are assumed as 1)   (2)
In real system $K_a = K_x * K_\gamma = c_B / c_A * \gamma_B / \gamma_A,$ γ_A = activity coefficient of A   (3)

As a preliminary attempt to take the non-ideality of the system into account the activity coefficients were estimated with UNIFAC group contribution method, using parameters specially determined for typical molecular groups of sugars [4]. This method was chosen because it had suitable parameters for sugars, because there is not quite much thermodynamic data from sugars available. Estimated activity coefficients were used to calculate the K_γ and then K_a was calculated as a product from K_x (from measurements) and K_γ (from estimated activities) (eq 3). One example of all calculated values are shown in figure 1.

Figure 1. Effect of sugar concentration on equilibrium constant.
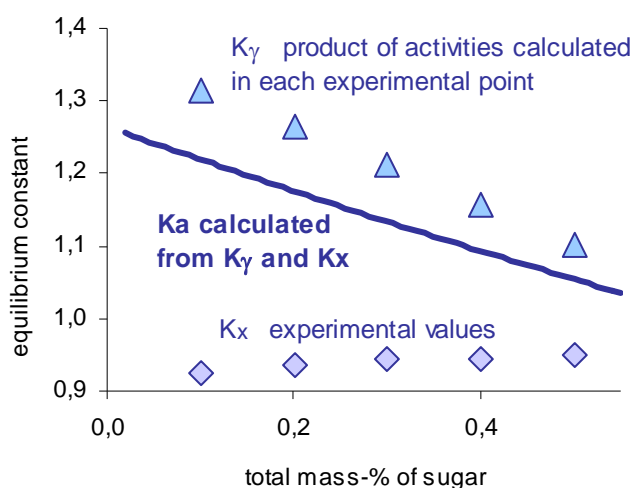
In summary from the experimental results and from the estimation of activity coefficient it can be concluded that the reaction system is non-ideal, which explains the effect of reaction medium on equilibrium. So there is a clear need to use activities instead of concentrations in calculation of reaction equilibrium and reaction rate. However, the UNIFAC method, which is initially developed for gas-liquid equilibrium for non-polar or slightly polar hydrocarbons, is an estimation method and not best suited for aqueous solutions. So there is a need to try some other methods for calculation of liquid activity coefficients.

1   K.M. Vilonen, A. Vuolanto, J.Jokela, M.S.A. Leisola and A.O.I. Krause, *Biotechnol.Prog.*, **2004**, 20 1555-1560.
2   K. Visuri, and A.M. Klibanov, *Biotechnol. Bioeng.*, **1987**, 30, 917-920
3   K.G.I. Nilsson, K. Mosbach and K. Sakaguchi, *Biotechnol. Lett.*, **1991**, 13, 787-792.
4   N. Spilitios and D. Tassios, *Fluid Phase Eq.*, **2000**, 173, 39-55.

DNA-Based Catalytic Enantioselective C-C Bond Forming in Water

David Coquière, A. J. Boersma, Ben L. Feringa, and Gerard Roelfes

Department of Organic and Molecular Inorganic Chemistry, Stratingh Institute for Chemistry,
University of Groningen, Nijenborgh 4, 9747 AG Groningen (The Netherlands).
Fax: (+31) 50-363-4296; Tel: (+31) 50-363-4256; E-mail: D.Y.G.Coquiere@rug.nl

The association of catalytic transition metal center with natural chiral biopolymers has given rise to a new powerful generation of hybrid catalyst. The double helix of DNA represents a very attractive scaffold for hybrid catalyst design and we have recently demonstrated that its chirality's can be transferred efficiently to the Cu^{2+} catalytic asymmetric Diels-Alder reaction.[1] This was achieved by binding a copper complex, based on a non-chiral ligand, to DNA in a non-covalent fashion (scheme 1). The DNA closed to the catalytic center provides the chiral environment and induce the enantioselectivity of the catalytic reaction. Using this method, up to 99% e.e. was obtained in the Diels-Alder reaction. Furthermore, this reaction could be performed on a synthetically relevant scale.

Given the excellent chiral discrimination induced by natural DNA in the Diels-Alder reaction, we decided to further explore the scope and versatility of the DNA-based catalysis concept by applying it to other catalytic enantioselective reactions in water. We are particularly interested in C-C bond forming reaction like the Michael reaction. During this lecture, we will present the recent results obtained with DNA-based asymmetric catalysis with a particular focus on the catalytic enantioselective Michael reactions in water, which gave up to 99% e.e..[2]
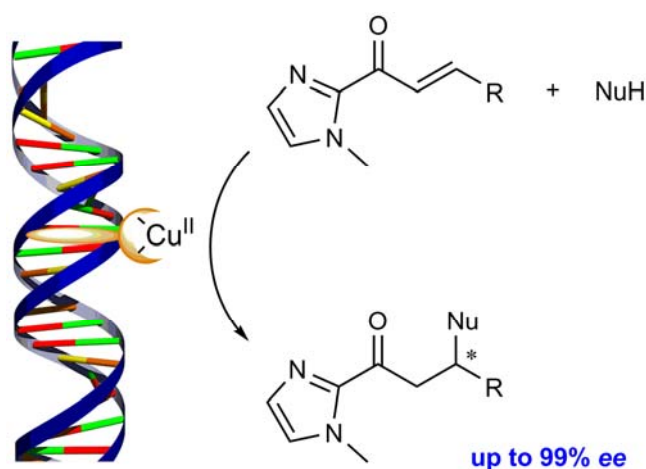
Scheme 1: Schematic representation of the asymmetric Michael addition reaction catalyzed by copper-achiral ligand complexes in the presence of DNA.

1 G. Roelfes, B. L. Feringa, *Angew. Chem. Int. Ed.* **2005**, *44*, 3230-3232; G. Roelfes, A. J. Boersma, B. Feringa, *Chem. Commun.* **2006**, 635-637; A. J. Boersma, B. L. Feringa, G. Roelfes, *Org. Lett.* **2007**, *9*, 3647-3650.
2 D. Coquière, B. L. Feringa, G. Roelfes, *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.200703459.

Synthesis and catalytic activity of water-soluble Au(I)-NHC complexes
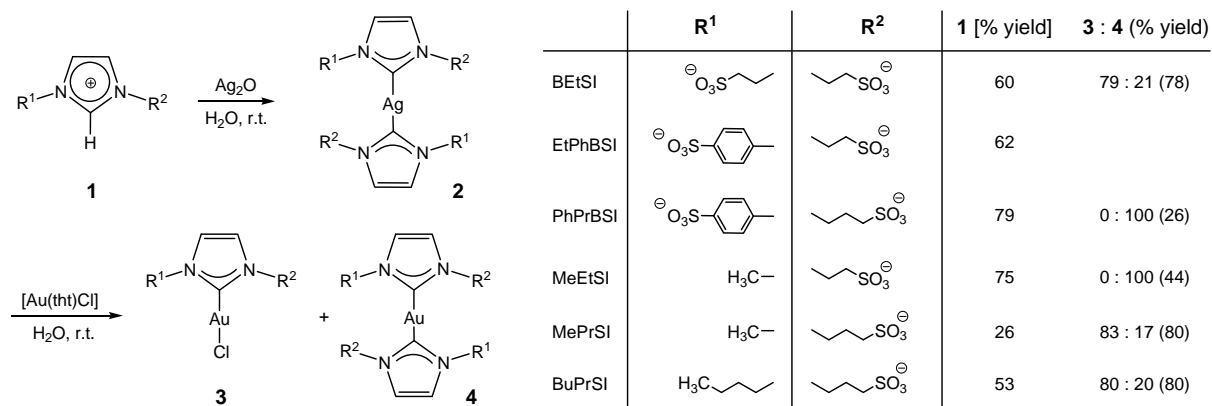
Ambroz Almássy,[a] **Ferenc Joó**[a]

[a] *Department of Physical Chemistry, University of Debrecen, Egyetem tér 1, 4010 Debrecen, Hungary; Fax: +52 512-915; Tel: +52 512-900/22382;*
E-mail: almassy@fns.uniba.sk

Complexes of gold have been long time considered to be catalytically inactive. Recently, many publications reported using of Au(I) phosphine complexes in homogeneous catalysis [1]. Although, coordination of electron-donating *N*-heterocyclic carbene (NHC) ligands increases oxidative and thermal stability of Au(I) complexes [2], no use of water-soluble Au(I)-NHC complexes was reported up to now. The aim of our research was to prepare them and explore their utilization in homogeneous catalysis.
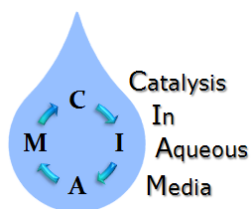
Required carbene ligand precursors – imidazolium sulfonate betaines **1** were prepared by condensation of corresponding amino sulfonic acid with glyoxal and paraformaldehyde (BEtSI, BPhSI) or by *N*-alkylation [3] of imidazole (BPrSI), *N*-methylimidazole (MeEtSI, MePrSI), *N*-butylimidazole (BuPrSI) and *N*-(phenylsulfonate)imidazole (EtPhBSI, PhPrSI).

On treatment of Ag$_2$O carbene transfer [Ag] complexes **2** were prepared. Silver coordinates two NHC-ligands in all cases and sulfonate group of one ligand serves as a counter ion of positively charged silver atom. Transmetallation with [Au(SMe$_2$)Cl] or [Au(tht)Cl] provides mono- and bis-carbene Au(I) complexes **3** and **4**, respectively.

Bis-carbene complexes are catalytically inactive. In mono-carbene Au(I) complexes second coordination position is occupied by Cl. This is essential for a catalytic activity in hydration of terminal alkynes [4]. Markovnikov addition of water on terminal alkynes provides corresponding methylketones. The best activity was achieved in hydration of *p*-ethynylanisole with 0.1 mol% of [Au(BEtSI)Cl] complex (TOF = 400.2 h^{-1}).

	R^1	R^2	1 [% yield]	3 : 4 (% yield)
BEtSI	$^{\ominus}O_3S\diagup$	$\diagup SO_3^{\ominus}$	60	79 : 21 (78)
EtPhBSI	$^{\ominus}O_3S$—⬡—	$\diagup SO_3^{\ominus}$	62	
PhPrSI	$^{\ominus}O_3S$—⬡—	$\diagdown\diagup SO_3^{\ominus}$	79	0 : 100 (26)
MeEtSI	H_3C—	$\diagup SO_3^{\ominus}$	75	0 : 100 (44)
MePrSI	H_3C—	$\diagdown\diagup SO_3^{\ominus}$	26	83 : 17 (80)
BuPrSI	$H_3C\diagdown\diagup$	$\diagdown\diagup SO_3^{\ominus}$	53	80 : 20 (80)

1   E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, *Angew. Chem. Int. Ed.* **2002**, *41 (23)*, 4563- 4565.
2   Lin, I. J. B.; Vasam, C. S. *Can. J. Chem.* **2003**, *83*, 812-825.
3   Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Ofele, K. U.S. Patent 5,728,839, **1998**.
4   Sanz, S.; Jones, L. A.; Mohr, F.; Laguna, M. *Organometallics*, **2007**, *26*, 952-957.

Aqueous phase catalysis, organometallic reactivity and much more: the renaissance of the water soluble monodentate phosphine PTA

Luca Gonsalvi[a] and **Maurizio Peruzzini**[a]

[a] *Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy. Fax: 0039 055 5225203; Tel: 0039 055 5225251; E-mail: l.gonsalvi@iccom.cnr.it*

The cage-like water soluble monodentate phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) has received renewed interest in the recent literature due to its properties to solubilize transition metal complexes in aqueous phase,[5] allowing for application of Rh, Ru and Pd-PTA complexes in aqueous phase or biphasic homogeneous catalysis, antitumoral tests (Ru and Pt) and photoluminescence (Au-PTA).

In the past few years we have investigated many aspect of this class of ligands, from the donor capacities of the potentially multidentate triaza phosphaadamantane moiety, resulting for example in a stable water soluble heterobimetallic coordination polymer,[6] or in the boranyl adduct[7] PTA-BH3 and related metal complexes, to the study of coordination chemistry to Ru(II),[8,9] Re(V),[10] Rh(I), Rh(III) and Ir(III), mainly bearing cyclopentadienyl coligands. In some cases, water soluble transition metal hydrides were identified by HP NMR techniques and rationalised via DFT calculations in the solvent media.[11]

Recently we have focused our attention on the functionalisation of the PTA skeleton, in order to obtain bidentate open-cage analogues PTN(R) (R = Ph, Me),[12] and diastereomerically enriched versions of PTA. The main results in this area, including data on catalytic hydrogenations and hydroformylations in aqueous or biphasic media will be presented.

[5] A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.* **2004**, 248, 955.

[6] C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano-Ruiz, L. Gonsalvi, M. Peruzzini, *Angew. Chem. Int. Ed.* **2005**, 44, 2568.

[7] S. Bolaño, A. Albinati, J. Bravo, L. Gonsalvi and M. Peruzzini, *Inorg. Chem. Comm.* **2006**, 9, 360.

[8] D. N. Akbayeva, L. Gonsalvi, W. Oberhauser, M. Peruzzini, F. Vizza, P. Brüggeller, A. Romerosa, G. Sava. A. Bergamo, *Chem. Commun.* **2003**, 264.

[9] S. Bolaño, L. Gonsalvi, F. Zanobini, F. Vizza, V. Bertolasi, A. Romerosa, M. Peruzzini, *J. Mol. Catal. A: Chem.* **2004**, *224*, 61.

[10] S. Bolaño, L. Gonsalvi, P. Barbaro, A. Albinati, S. Rizzato, E. Gutsul, N. Belkova, L. Epstein, E. Shubina, M. Peruzzini, *J. Organomet. Chem.* **2006**, 691, 629.

[11] A. Rossin, L. Gonsalvi, A. D. Phillips, O. Maresca, A. Lledos, M. Peruzzini, *Organometallics* **2007**, *26*, 3289.

[12] A. D. Phillips, S. Bolaño, S. S. Bosquain, J.-C. Daran, R. Malacea, M. Peruzzini, R. Poli, L. Gonsalvi, *Organometallics* **2006**, *25,* 2189.

Tackling a 30 year old problem : Fast reactions of medium chain-length alkenes under aqueous biphasic conditions with rapid phase separation

Simon L. Desset,[a] David. J Cole-Hamilton[a] and Douglas F. Foster[b]

[a] *EaStCHEM, Schoolof Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, Scotland. Fax: 44 1334 463808; Tel:44-1334-463805; E-mail: djc@st-and.ac.uk*

[b] *Sasol Techmology (UK) Ltd., Purdie Building, North Haugh, St. Andrews, Fife, KY16 9ST, Scotland. Fax: 44 1334 460939; Tel: 44 1334 460933; E-mail: Douglas.foster@UK.sasol.com*

Many homogeneous catalysts can show very high rates and selectivities towards desired products, but some of then suffer from serious problems associated with the separation of the product from the catalyst and any solvent. Several strategies have been proposed for effecting the desired separation. These involve immobilising the catalyst on a soluble or insoluble polymer, inorganic oxide or dendrimer support, or on the use of biphasic systems.[1,2]

One of the few alternative separation strategies (to distillation) for homogeneous catalysis that has been commercialised is the Ruhrchemie / Rhône-Poulenc process for the hydroformylation of propene, which is carried out in water using $P(C_6H_4SO_3Na)_3$ (TPPTS) as the ligand for rhodium based catalysts.[3] The aldehydes formed phase separate from the water and are removed in a decanter. The aqueous catalyst solution is returned to the reactor with < 1 ppb of Rh losses. Attempts to apply this technology to the hydroformylation of medium and long chain alkenes have been unsuccessful because the solubility of the alkenes in water is so low that mass transport across the interface renders the reactions too slow to be of commercial interest.

We shall describe new additives which allow aqueous biphasic hydroformylation (Scheme 1) to be carried out with commercially interesting rates, low rhodium losses and fast phase separation.[4,5] These additives are intermediate chain length imidazolium or pyridinium salts. They can increase the rate of an aqueous biphasic reaction by 30x (Figure 1), yet the phase separation occurs within one minute and the rhodium content of the organic product can be <100 ppb. The mechanism by which the additives operate will be discussed.

We shall also describe an alternative approach involving a new method for switching the catalyst between phases. The catalyst is designed to be soluble in the organic phase during the reaction, but switches into the aqueous phase on bubbling CO_2. After phase separation, the CO_2 can be removed by bubbling argon and the catalyst switches back into the organic phase (Figure 2).[5]
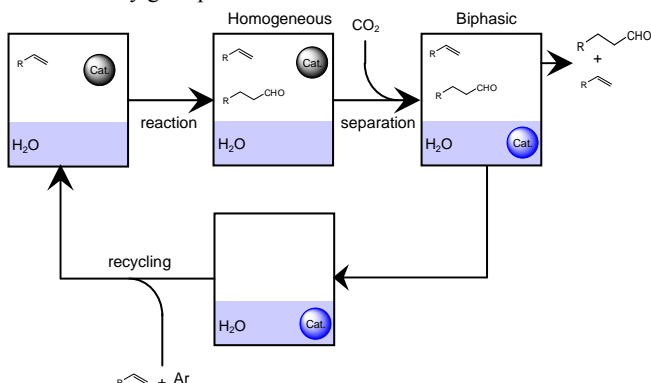
.
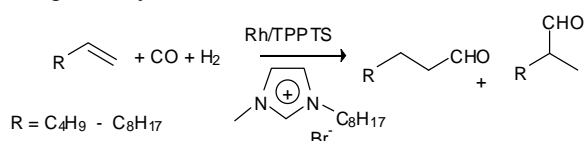
Scheme. 1 The hydroformylation of medium chain alkenes in the presence of [OMIM]Br under aqueous biphasic conditions
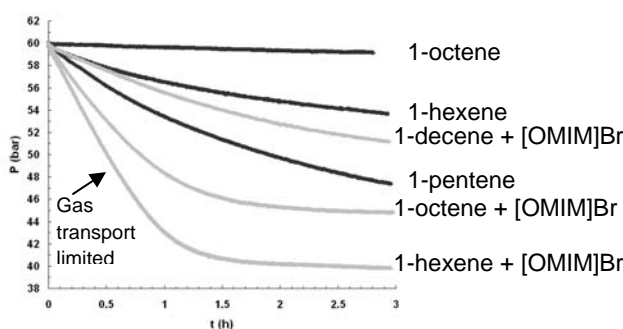
Figure 1 Effect of adding 1-octyl-3-methylimidazolium bromide ([OMIM]Br) on the aqueous biphasic hydroformylation of intermediate chain length alkenes, as indicated by gas uptake curves

Figure 2 Phase switching of a catalyst using CO_2

1   D. J. Cole-Hamilton, *Science*, **2003**, *299*, 5613;

2   *Catalyst Separation, recovery and recysling: Chenistry and Process Design,* Eds.D. J.Cole-Hamilton and R. P.Tooze, Springer: Dordrecht, 2005.

3   E. Wiebus, and B. Cornils, in *Catalyst separation, recovery and recycling: Chemistry and process design*; Eds. D. J. Cole-Hamilton and R. P. Tooze, Springer: Dordrecht, 2005, pp 105 et seq.

4   S. L. Desset D. F. Foster and D. J. Cole-Hamilton, *Chem. Commun.,* **2007**, 1933

5   S. L. Desset D. J. Cole-Hamilton, *Eur. Pat Appl.*

# Biphasic Catalysis Promoted by Modified Cyclodextrins: Current Scope and Future Developments

Frédéric Hapiot,[a] Anne Ponchel,[a] Sébastien Tilloy[a] and Eric Monflier[a]

[a] Université d'Artois, Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Faculté Jean Perrin, rue Jean Souvraz, S.P. 18, 62307 Lens Cedex, France. Fax: 33(0)321791755; Tel: 33(0)321791772; E-mail: monflier@univ-artois.fr

The twelve principle of Green Chemistry have been defined in 1998 by Anastas and Warner to aid one in assessing how green a chemical, a reaction or a process is. Among these principles, some of them are devoted to reusability and catalysis with potential outcomes in reducing toxicity, pollution and waste and improving energy efficiency and resource use. In this context, biphasic catalysis in an aqueous/organic two-phase system appears to be an economical and safe approach for the production of industrially valuable products. The biphasic rhodium-catalyzed hydroformylation of terminal alkenes has especially been the subject of numerous studies.

n = 0, 1, 2...   linear aldehyde (l)   branched aldehyde (b)
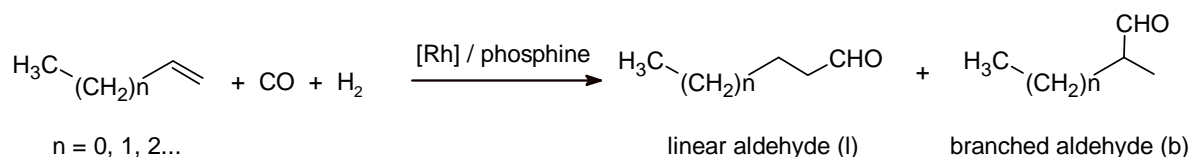
Unfortunately, the industrial viability of the biphasic hydroformylation process has only been demonstrated in the case of lower olefins such as propene and butene with a Rh/TPPTS (TPPTS=tris(m-sulfonatophenyl)phosphine trisodium salt) catalytic system. For higher olefins (five or more carbon atoms), their solubility is water is too low for industrially important rates to be achieved. In order to circumvent this crucial problem, we developed the use of chemically modified cyclodextrins as mass transfer promoters.[2]

G: H or R
n = 6 or 7
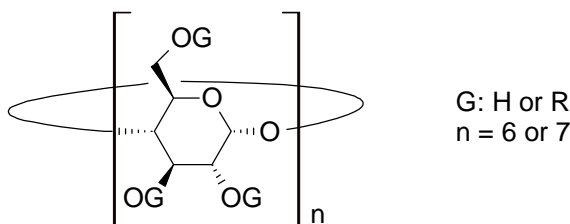
Their contribution in biphasic rhodium-catalysed hydroformylation of hydrophobic terminal alkenes will be tackled, taking into account previous results and new experimental data. The role of the cyclodextrins will be emphasized and discussed through the analysis of NMR results and association constants between the cyclodextrins and the organic substrates. Outlooks will also be presented.[3]

1 P.T. Anastas and J.C. Warner *Green Chemistry Theory and Practice*, Oxford University Press, New York, **1998**.

2 E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, *Angew. Chem. Int. Ed*. **1995**, *34*, 2269; D. Kirschner, T. Green, F. Hapiot, S. Tilloy, L. Leclercq, H. Bricout, E. Monflier, *Adv. Synth. Catal*. **2006**, *348*, 379; E. Monflier, H. Bricout, F. Hapiot, S. Tilloy, A. Aghmiz, A.M. Masdeu-Bultó, *Adv. Synth. Catal*. **2004**, *346*, 425; L. Leclercq, F. Hapiot, S. Tilloy, K. Ramkisoensing, J.N.H. Reek, P.W.N.M. van Leeuwen, E. Monflier, *Organometallics* **2005**, *24*, 2070.

3 C. Machut, J. Patrigeon, S. Tilloy, H. Bricout, F. Hapiot, E. Monflier, *Angew. Chem. Int. Ed.* **2007**, *46*, 3040; A. Nowicki, Y. Zhang, B. Léger, J.-P. Rolland, H. Bricout, E. Monflier, A. Roucoux, *Chem. Commun.* **2006**, 296; A. Cassez, A. Ponchel, F. Hapiot, E. Monflier, *Org. Lett.* **2006**, *8*, 4823.
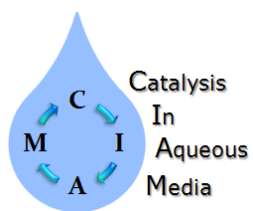
Hydrogen production by aqueous-phase reforming of Glycerol on supported metal catalysts

Aonsurang Wawrzetz, Andreas Jentys, Johannes A. Lercher

Technische Universität München, Department Chemie, Lehrstuhl II für Technische Chemie, Lichtenbergstraße 4, 85747 Garching, Germany

Fax: 49 089 289 13544; Tel: 49 089 135 38; E-mail: andreas.jentys@ch.tum.de

The full environmental benefit of hydrogen fuel cells is only achievable if hydrogen is produced from sustainable resources such as biomass. Glycerol is the main biomass-derived product formed during bio-diesel production. Nowadays the worldwide trend of increasing production of bio-fuels results in an overproduction of glycerol.

In the work presented hydrogen production from glycerol by the aqueous-phase reforming process at low temperatures and high pressures on various supported catalysts including Pt/Al_2O_3, Pd/Al_2O_3, Ni/Al_2O_3, Ru/Al_2O_3 and Rh/Al_2O_3 was studied. The apparent activation energies of the metals supported on γ-alumina were examined. The temperature was varied from 473 K to 793 K. The conversion was kept below 10%. The activation energy of each catalyst was calculated according to Arrhenius equation. The activation energies of the catalysts were in the order Pt < Pd < Ru < Ni < Rh. The selectivity of hydrogen and alkane are shown in the figure 1. The hydrogen selectivities of various metals supported on γ-Al_2O_3 were in the order Pt > Pd > Ru > Rh > Ni at 498 K and 26.5 bar. The H_2 selectivity of Pt supported on γ-Al_2O_3 was above 90%, with the lowest alkane selectivity and CO formation.
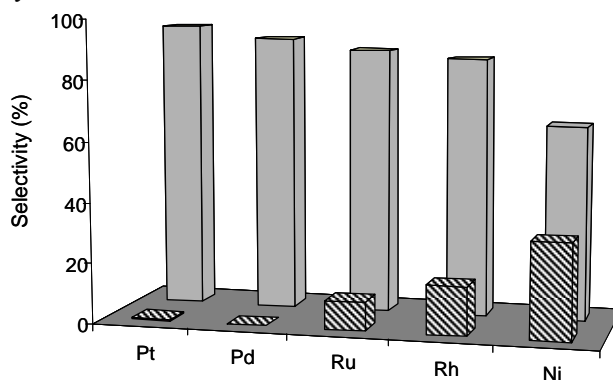

Figure 1: Hydrogen and alkane selectivity of the catalysts.
The hashed bars represent alkane selectivity and the gray bars hydrogen selectivity

The stability test of catalyst with the highest hydrogen selectivity (Pt/γ-Al_2O_3) was carried out at 20% glycerol concentration for 100 h at 498 K and 29 bar. During this time the activity of the catalyst was almost constant as shown in Figure 2.
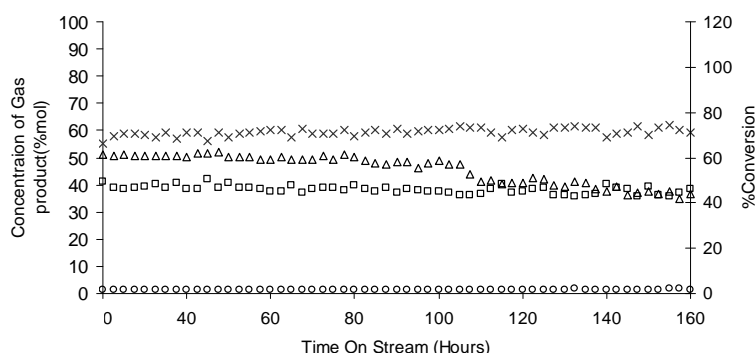

Figure 2. Conversion of glycerol (Δ) and concentration of gas products
H_2 (×) CO_2: (□); CH_4 (○) versus reaction time

The slow deactivation of γ-Al_2O_3 in aqueous media results from the formation of aluminium-oxide-hydroxide (Boehmite), which was confirmed by XRD. The loss of metal and a decrease in the surface area were also observed. As deterioration of support material was identified as the main reason for the deactivation of the catalyst, Pt supported on various other supports including ZrO_2, Carbon, Fe_2O_3, ASA, CeO_2 and TiO_2 were investigated.

In the oral communication the activity of these materials will be discussed together with the different reaction pathways leading to gaseous and liquid phase products.

Pd(TPPTS)$_3$ reactions with butenols and butadiene in water

N. Legagneux, C. Lucas, E. Kuntz[*]

Laboratoire C2P2, Equipe LCOMS, CPE-Lyon, 43 Bd du 11 Novembre1918, 69616 Villeurbanne Cedex, France
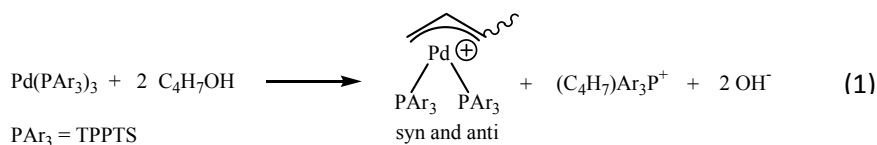
Corresponding author: Kuntz@cpe.fr

Palladium catalysts based on hydrosoluble phosphines TPPTS and TPPMS were mainly used in the functionalization and telomerization of dienes[1] and in the Tsuji-Trost nucleophilic substitution of allylic compounds[2]. However, metallic palladium precipitation often occurred during the catalysis. The exact reasons for this phenomenon are still not well understood. In this line, the reactions between the Pd(TPPTS)$_3$ complex and butadiene or butenols (trans-2-buten-1-ol, cis-2-buten-1-ol and 3-buten-2-ol) have first been investigated.

In the presence of butenols, two reactions occur with the Pd(TPPTS)$_3$ complex: first, easy ionisation of butenols in water at room temperature over a wide range of pH to yield HO$^-$ and TPPTS along with syn and anti allyl palladium complexes (see eq. 1). Then, the released TPPTS reacts with palladium cationic complexes to produce three isomeric butenylphosphonium salts of TPPTS $[(C_4H_7)Ar_3P^+]$, the relative proportions of syn and anti isomers and of the phosphonium salts depend on the starting butenol.
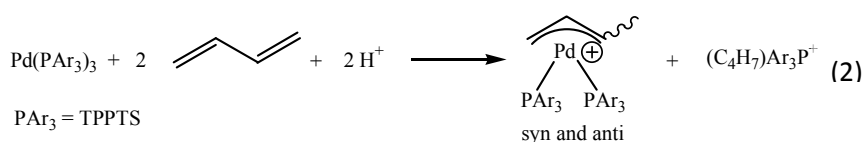
Reaction of gaseous butadiene with Pd(TPPTS)$_3$, in aqueous solution at room temperature, leads to a proton consumption, even in basic medium, with formation of the same allyl palladium complexes and phosphonium salts as discussed above (see eq. 2). The distribution of these products is different than those obtained with butenols. The reaction is dependent on pH and proceeds even at pH 11. The major role of the pH on the kinetics of reactions (1) and (2) has been highlighted.

Isomerization of phosphonium salts 4a$_{1trans}$, 4a$_{1cis}$ and 4a$_3$ (see eq. 3) and isomerization of palladium complexes (anti - syn) can be observed (see eq. 4).
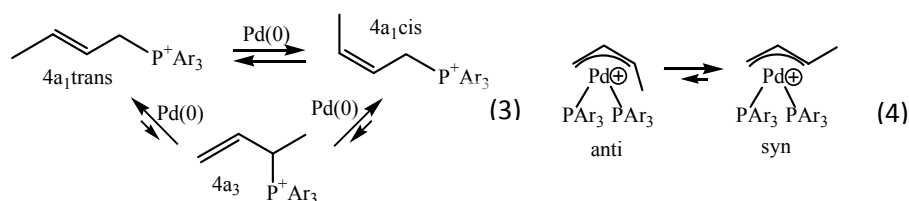
Our study outlines the basis for a better understanding of the mechanism involving TPPTS or TPPMS palladium catalysts in Tsuji-Trost reaction and in the functionalization and telomerization of dienes in aqueous media.

$$Pd(PAr_3)_3 \ + \ 2 \ C_4H_7OH \ \longrightarrow \ \underset{\substack{\\ syn \ and \ anti}}{[allyl\text{-}Pd(PAr_3)_2]^+} \ + \ (C_4H_7)Ar_3P^+ \ + \ 2 \ OH^- \qquad (1)$$

PAr$_3$ = TPPTS

Equation 1 : Reaction of butenols with Pd(PAr$_3$)$_3$

$$Pd(PAr_3)_3 \ + \ 2 \ \text{(butadiene)} \ + \ 2 \ H^+ \ \longrightarrow \ \underset{\substack{\\ syn \ and \ anti}}{[allyl\text{-}Pd(PAr_3)_2]^+} \ + \ (C_4H_7)Ar_3P^+ \qquad (2)$$

PAr$_3$ = TPPTS

Equation 2 : Reaction of butadiene with Pd(PAr$_3$)$_3$

Equations 3 and 4 : Isomerization of phosphonium salts and of π-allylPd(PAr$_3$)$_2$ complexes

Bibliography

[1] (a) Kuntz, E. G. (Rhône-Poulenc Ind), FP 2 366 237, 07 27 **1976**. (b) Yoshimura, N. *Aqueous –Phase Organometal Catalysis: Concepts and Applications;* Cornils, B.; Herrmann, W. A., Eds.; Wiley-VCH: Wienheim*, ,* **2003***;*540-549.

[2] (a) Blart, E.; Genet, J.P.; Safi, M.; Savignac, M.; Sinou, D. *Tetrahedron.* **1994**, 50, 505-514. (b) Kuntz, E. G.; Amgoune, A.; Lucas, C.; Godard, G. *J. Mol. Cat.* A **2006**, *244*, 124-136.

A recyclable multi-substrates catalytic system for enantioselective reduction of ketones in water

Jacqueline Collin,*[a] **Jean-Claude Fiaud**,[a] **Saoussen Zeror**[a] **and Louisa Aribi Zouioueche***[b]

[a] *Equipe de Catalyse Moléculaire, ICMMO, UMR 8182,, Université Paris-Sud, 91405 Orsay, France; Tel: 33 (0)1 69154740*
E-mail: jacollin@icmo.u-psud.fr
[b] *Groupe de Synthèse Asymétrique et Biocatalyse, LCOA, Université Badji Mokhtar, 23000 Annaba Algérie; E-mail: lzouioueche@yahoo.fr*

Nowadays a major concern for chemists is the design of new low cost and highly sustainable methodologies following green chemistry principles which requires atom economy, use of environmental friendly methods, safe reagents and solvents, recyclability of catalysts and easy separation of reaction products. Asymmetric transfer hydrogenation fulfill most of these requirements for the easy preparation of enantiomerically enriched alcohols and catalysts for enantioselective hydride transfer reactions in water have been recently developped.[1]

A system *in situ* prepared from $[RuCl_2(p\text{-cymene})]_2$ and *N*-phenyl-(*L*)-proline amide has been reported as an enantioselective catalyst for the reduction of *ortho*-substituted acetophenone in water.[2] We have studied the reduction in water of a variety of aromatic ketones with this ruthenium catalyst and found high asymmetric inductions in several cases. The reusability of this catalyst has been demonstrated by 15 consecutive reductions of *o*-methoxyacetophenone with high enantiomeric excesses. The consecutive reduction of seven different aromatic ketones reusing the same recovered catalyst furnishes successively seven alcohols each with similar enantiomeric excess than the one recorded in a single run.[3]
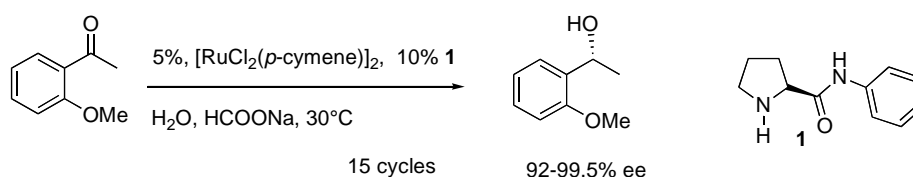

We next present a simple method allowing the evaluation of the enantiomeric excesses of six alcohols by a single chromatographic analysis. We have investigated various ligands for the ruthenium-catalyzed enantioselective reduction of ketones in water.[4] Different proline amides and aminoalcohols have been compared for one-pot reductions of two sets of six ketones, and the proline amide derivative prepared from (1*R*, 2*S*)-*cis*-aminoindanol has been selected as the best ligand. The latter has been employed for the enantioselective reduction of a variety of other aromatic ketones and in all cases the enantioselectivity was improved compared to that obtained with phenyl proline amide. This really demonstrates the interest of our method for optimising ligands for asymmetric hydride transfer.

1 X. Wu, J. Xiao, *Chem. Commun.* **2007**, 2449.
2 H. Y. Rhyoo, H-J. Park, Y.K. Cheng, *Chem. Commun*, **2001**, 2064.
3 S. Zeror, J. Collin, J-C Fiaud, L. Aribi-Zouioueche. *J. Mol. Cat. A*, **2006**, *256*, 85.
4 S. Zeror, J. Collin, J-C. Fiaud, L. Aribi-Zouioueche, *Adv. Synth. Catal.* **2007**, in press, DOI : 10.1002/adsc.200700272.
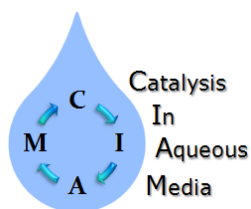
Synthesis and Characterization of Novel Iridium Complexes with Water-Soluble Phosphine Ligands

Vanessa R. Landaeta,[a,b] **Mikael Erlandsson,**[a] **María E. Vásquez-Pérez,**[b] **César A. Urbina-Blanco,**[b]
Andrew D. Phillips,[c] **Luca Gonsalvi**[a] **and Maurizio Peruzzini.**[a]

[a] *ICCOM- CNR, Via Madonna del Piano 10, 50019, Sesto Fiorentino, Italy, Fax:+39 055 5225203; Tel:+39 055 522528.*
[b] *Current Address: Departamento de Química, Universidad Simón Bolívar. Valle de Sartenejas, Baruta. Apartado 89000, 1080A. Caracas, Venezuela. Fax:+58 212 9063961; Tel:+58 212 9063984. E-mail: vlandaeta@usb.ve*
[c] *EPFL - LCOM, BCH 2405, CH-1015 Lausanne, Switzerland, Fax: +41 21 6939885; Tel: +41 21 6939853.*

Water-soluble phosphine ligands have attracted lots of attention recently,[1] since they not only lead to hydrosoluble transition metal complexes but also permit the development of water-soluble catalysts, which is a highly desirable matter in "green chemistry". Typical examples of water-soluble phosphine ligands are the sodium salts of sulfonated triphenylphosphine (TPPMS, TPPDS or TPPTS), 1,3,5-triaza-7-phosphaadamantane (PTA) or 1-methyl-1,3,5-triaza-7-phosphaadamantane (mPTA). Some success has already been achieved in this field with the Rhurchemie/Rhône-Poulenc hydroformylation process, which is catalyzed by the rhodium complex $[RhH(CO)(TPPTS)_3]$.[1b]

Our group has been very interested in the chemistry of PTA ligand.[2,3] Rh-PTA complexes have attracted a lot of attention due to their biological activity[4] and their potential as catalysts for aqueous biphasic processes, and a variety of Cp'Ru and Rh complexes (Cp' = Cp, Cp*) has been synthesized and some catalytic and biological studies have been reported.[2,3] Only a few examples of Ir-PTA species are known,[5] and, up to our knowledge, only a brief study on the intramolecular hydroamination of 4-pentyn-1-amine catalyzed by $[IrCl(CO)(PTA)_3]$ and $[Ir(CO)(PTA)_4]Cl$ has been reported so far.[5b]

Thus, it seemed of interest to extend these studies to iridium at first looking for the synthesis of new Cp'Ir (Cp' = Cp*, Ind) complexes bearing water-soluble phosphine ligands, such as PTA, mPTA or TPPMS, and then investing their chemical reactivity and their catalytic behavior in biphasic processes such as hydrogenation and C-H bond activation. Here, we report the synthesis and the characterization of novel Ir-PTA complexes bearing Cp* ligand, and the first steps towards the isolation of iridium-indenyl species with PTA and TPPMS.

Cp*Ir-PTA compounds were straightforwardly prepared by treating solutions of the iridium dimer $[Cp*IrCl_2]_2$ with one or two equivalents of PTA.[6] These tests led to the isolation of new Cp*Ir-PTA complexes, namely $[Cp*IrCl_2(PTA)]$ (**1**) (2 PTA equivalents, CH_2Cl_2, room temperature) and $[Cp*IrCl(PTA)_2]Cl$ (**2**) (4 equivalents, 2-$MeOCH_2CH_2OH$, reflux). Both compounds were synthesized in good yields, and characterized by elemental analysis, multinuclear NMR spectroscopy and their crystal structure determined by X-ray crystallography. The solubility of these species in water has been determined at room temperature. One PTA ligand, as in $[Cp*IrCl_2(PTA)]$ (**1**), leads to a solubility of 2.20 mg/mL. When a second PTA ligand coordinates to iridium, as in $[Cp*IrCl(PTA)_2]Cl$ (**2**), the water solubility increases dramatically to 27.5mg/mL. The reaction between **1** and $NaBH_4$ led to hydride species $[Cp*Ir(H)_2(PTA)]$ (**3**). Protonation tests (low temperature) on **3**, using weak acids such as fluorinated alcohols, indicate the occurrence in solution of weak interactions similar to hydrogen bonding. We are also investigating the chemistry of **1** and **3** towards copper, silver and gold fragments as our protonation studies indicate, in the case of **3**, that some interaction through the hydride ligands might occur. In fact, preliminary tests with Au(P) (P = PPh_3 and PTA) fragments indicate changes in the hydride region of the ^1H NMR spectra for **3**, and a strong interaction with **1**. Preliminary tests *in situ* by NMR on the chemistry of indenyl ligand towards iridium and PTA or TPPMS show that (Ind)Ir-phosphine species can be stabilized.

Further work will focus on studying the interaction of **1-3** with Cu, Ag and Au fragments, and to extend this study to other coinage metals species. Additional synthetic approaches will also be developed to isolate Ir-indenyl complexes with the water soluble ligands. In parallel, we will also explore the potential of our complexes as catalyst precursors[5] for a variety of reactions.

1. a) F. Joó, *Aqueous Organometallic Catalysis*, Kluwer, Dordrecht, **2001**. b) B. Cornils. *Org. Process Res. Dev*. **1998**, *2*, 121-127.
2. A. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini. *Coord. Chem. Rev.*, **2004**, *248*, 955.
3. See for example: D. Akbayeba, L. Gonsalvi, W. Oberhauser, M. Peruzzini, F. Vizza, P. Brüggeller, A. Romerosa, G. Sava, A. Bergamo. *Chem. Comm.*, **2003**, 264.
4. A. Dorcier, W. H. Ang, S. Bolaño, L. Gonsalvi, L. Juillerat-Jeannerat, G. Laurenczy, M. Peruzzini, A. D. Phillips, F. Zanobini, P. J. Dyson. *Organometallics,* **2006**, *25*, 4090-4096.
5. (a) D. A. Krogstad, J. A. Hilfen, T. J. Terry, V. G. Young Jr, *Inorg. Chem.* **2001**, *30*, 463-471. (b) D.A. Krogstad, A. J. DeBoer, W. J. Ortmeier, J. W. Rudolf, J. A. Halfen. *Inorg. Chem. Commun,* **2005**, *8*, 1141
6. M. Erlandsson, V. R. Landaeta, L. Gonsalvi; M. Peruzzini, A. D. Phillips, P. J. Dyson, G. Laurenczy, *Eur. J. Inorg. Chem,* in press.

Transition Metal-N-Heterocyclic Carbene Complexes as Catalysts of Hydrogenation, Transfer Hydrogenation, Hydration and Redox Isomerization in Homogeneous and Biphasic Media

Ferenc Joó

University of Debrecen, Institute of Physical Chemistry and Hungarian Academy of Sciences, Research group of Homogeneous Catalyis, Debrecen 10, P.O.Box 7, H-4010 Hungary. Fax: 36 5251 2915; Tel.: 36 5251 2900; E-mail: fjoo@delfin.unideb.hu

N-Heterocyclic carbene (NHC) complexes of transition metals play an important role in homogeneous catalysis [1]. The NHC ligands are often compared to tertiary phosphines which, for a long time, were used as primary flexible components for tayloring the catalytic properties of homogeneous organometallic catalysts. Some time ago our laboratory initiated the study of water-soluble transition metal phosphine complexes [2] and this approach resulted in a considerable success in homogeneous catalysis in water and in aqueous-organic biphasic catalysis [3]. Recently we also started the investigation of water-soluble transition metal – NHC complexes with the aim of developing active and durable homogeneous catalysts for aqueous phase and biphasic processes [4,5].

Several water-soluble N-heterocyclic carbene complexes containing Rh(I), Ru(II), Ir(I) and Au(I) central ions were synthesized starting with simple precursors such as [{RhCl(COD)}$_2$], [{RuCl$_2$(*p*-cymene)}$_2$], [{Ir(OMe)(COD)}$_2$], and [AuCl(tht)] (COD = 1,5-cyclooctadiene, *p*-cymene = 4-isopropyl-toluene, tht = tetrahydrothiophene), either in the reaction of the metal complex precursor with the proper 1,3-dialkylimidazolium salt or using the Ag(I) carbene-transfer methodology. The water-solubility of some of the complexes was due to the formation of complex cations by halide dissociation, others contained ligands carrying the strongly hydrophilic sulfonate substituent. The catalytic properties of the complexes were tested in hydrogenation and hydration as well as in the redox isomerization of allylic alcohols. The latter process is characterized by 100% atom economy, while the use of aqueous-organic biphasic reaction mixtures gives a general possibility of separating and recovering the catalyts in the aqueous phase. The Rh(I)-complexes showed good catalytic activity in the hydrogenation of C=C bonds, while the highest activities and selectivities in the redox isomerization of allyl alcohols (Fig. 1) as well as in the transfer hydrogenation of acetophenone (Fig. 2) were observed with Ru(II)-NHC complexes as catalysts. The novel water-soluble Au(I)-NHC complexes proved excellent catalysts for the hydration of alkynes [6].
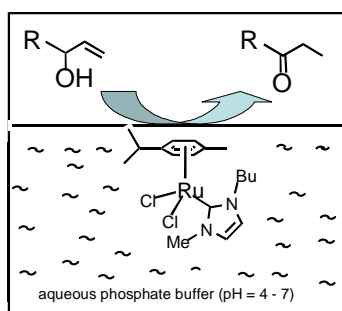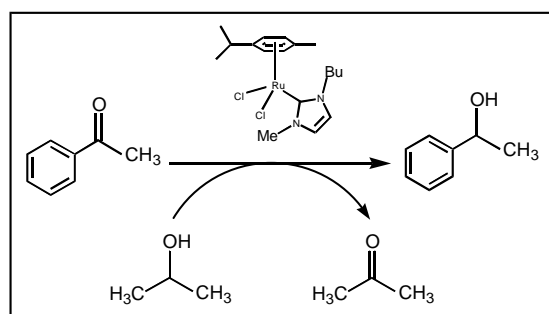

Figure 1.

Figure 2.

1   W. A. Herrmann, C. Kocher, *Angew. Chem. Int. Ed.*, **1997**, *36*, 2163; M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc*., **2001**, *123*, 6543; P. de Frémont, N. M. Scott, E.D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Aberbethy, S. P. Nolan, *Organometallics*, **2005**, *24*, 6301; D. Gnanamgari, A. Moores, E. Rajaseelan, R. H. Crabtree, *Organometallics*, **2007**, *26*, 1226; V. Dragutan, I. Dragutan, L. Delaude, A. Demonceau, *Coord. Chem. Rev.,* **2007**, *251*, 765.

2   F. Joó, Z. Tóth and M.T. Beck, *Inorg. Chim. Acta,* **1977**, *25*, L61 .

3   F. Joó, *Aqueous Organometallic Catalysis*, Kluwer, Dordrecht, The Netherlands, 2001.

4   P. Csabai and F. Joó, *Organometallics,* **2004**, *23*, 5640.

5   M. Fekete and F. Joó, *Catal. Commun.,* **2006**, *7*, 783.

6   See also the contribution of A. Almássy at this conference.
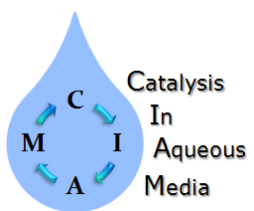
Poster Contributions

Comparative kinetic and DFT studies on the stabilisation of pyrammidal tautomers of low-valent phosphorus acids

A. G. Algarra,[a] **M. G. Basallote,**[a] **M. J. Fernández-Trujillo,**[a] **R. Hernández-Molina,**[b] **and V. S. Safont**[c]

[a]*Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica, Facultad de Ciencias, Universidad de Cádiz, Avd. República Saharahui, s/n, Puerto Real, 11510 Cádiz, Spain. andres.algarra@uca.es*

[b]*Departamento de Química Inorgánica, Facultad de Farmacia, Universiad de LaLaguna, 38200 La Laguna, Tenerife, Spain.*

[c]*Departament de Química Física i Analítica, Universitat Jaume I, Campus de Riu Sec,P. O. Box 224, 12071 Castelló, Spain.*

Acids of phosphorus in low oxidation state, as hypophosphorous (H_3PO_2) or phosphorous (H_3PO_3) acids, are known to exist as tetrahedral molecules (*tet*) with a P=O group. However, some years ago it has been observed the existence of an alternative unestable pyramidal form (*pyr*) of these acids, $HP(OH)_2$ and $P(OH)_3$, was proposed decades ago and confirmed in recent years for some ases in which they are P-coordinated to soft metal centers.[1] The existence of this new kind of complexes can provide an entry into a coordination chemistry very similar to the chemistry of the phosphine complexes, but with the advantages of the water solubility and the existence of OH groups able to promote additional hydrogen bonding. In fact, the heterolytic activation of H-X (X = H, Si, B) by using the 16-electron $[Ru(P(OH)_3)(dppe)_2][OTf]_2$ (dppe= $Ph_2PCH_2CH_2PPh_2$) complex has been described recently .[2]

As a continuation of our interest in the mechanistic aspects of reactions of M_3Q_4 and $M_3M'Q_4$ clusters (M=Mo, W; M'=Ni, Pd; Q= S, Se), we have studied the reaction between $[Mo_3S_4Pd(H_2O)_{10}]^{4+}$ (**1**) and H_3PO_2 to give $[Mo_3S_4Pd[PH(OH)_2](H_2O)_9]^{4+}$ (**2**) by using experimental and DFT methods.[3] The reaction of **1** with an excess of *tet*-H_3PO_2 in aqueous solution (25.0ºC, 2 M Hpts/Lipts, pts⁻=p-toluenesulfonate) takes place with biphasic kinetics, and surprisingly the rate constants of each step show a first-order dependence with respect to the acid concentration (see Scheme 1). Both kinetic and NMR spectroscopic data indicate that the first step is a simple substitution leading to a complex (**I**) containing O-coordinated *tet*-H_3PO_2.

1   **I**   **2**
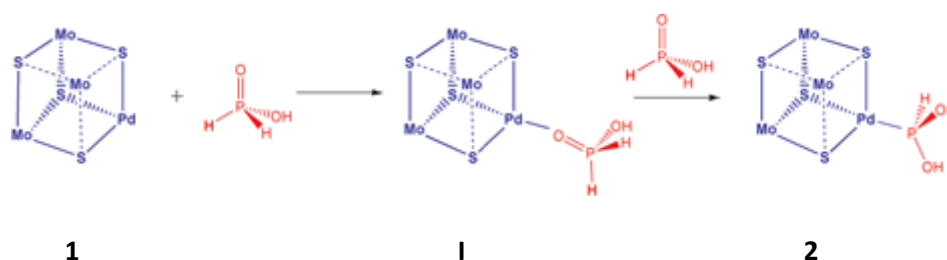
Scheme 1. Mechanism of the reaction between *tet*-H_3PO_2 and **1**. For simplicity, the water molecules are not shown, they complete the coordination environment of Mo and Pd atoms.

In order to elucidate the mechanism of tautomerization between **I** and **2** and to understand the necessity of a second H_3PO_2 molecule, theoretical calculations have been carried out. On the basis of these results, the proposed mechanism indicates that tautomerization implicates an 1,2-H shift from the P-H bond to the oxygen of the P=O group (giving an O-coordinated pyr-form) and then isomerization to the P-coordinated form in **2**. The activation barrier is determined by the 1,2-H shift and, actually the latter isomerization shows a very low activation barrier of only 2.5 Kcal/mol (all the energy values are given in aqueous solution). The role of the second *tet*-H_3PO_2 is to catalyze the hydrogen shift because of its capability to act as a base in aqueous solution forming $H_4PO_2^+$, which then acts as an acid and transfers the proton to the oxygen atom in the P=O group. While the activation barrier for these two proton transfers in presence of the second *tet*-H_3PO_2 is 22.4 Kcal/mol, a transition state for the direct conversion with an activation barrier of 63.2 Kcal/mol has been calculated. Comparative studies on the tautomerisation of H_3PO_3 will be also presented and discussed.

1   M. N. Sokolov, A. V. Virovets, D. N. Dybtsev, E. V. Chubarova, V. P. Fedin and D. Fenske, *Inorg. Chem.*, **2001**, *40*, 4816; M. N. Sokolov, R. Hernández-Molina, W. Clegg, V. P. Fedin and A. Mederos, *Chem. Commun.*, **2003**, 140; R. Hernández-Molina, M. N. Sokolov, M. Clausen and W. Clegg, *Inorg. Chem.*, **2006**, *45*, 10567; R. Hernández-Molina, I. Kalinina, M. N. Sokolov, M. Clausen, J. González Platas, C. Vicent and R. Llusar, *Dalton Trans.*, **2007**, 550; C. M. Nagaraja, M. Nethaji and B. R. Jagirdar, *Inorg. Chem.*, **2005**, *44*, 4145; D. N. Akbayeva, M. Di Vaira, S. S. Costantini, M. Peruzzini and P. Stoppioni, *Dalton Trans.*, **2006**, 389.
2   C. M. Nagaraja, P. Parameswaran, E. D. Jemmis, B. R. Jagirdar, *J. Am. Chem. Soc.*, **2007**, 5587.
3   A. G. Algarra, M. G. Basallote, M. J. Fernández-Trujillo, R. Hernández-Trujillo, V. S. Safont, *Chem. Commun.*, **2007**, 3073.

Aqueous-biphasic hydroformylation: How to bring higher alkenes into play ?

Simon L. Desset,[a] **and David J. Cole-Hamilton**[a]

[a] *School of Chemistry, University of St. Andrews, St. Andrews, Scotland. Tel: 0044 1334 46 3805; E-mail: djc@st-andrews.ac.uk*

Organometallic catalysts allow reactions to proceed under mild conditions and with high selectivity. However for industrial applications they are outweighed by heterogeneous catalysts due to the ease of reuse of the latter. Recycling of the catalyst constitutes, therefore, one of the major challenges for implementing homogeneous catalysis as a viable technology for large scale chemical production.

Among the different approaches already developed to tackle this problem, aqueous-biphasic catalysis has been brought to the industrial scale for the hydroformylation of propene with a production of 800 000 t/y. Neverthess, this attractive process is limited to the hydroformylation of propene and butene due to the poor solubility in water of their higher counterparts.[1]

To address this limitation, we have developed two main strategies.

Firstly, we found that ionic additives consisting of an imidazolium, trimethylammonium or pyridium unit bearing aliphatic chains have a dramatic effect on both reaction rate and selectivity. For example, addition of 1-octyl-3-methylimidazolium bromide, OctMImBr, to the aqueous biphasic system allows hydrophobic substrates such as 1-octene to be converted at high rate with excellent phase separation and retention of the metal in the aqueous phase (Figure 1)[2].
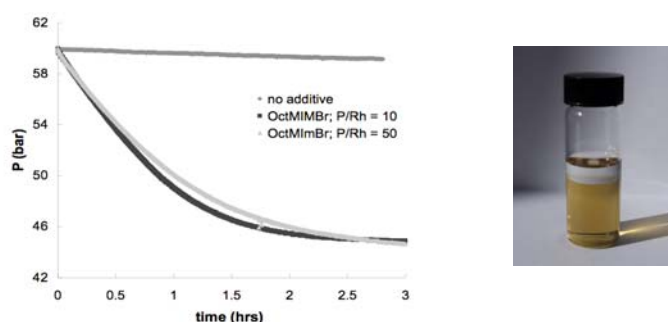

Figure 1   Effect of OctMImBr addition on the gas uptake from a ballast vessel in the aqueous-biphasic hydroformylation of 1-octene.
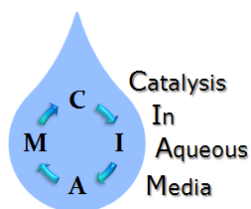
Secondly, we developed ligands for which the solubility in water can be switched by reversible reaction with CO_2. This allows the reaction to be carried out in a homogeneous fashion, avoiding solubility and mass transfer limitation, but the catalyst can be extracted into an immiscible aqueous phase after the reaction. The catalyst can then be extracted back into a phase containing fresh substrate.
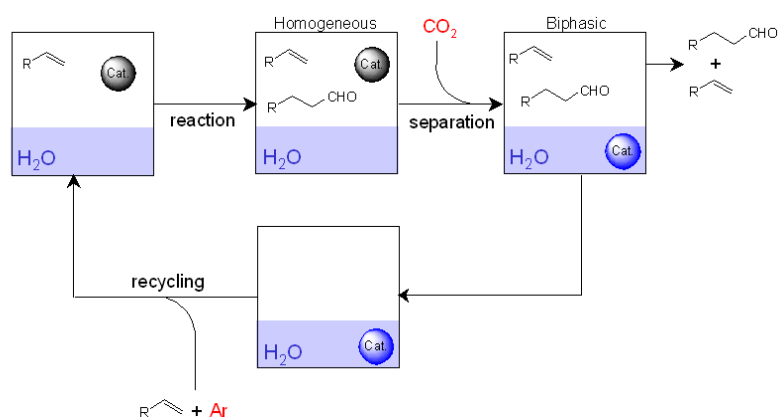
1 E. Wiebus and B. Cornils, in '*Catalyst separation, recovery and recycling: Chemistry and process design*', ed. D. J. Cole-Hamilton and R. P. Tooze, Springer, Dordrecht, **2005**.
2   S. L. Desset, D. J. Cole-Hamilton and D. F. Foster, *Chem. Commun.*, **2007**, 1933-1935.

Comparative studies for the catalytic water phase carbon dioxide hydrogenation using iridium and ruthenium PTA complexes (PTA = 1,3,5-triaza-7-phosphaadamantane)

Mikael Erlandsson,[a] **Vanessa R. Landaeta,**[a] **Sylvain S. Bosquain,**[a] **Antoine Dorcier,**[b] **Andrew D. Philips,**[a] **Paul J. Dyson,**[b] **Gábor Laurenczy,**[b] **Luca Gonsalvi,**[a] **and Maurizio Peruzzini**[a]

[a] *ICCOM- CNR, Via Madonna del Piano 10, 50019, Sesto Fiorentino, Italy, Fax:+39 055 5225203; Tel:+39 055 522528.*
E-mail: mikael.erlandsson@iccom.cnr.it
[b] *EPFL - LCOM, BCH 2405, CH-1015 Lausanne, Switzerland, Fax: +41 21 6939885; Tel: +41 21 6939853*

The fixation of carbon dioxide is an important chemical and environmental question. CO_2 is widely available in the atmosphere and its conversion into useful organic C_1 building blocks such as methanol or formate is a great challenge for chemistry.[13] Several platinum metal group complexes were shown to catalyze the hydrogenation of CO_2 to formic acid under both conventional and supercritical conditions and in particular some ruthenium complexes were found to be highly active for this process.[14] $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene, *p*-cymene) complexes have been used as catalyst precursors together with various ligands in the hydrogenation of CO_2 in organic solvents[15] and in water.[16] Iridium complexes have been less investigated for use in hydrogenation of CO_2 despite the fact that Ir complexes have been shown to have activities superseding many Ru complexes.[13]

We have been interested for some years in the applications of arene and cyclopentadienyl Ru and Ir complexes bearing the water soluble monodentate phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) in selective hydrogenation reactions, medicinal applications and recently extended these studies to other transition metals and applied ligand structural modifications to observe a variety of coordination modes and their implications in catalysis.[17,18]

The study presented here shows that catalytical amounts of a water soluble ruthenium(II) complex, i.e. $[Cp'RuX(PTA)_2]Y$ and $[CpRuCl(PPh_3)(mPTA)]OTf$ (Cp' = Cp, Cp*, X = Cl, Y = null; X = MeCN, Y = PF_6 or the iridium (III) complex $[Cp*Ir(PTA)_2Cl]Cl$; PTA = 1,3,5-triaza-7-phosphaadamantane; mPTA, 1-methyl-1,3,5-triaza-7-phosphaadamantane) are moderately active catalysts for the hydrogenation of CO_2 and bicarbonate in aqueous solutions, in the absence of amines or other additives, under relatively mild conditions (100 bar H_2, 30-80 ºC).[19] Kinetic studies showed that the hydrogenation of HCO_3^- proceeds without an induction period, and that the rate strongly depends on the pH of the reaction medium. ^1H and ^{31}P HPNMR studies showed that hydrides $Cp*Ru(PTA)_2H$, $CpRu(PTA)_2H$, $Cp*Ir(PTA)H_2$ and $[Cp*Ir(PTA)_2H]^+$ were formed *in situ* under H_2 pressure.[7,8]

It was concluded that complexes $Cp*RuCl(PTA)_2$ and $[Cp*IrCl(PTA)_2]Cl$ had similar activities for the reduction of CO_2 and bicarbonate in aqueous solutions.

[13] P. G. Jessop, F. Joó, C.-C. Tai, *Chem. Rev.*, **2004**, *248*, 2425.
[14] (a) X. Yin, J. R. Moss, *Coord. Chem. Rev.*, **1999**, *181*, 27. (b) B. Cornils, W. A. Herrmann, Eds., *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1-2, VCH, **1996**.
[15] C.-C. Tai, J. Pitts, J. C. Linehan, A. D. Main, P. Munshi, P. G. Jessop, *Inorg. Chem.* **2002**, *41*, 1606.
[16] F. Joó, *Aqueous Organometallic Catalysis*, Kluwer, Dordrecht, 2001.
[17] A. D. Phillips, S. Bolaño, S. S. Bosquain, J-C, Daran, R. Malacea, M. Peruzzini, R. Poli, L. Gonsalvi, *Organometallics*, **2006**, *25*, 2189.
[18] A.D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.,* **2004**, *248*, 955.
[19] S. S. Bosquain, A. Dorcier, P. J. Dyson, M. Erlandsson, L. Gonsalvi, G. Laurenczy, M. Peruzzini. *Appl. Organometal. Chem.* **2007**, *21*, 947;
[8] M. Erlandsson, V. R. Landaeta, L. Gonsalvi; M. Peruzzini, A. D. Phillips, P. J. Dyson, G. Laurenczy, *Eur. J. Inorg. Chem,* in press.

# Photochemical Behaviour of the Water Soluble Complex [RuCl$_2$(PTA)$_4$]

Antonio Romerosa, [a] **Rugiada Girotti,**[a] **Sonia Mañas and Robin N. Perutz**[b]

[a] *Área de Química Inorgánica. Universidad de Almería, 04120, Almería, Spain.. Fax: +34 950015008; Tel: +34 950015305; E-mail: romerosa@ual.es* [b]
Department of Chemistry, University of York, York YO10 5DD, UK. Fax: +44 (0)1904 432516; Tel: +44 (0)1904 432549; E-mail: rnp1@york.ac.uk

One of the key challenges of the millennium is to combine the technological progress with environmental protection. One of the most efficient strategies to achieve benign chemical processes proposes the replacement of organic solvents by alternative reaction media such as ionic liquids, supercritical fluids and absence of reaction media (solvent-free conditions), but the simplest and cheapest way is the use of water as a solvent.

For this reason, as part of our interest in the synthesis and reactivity of new water soluble metal complexes, in the latest years our research has been focused on the synthesis of ruthenium complexes containing PTA (1,3,5-triaza-7-phosphaadamantane) and its methylated derivatives.[1]

Initially the photoisomerization of the well known *trans*-[RuCl$_2$(PTA)$_4$][2] (*trans*-**1**) to *cis*-**2** has been studied in chloroform at various wavelengths (Scheme 1, Figure 1), and in this case a reversible equilibrium has been observed.
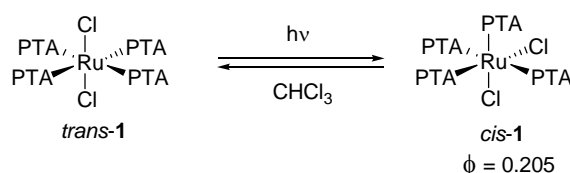
Scheme 1. *trans*-**1** to *cis*-**1** photoisomerization
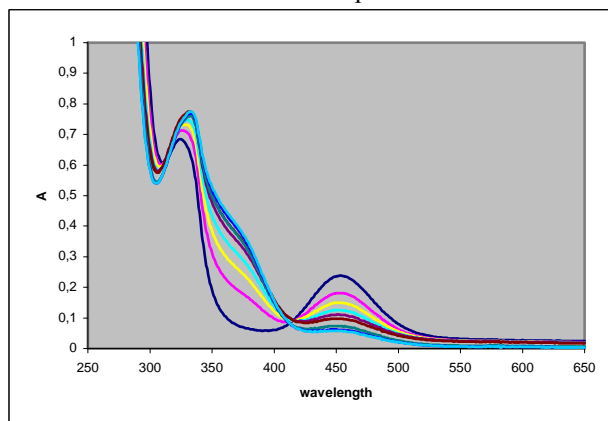

Figure 1. Study by UV spectra of the *trans*-**1** photoisomerization in CHCl$_3$ (irradiation with $\lambda > 416$ nm)

The study has been extended in water (Scheme 2): in this case the photoisomerization occurred followed by an exchange of a chloride with a water molecule to obtain the complex **2**, which was in a concentration-dependent equilibrium with *cis*-**1**. It was possible to isolate the pure aqua-complex **3** adding to the reaction mixture one equivalent of AgOTf.
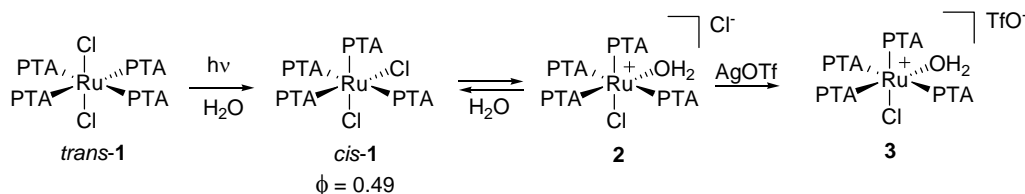
Scheme 2. Reactivity of the *trans*-**1** in water under light irradiation.

1   a) Saoud, M. *et al. Eur. J..Inorg. Chem.* **2003**, 1614-1619, b) Bolaño, S. *et al J. Mol Cat.* **2004**, *224*, 61-70. c) D. Akbayeva *et al.*, *Chem. Comm.* **2003**, 264-265. d) A. Romerosa *et al. Inorg. Chem.* **2006**, *45*, 1289-1298.
2   a) Mebi, C.A. ; Frost, B.J. ; *Inorg. Chem.* **2007**, 7115-7120; Darensbourg, D. J.; b) Darensburg, D.J. Joo, F. ; Kannisto, M. ; Katho, A. ; Reibenspies, J. H.; Daingle, D.J.; *Inorg. Chem.* **1994**, 200-208; c) Joo, F. ; Kannisto, M. ; Katho, A. ; Reibenspies, J. H. *Inorg. Chem.* **1992**, 1990-1993.

Theoretical investigation of the stereoselective reduction of diphenylacetlyene in acidic aqueous solutions catalyzed by water soluble ruthenium(II) phosphine complexes

G. Kovács[a,b], G.Ujaque[a], A. Lledós[a], F. Joó[b,c]

[a]*Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona) Spain*
[b]*Institute of Physical Chemistry, University of Debrecen, Debrecen 10, H-4010 Hungary*
[c]*Research Group of Homogeneous Catalysis, Hungarian Academy of Sciences, Debrecen 10, P.O. Box 7, H-4010 Hungary*
*e-mail: gabor@klingon.uab.cat*

New prospects have been provided in organometallic catalysis by using aqueous and especially aqueous-organic biphasic systems, since one major problem of homogenous catalysis, that is, the separation of the catalyst from the products can be easily achieved. One well-described family of water-soluble complexes catalyzing different hydrogenation reactions are rhodium and ruthenium complexes prepared with sulfonated aromatic phosphine ligands.

A series of articles have published by ourselves, in which, we intended to describe aqueous phase organometallic catalytic processes involving such complexes by means of theoretical methods[1]. As a continuation of the aforementioned works, in the present study, the mechanism of the hydrogenation of 1,2-diphenylacetylene is analyzed by means of theoretical methods, with the intention to explore the origin of the observed *stereoselectivity*.

It has been published by Joó and co-workers recently[2] that diphenilacetylene was hydrogenated under mild conditions in aqueous-organic biphasic systems with [{RuCl$_2$($m$tppms)$_2$}$_2$] as catalyst in the presence of $m$tppms ligands. In acidic solution the major product of the reaction was found to be *Z*-stilbene with only traces of the *E*-stereoisomer and only a slight overreduction to 1,2-diphenylethane was observed. Nevertheless, basic conditions favoured the formation of *E*-stilbene and the major product was 1,2-diphenylethane. These observations were explained by the distribution of the catalytically active hydride species that are present in the solution as a function of the pH.

In this work, theoretical (DFT) methods were applied to account for the observed stereoselectivity under *acidic* aqueous reaction conditions. [RuHCl(PH$_3$)$_3$] was applied as model for the spectroscopically detected [RuHCl($m$tppms)$_3$] complexes. The calculations show that the hydrogenation proceeds by the participation of both the hydride ligand and the hydroxonium ions present in acidic solutions at reasonable concentration. Since it was already known that appropriate inclusion of the solvent environment in the calculations is required for obtaining reasonable energetics, thus small clusters of water molecules were applied for modelling proton transfer reactions between the solvent and the catalytic intermediates. The stereoselectivity was explained on the basis of the different energy profiles gained for the possible reaction pathways.
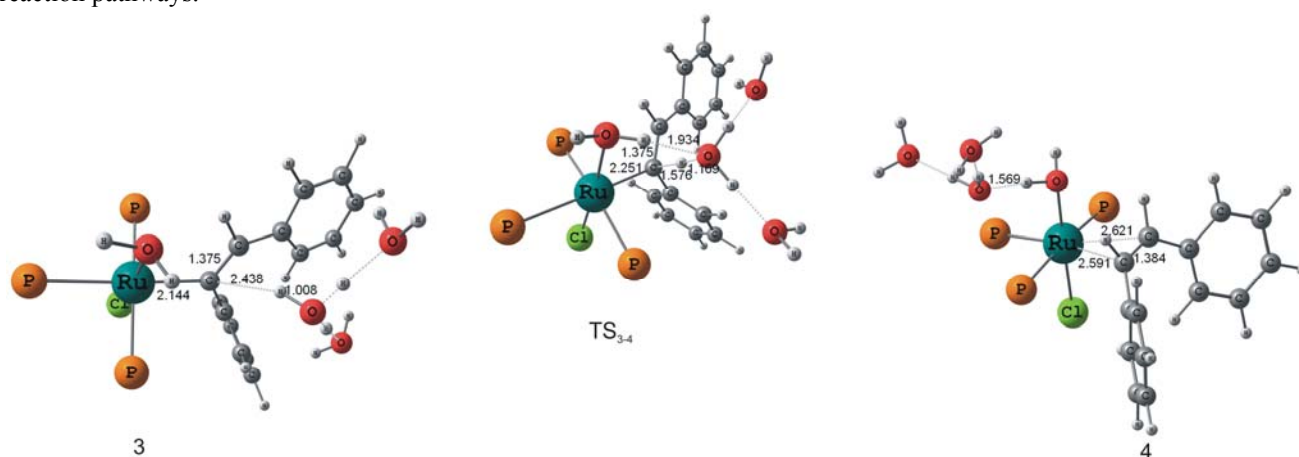
Figure 1. Structures representing the protonation of the carbon-carbon bond leading to the formation of *Z*-stilbene

[1] a) Kovács, G.; Schubert, G.; Joó, F.; Pápai, I. *Organometallics* **2005**, *24*, 3059. b) Kovács, G.; Schubert, G.; Joó, F.; Pápai, I. *Catal. Today* **2006**, *115*, 53. c) Kovács, G.; Ujaque, G.; Lledós, A.; Joó, F. *Organometallics* **2006**, *25*, 862. d) Rossin, A.; Kovács, G.; Ujaque, G.; Lledós, A.; Joó, F. *Organometallics* **2006**, *25*, 5010.
[2] Horvath, H. H.; Joó, F. *Reaction Kinetics and Catalysis Letters* **2005**, *85*, 355.

# Consecutive palladium-catalyzed Hiyama-Heck reactions in aqueous media under ligand-free conditions

Álvaro Gordillo,[a] Carmen López-Mardomingo[a] and Ernesto de Jesús[b]

[a] Departamento de Química Orgánica [b] Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E28871 Alcalá de Henares (Madrid), Spain. Fax: (+34) 91 885 4683; Tel: (+34) 91 885 4616; E-mail: carmen.lopezm@uah.es

Palladium-catalyzed carbon–carbon couplings, which are some of the most common transition-metal-catalyzed processes, are more and more often being performed in aqueous or biphasic media.[1] We have recently described the Hiyama arylation of bromoarenes in water using a variety of Pd precatalysts and aryl siloxanes activated with sodium or potassium hydroxide.[2] The most interesting results from these investigations suggested that bromides might react efficiently with aryl siloxanes at high temperatures in the presence of relatively low concentrations of palladium salts and in the absence of phosphanes or other expensive or toxic ligands (ligand-free conditions) (Scheme 1a).

In this work, we show that this attractive and unique combination of accessible and stable organosiloxanes, aqueous media, low Pd loadings, and aerobic and fluoride- and ligand-free conditions are also valid for sequential reactions that afford more complex products in a one-pot synthesis.[3] The vinylation of bromoarenes (**1**), with vinylsiloxanes (**2**) is complicated by the fact that palladium catalysts promote the Heck-Mizoroki coupling of aryl halides and alkenes under conditions similar to those of the Hiyama reaction. The selective synthesis of vinylarenes (**3**) therefore requires close control of the relative kinetics of the Hiyama and Heck reactions in order to minimize the formation of (*E*)-1,2-diarylethenes (**4**) and other Heck by-products (Scheme 1b). A number of vinylarene derivatives (**3**) was prepared in good yields by mixing the corresponding bromoarene with 2-4 equiv. of triethoxy(vinyl)silane, 0.1-0.5 mol of palladium(II) acetate, and 3-5 equiv. of 0.5 M NaOH, and stirring at 140-150 ºC for 2-3 h in a pressure tube. It should be stressed that the addition of poly(ethylene glycol) (PEG M_w = 2000) greatly enhanced the selectivity for the vinyl compound even in the presence of smaller excesses of silane. In contrast, symmetric (*E*)-1,2-diarylethenes (**4**) were selectively obtained simply by varying the aforementioned conditions. This variation essentially consisted of using a stoichiometric amount or a slight excess of the vinylsilane, and allowed the preparation of such symmetric alkenes by consecutive Hiyama-Heck reactions. We subsequently attempted the one-pot synthesis of asymmetric (*E*)-1,2-diarylethenes (**5**) by combining the Hiyama vinylation of the bromoarenes (**1a**) with the in situ Heck reaction of the resulting vinylarenes (**3**) (Scheme 1c). The selectivity for asymmetric (*E*)-stilbenes or stilbazoles (**5**) was notable, as can be inferred from the high yields of isolated products (81-91%).

The efficiency of the reactions described in water competes favourably with those reported in organic solvents, but the use of water has specific advantages over conventional organic solvents: (a) the activation of aryl bromides under ligand-free conditions relies on the use of high temperatures for which a non flammable solvent such as water is superior on safety grounds; (b) many of the alkenes reported, especially 1,2-diarylethenes, are solids that precipitate from the aqueous reaction medium and can therefore be separated by simple filtration to afford crude products that, in many cases, are pure by ^{1}H NMR spectroscopy.
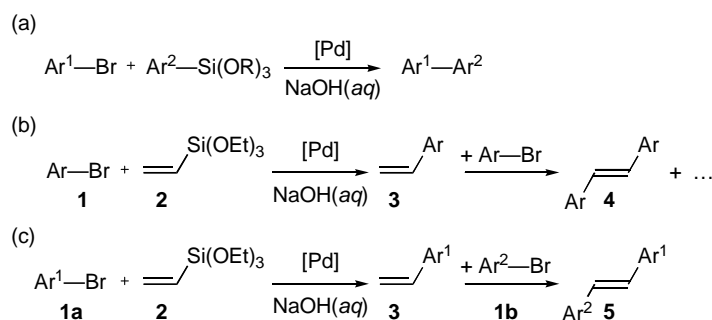
Scheme 1

1   C.-J. Li, *Chem. Rev.* **2005**, *105*, 3095-3165.
2   A. Gordillo, E. de Jesús, C. López-Mardomingo, *Org. Lett.* **2006**, *8*, 3517-3520.
3   A. Gordillo, E. de Jesús, C. López-Mardomingo, *Chem. Commun.* **2007**, 4056-4058.

Highly efficient Suzuki-Miyaura cross coupling in aqueous media catalyzed by *trans*-[Pd{NH(CH₂CH₂OH)₂}₂(Cl)₂]$^{(1)}$ complex

Galicia López Oscar, David Morales Morales

Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Circuito Exterior, Coyoacán, 04510, México, DF, México.
Fax: +52 55 56162217; Tel: +52 55 56224514; E-mail: damor@servidor.unam.mx

The last decade has witnessed the steadily advance and progress of cross coupling reactions, reaching now a days the status of corner stone in organic synthesis, this being particularly true for the case of the Heck-Mizoroki[2,3] and Suzuki-Miyaura[4] type reactions. For most of the cases, palladium based catalyst have been the choice to carry out these processes. However, most of these systems involve toxic solvents and expensive transition metal catalysts.[5] Thus, the use of more readily available and potentially recoverable catalysts instead of expensive and sensitive catalysts as well as non-organic solvents is highly desirable. On the other hand, performing organic reactions in more environmentally benign ways is an important goal from an ecological point of view.[6,7] Hence, utilizing water as the reaction media has attracted many synthetic organic chemists because it is one of the best ways to avoid many environmental problems that can occur with industrial organic synthesis.[8] Moreover, the use of water facilitates the separation of the products from a water soluble catalyst, since for most of the cases, the catalyst remains in the aqueous layer thus enabling it for further use (recycling). Thus the present work describes our findings on the use of the very facile to synthesize system *trans*-[Pd{NH(CH₂CH₂OH)₂}₂(Cl)₂][9] as efficient catalyst for the Suzuki-Miyaura couplings of a series of halobenzenes in water.
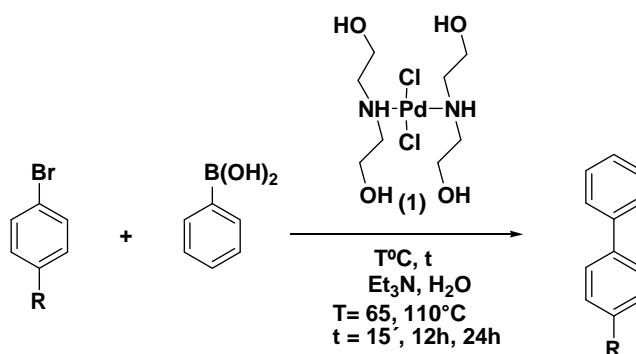

R = OMe, Me, H, Cl, CHO, COMe, CN

1- Diethanolamine is non-expensive, non-toxic commencially available starting material which is used in a number of consumer products, such as shampoos, cosmetics, and pharmaceuticals. US Enviromental Protection Agency. http://www.epa.gov/ttn/atw/hlthef/diethano.html#ref7
2- R. F Heck, Jr. J. P.Nolley, *Journal of Organic Chemistry,*.**1972**, 37*(14)*, 2320.
3- T.Mizoroki, K. Mori; A. Ozaki, *Bulletin of the Chemical Society of Japan*, **1971**, 44, 581.
4- (a) N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Letters*, **1979**, 20, 3437, (b)N. Miyaura and A. Suzuki, Journal of Chemical Society, Chemical Communication, 1979, 866.
5- K. H. Shaughnessy, R. B. DeVasher, *Current Organic Chemistry*, **2005**, 9, 585.
6- R. A. Sheldon, *Green Chemistry*, **2005**, 7, 267.
7- R. Franzén, Y. Xu, *Canadian Journal of Chemistry*, **2005**, 83, 266.
8 Chao-Jun Li, *Chemical Reviews*, **2005**, 105, 3095.
9- Z. D. Prtrovic, M. I. Djuran, F.W. Heinemann, S. Rajković, S. R. Trifunović, *Bioinorganic Chemistry*, **2006**, 34, 225.

Catalysis in biphasic (water-CH$_2$Cl$_2$) medium and in water with core/shell bimetallic Rh-Pd nanoparticles.

Christian Bergounhou, Claudine Blandy, <u>Christian Lorber</u> and Jean- Louis Pellegatta

Laboratoire de Chimie de Coordination du CNRS (UPR 8241)- 205, route de Narbonne, 31077, Toulouse Cedex 4, France. Tel: 33 5 6133 3144 ; E-mail: lorber@lcc-toulouse.fr

The organometallic one pot route from the redox properties of the vanadocene and a variable mixture of two [M(I)-Cl]$_2$ (M = Rh(C$_2$H$_4$)$_2$, Pd(allyl)) in the presence of PVP gives core/shell Pd/Rh bimetallic nanoparticles of different composition and similar size (nearly 2 nm).[1]

$$(x+y)Cp_2V + x[Rh (C_2H_4)_2Cl]_2 + y[Pd (\eta^3\text{-allyl})Cl]_2 \rightarrow Rh_xPd_y/PVP + (x+y) Cp_2VCl$$
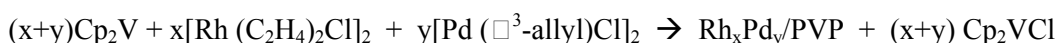
TEM and HRTEM show well dispersed microcrystalline particles; the average size from electron microscope observations was approximatively 1.9 nm with a relatively narrow size distribution.
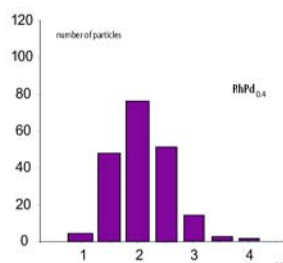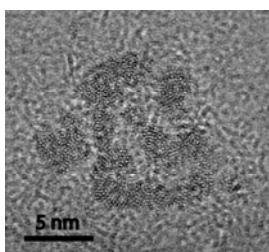
Characterization of the surface composition was realized by chemical probes such as carbon monoxide chemisorption experiments (followed by IR spectroscopic studies) and catalytic hydrogenation reaction studies.

Catalytic hydrogenation reactions of quinoline and phenylacetylene followed by GC, confirm the presence of core/shell structured bimetallic colloids with Pd atoms surrounded by Rh atoms.

All the catalytic results of the hydrogenation of quinoline show unambiguously a significant enhancement of the activity of the bimetallic colloids, by comparison to the linear additive effect of Rh and Pd observed for the physical mixtures. For the hydrogenation of the phenylacetylene, Rh atoms could be considered as inhibitors for the bimetallic catalyst. The maximum or the minimum activity for the bimetallic colloids is exhibited at nearly RhPd$_4$, depending on the substrate. For highest Rh content, the activity of the bimetallic colloids could be considered as monotonic and similar to the pure rhodium colloids. This suggests that Rh atoms are on the surface on the bimetallic colloids as a shell, which can serve as a catalytic promoter for the quinoline or *a contrario*, a protective shell over the palladium core which prevents the catalytic hydrogenation of the phenyl acetylene.
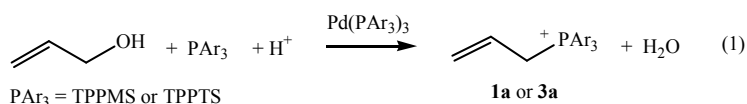
Catalytic reactions (mainly hydrogenation reactions) using these nanoparticles, in biphasic medium and in water as solvent, will be presented.

1   *New J. Chem.* **2003**, 27, 1528 - *New J. Chem.* **2007**, 31, 218.

Stability of allylphosphonium chloride salt of TPPTS

C.Lucas*, N.Legagneux, E. Kuntz

*C2P2- LCOMS-CPE, 43 Bld du 11 Novembre 1918, 69616 VILLEURBANNE Cedex, E-mail : lucas@cpe.fr*

Allyl phosphonium salts of TPPMS (**1a**) and TPPTS (**3a**) are produced from allyl alcohol and the 2 ligands TPPTS and TPPMS with palladium catalyst (eq.1).[1, 2]

$$\text{\Huge\diagdown\diagup}OH \; + \; PAr_3 \; + H^+ \; \xrightarrow{\;Pd(PAr_3)_3\;} \; \text{\Huge\diagdown\diagup}^+PAr_3 \; + \; H_2O \qquad (1)$$

PAr_3 = TPPMS or TPPTS   **1a** or **3a**

It appears that the stability of phosphonium salts is a crucial point for the understanding of the stability of hydrosoluble TPPTS and TPPMS palladium catalysts (Tsuji-Trost reaction and diene telomerization). An irreversible destruction of phosphonium salts should lead to the decomposition of the ligand excess, and therefore to the metallic palladium precipitation.

The study of the stability of **3a** aqueous solutions *versus* pH and temperature revealed the existence of several transformations (Scheme **a**). **3a** decomposition into the oxide **2a** and propylene is very fast in sodium hydroxide solutions. **3a** can also isomerize into the vinylic species **3b,** which can be hydrated into **3c**. **3b** and **3c** are also transformed into the oxides **2b** and **2c,** respectively.

Schemes **a** and **b**.
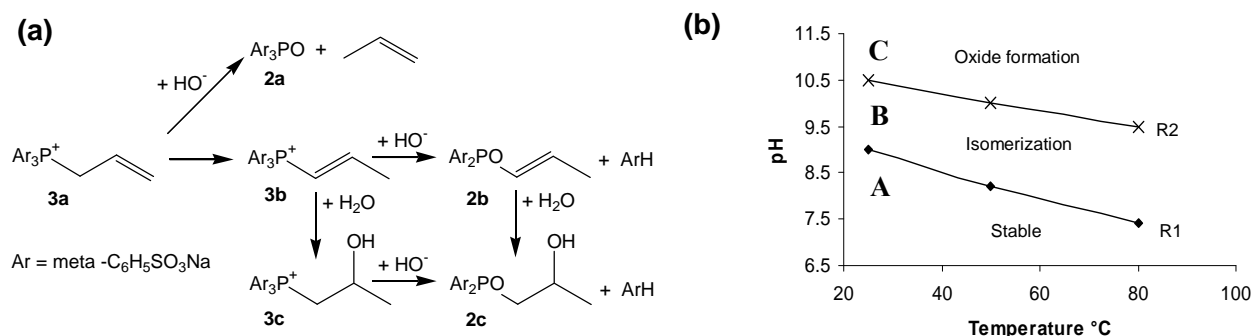
Temperature-pH diagram of these degradation reactions of **3a** are represented (Scheme **b**).Temperature and high pH have an adverse effect. In the area **C,** oxides formation is fast. In **B,** isomerization of **3a** occurs. In **A**, **3a** is stable (pH<9 at 25°C and at pH<7.5 at 80°C).

The metallic palladium precipitation in Tsuji-Trost reaction or diene telomerization has probably several causes. Our results are in agreement with the fast palladium precipitation observed in basic medium during phenol C-allylation or butadiene hydrodimerisation at 80°C (pH>10.5), due to the rapid decomposition of TPPTS. On the contrary, the addition of acid or carbon dioxide pressure (Tsuji-Trost reaction at low pH or Kuraray process[1]) would maintain the pH to a value <9 (25°C) or <7.5 (80°C), ensuring the stability of phosphonium salts and consequently that of the palladium catalyst.

 (1) Yoshimura, N. In Aqueous –Phase Organometallic Catalysis: Concepts and Applications; Cornils, B.; Herrmann, W.A., Eds.; Wiley-VCH: Wienheim, **2003**, 540-549

(2) Kuntz, E. G.; Amgoune, A.; Lucas, C.; Godard, G. J. Mol. Cat. A **2006**, 244, 124-136.

Water soluble metalic compounds

Asun Luquin[a], Sascha Schäfer[a],Elena Cerrada[a], Aránzazu Mendía[b], Mariano Laguna[a]

[a] *Inorganic Chemistry Department, University of Zaragoza, Plaza S. Francisco s/n 50009 Zaragoza Spain. Fax: 34 976 761187; Tel: 34 976 761181; E-mail: aluquin@unizar.es*

[b] *Chemistry Department, Science Faculty, Plaza Misael Bañuelos s/n 09001 Burgos. Spain.*

Classical chemistry began with the use of water, both as a solvent and as a ligand for many organic and inorganic reactions. Due to this discipline advance, new reactions, ligands, complexes… were discovered and some of them required completely anhydrous conditions as well as special techniques and apparatus to keep water out of reaction[1].

Nowadays, water is experiencing a revival as a solvent in organic and inorganic chemistry and the main challenge today is the design and development of new complexes that are both soluble and stable in water. One of the strategies used to dissolve organic and inorganic complexes in water is to use of water soluble ligands such as some sulfonated phosphines, or phosphines like 1,3,5-triaza-7-phosphaadamantane (PTA)[2] or 3,7-diacetyl-1,2,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA)[3] and its salts, so that they can be used for instance, as catalysts both in biphasic or aqueous catalysis.

$R_1 = SO_3Na$, R_2, $R_3 = H$ TPPMS
R_1, $R_2 = SO_3Na$, $R_3 = H$ TPPDS
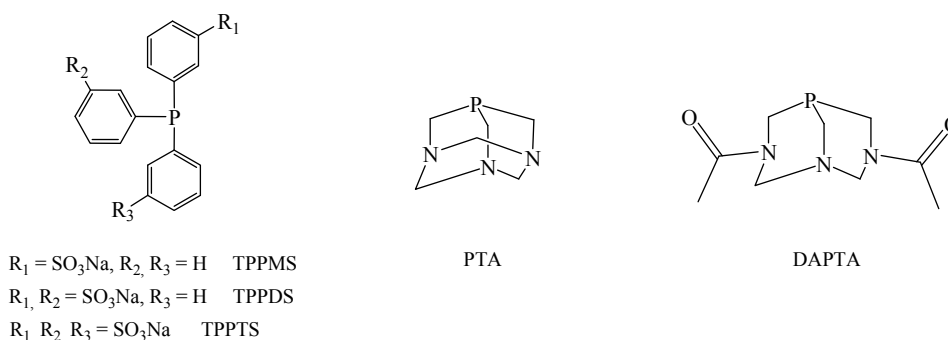R_1, R_2, $R_3 = SO_3Na$ TPPTS

PTA   DAPTA

Figure 1, Water soluble ligands used to make soluble organic and inorganic complexes.

In our group we have try to improve water solubility developing new PTA salts by addition of organic bromide or triflatos to the PTA. All the phosphine salts were obtained in an excellent yield. These salts and some old salts of this kind[4] were reacted with gold derivatives and a series of water soluble and stable gold complexes were synthesised. Some reactivity of complexes prepared is also reported.
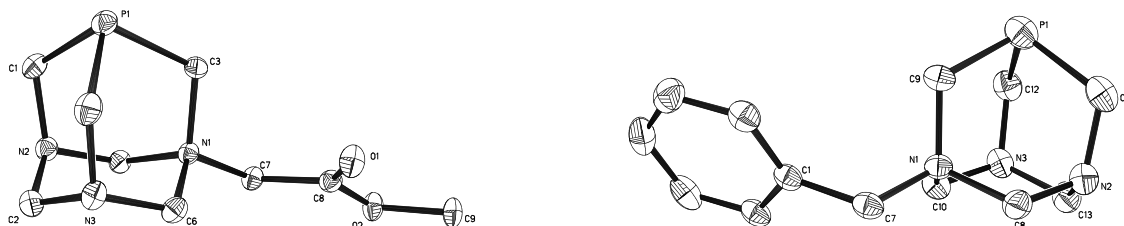

Figure 2, Crystal structure of $[PTACH_2COOMe]^+$ and $[PTACH_2Ph]^+$

1   D. Shriver, M. A. Drezdon, *The manipulation of air sensitive compounds*, John Wiley & Sons, New York, **1986**
2   D. J. Daigle, A. B. Peperman Jr., S. L. Vail, *J. Heterocyclic Chem.*, **1974**, *11*, 407.
3   D. J. Darensbourg, C. G. Ortiz, J. W. Kamplain, *Organometallics*, **2004**, *23*, 1747.
4   A. Mena-Cruz, P. Lorenzo-Luis, A. Romerosa, M. Salud, M. Serrano-Ruiz, *Inorg Chem* **2007**, *46*, 6120

Preparation and Characterization of Water-Soluble Ruthenium(II) Complexes Containing one Triisopropylphosphine

M. Martín,[a] E. Sola,[a] H. Horváth,[b,c] Á. Kathó,[b] F. Joó[b,c]

[a] *Departamento de Química de la Coordinación y Catálisis Homogénea, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain. Fax: +34 976761187; Tel: +34 976762026; E-mail: martam@unizar.es.* [b] *Institute of Physical Chemistry, University of Debrecen.* [c] *Research Group of Homogeneous Catalysis, Hungarian Academy of Sciences, Debrecen 10, P.O. Box 7, H-4010 Hungary.*

The application of metal catalysts in aqueous systems that enables an easy recovery of the catalyst by decantation, has recently attracted attention.[1] One commonly used strategy to impart water-solubility to a given metal complex involves the use of ligands possessing solubilizing groups or use of water-soluble ligands. The most numerous ligands used in such processes are water-soluble phosphines, however there has been paid less attention to the aqueous catalytic proprieties of phosphine complexes that are water-soluble as a consequence of the ionic nature of the compound.

Although there are several cationic acetonitrile ruthenium catalysts there are only a few instances of their use in aqueous solutions. Our interest in compounds with labile ligand to the substitution[2] motivated us to prepare acetonitrile ruthenium complexes. Here we reported our result on the synthesis, structural characterization and biphasic catalytic behaviour of water-soluble acetonitrile rutenium(II) complexes containing one triisopropylphosphine ligand.

1   (a) B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt, Eds. *Multiphase Homogeneous Catalysis*, Wiley-VCH, Weinheim, 2005. (b) F. Joó, *Aqueous Organometallic Catalysis*, Kluwer, Dordrecht, 2001.
2   (a) E. Sola, J.Navarro, J. A. López, F. J. Lahoz, L. A. Oro, H. Werner, *Organometallics,* **1999**, *18*, 3534. (b) M. Martín, E. Sola, S. Tejero, J. L. Andrés, L. A. Oro, *Chem. Eur. J,.* **2006**, *12*, 4043. (c) J. Navarro, M. Sági, E. Sola, F. J. Lahoz, I. T. Dobrinovitch, A. Kathó, F. Joó, L. A. Oro, Adv. Synth. Catal., **2003**, *345*, 1.

Deborronation of phosphines containing amine acids.
# Theoretical and experimental results.

Emma Petersen,[a] **Gabór Kovács**[b] , **Manuel Serano**[a]**, Agustí Lledós**[b]**, Antonio Romerosa**[b]**, Chiara Ciardi**[a]**,**
Gianna Reginato[c] **and Maruzio Peruzzini**[c]

[a] *Area Química Inorganica, Universidad de Almería,C/ La Cañada de San Urbano s/n, 04007 Almería, Spain. Fax: +34-950015008;*
Tel: =34-950015305; E-mail: romerosa@ual.es
[b] *Unitat Quimica Fisica, Universitat Autonoma de Barcelona ,08193 Bellatera, Barcelona, Spain; E-mail: agusti@klingon.uab.es*
[c] *ICCOM-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorention, Firenze, Italy.*

The use of water as a solvent is a rather new concept in chemistry, as for a long time it was seen as a containment, and should be get rid off. The use of water however has increased our attention as it could provide a cost reduction in synthetic processes and decrease their environmental impact. The chiral centre in it's turn can induce chirality into the reaction, and therefore enhance stereoselctivity ot the reaction. These complexes, designed for organic solvents, are unsuitable for use in water because they decompose or react with the solvent. The aim is to synthesize water soluble chiral complexes, which could induce chirality on the catalyzed reactions. There are essentially two ways to incorporate chirality into the complex, the first one is to make the complex chiral on the metal centre or you can introduce chirality through the incoming ligands.

We have synthesized new amine acid based phophine ligands from natural amine acids. They are watersoluble and they contain chiral centers. We transformed the amine acid to complex **3**[1] (scheme 1) which by reaction with [Rh(COD)Cl]$_2$ in methanol, without deprotecting the phosphine moiety, gave the same complex as the deprotected phosphine in DCM. It was known from literature that the phosphine boran cleavage is normally done with amines, however this is an equilibrium and the reaction should be done in two steps. Only Also an article was presented in which methanol is used as the deprotecting agent but in the presence of molecular sieves and in THF.[2]
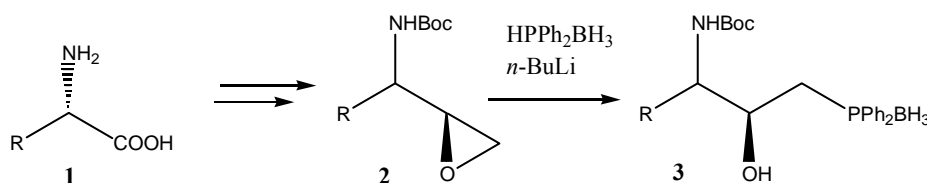
Scheme 1

Here we present the calculated difference in activation energy between dimethylamine and methanol with two different phosphines. We found that in all intstances the trancition state of the reaction, with both reactants, resembeles a S_N2 reaction type as can be seen in figure 1, but the activation energy for dimethylamine is lower than for methanol while the formation energy is lower for methanol.
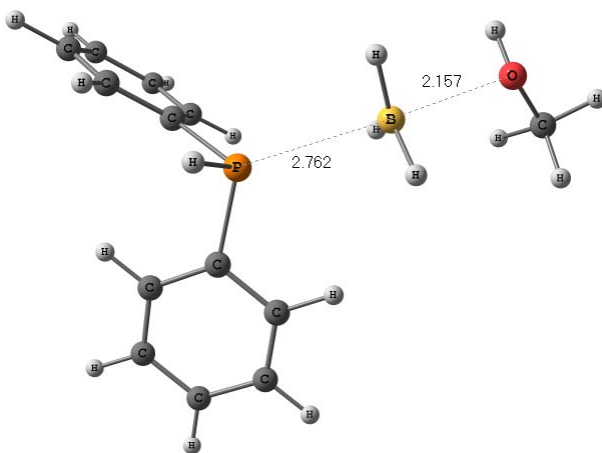
Figure 2 transition state of methanol and diphenylphosphine borane complex.

1   C. Ciardi, a. Romerosa, M, Serano, L. Gonsalvi, M, Peruzzini and G. Reginato, *Journal Organic Chemistry*, **2007**, *72(20)*, 7787.
2   M. Schröder, K. Nozaki, T. Hiyama, *Bull. Chem. Soc. Jpn.*, **2004**, *77(10)*, 1931.

# PTA ligands as end groups of water-soluble phosphorus dendrimers. Use of their Ru(II) complexes as catalysts

Paul Servin,[a] **Régis Laurent,**[a] **Luca Gonsalvi,**[b] **Maurizio Peruzzini,**[b] **Jean-Pierre Majoral,**[a] **and Anne-Marie Caminade**[a]

[a] *Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France. Fax: + 33 5 61 55 30 03; Tel: + 33 5 61 33 31 25; E-mails:* majoral@lcc-toulouse.fr, caminade@lcc-toulouse.fr

[b] *ICCOM CNR, Istituto di Chimica dei Composti Organo Metallici, Via Madonna del Piano, 10 Polo Scientifico di Sesto Fiorentino 50019 Sesto Fiorentino, Italy*

Today several industrial catalytic processes are running in biphasic systems (water/organic solvent)[1] and it is therefore of importance to develop the aqueous catalysis further. To accomplish this goal water soluble ligands such as PTA (1,3,5-triaza-7-phosphaadamantane)[2] can be used. This phosphine has received increased attention due to its ability to stabilize low metal oxidation states and to its high solubility in water.[3] These characteristics make it an excellent ligand for preparing water-soluble catalysts.

On the other hand, there is an increasing interest in using dendrimers as catalysts. Indeed, these hyperbranched and perfectly defined macromolecules can bear catalytically active entities as end groups, and combine the advantages of homogeneous (they are soluble) and of heterogeneous catalysts (they can easily be eliminated from the products and reused).[4] Furthermore, metal leaching is generally diminished by grafting a catalyst to a dendrimer.
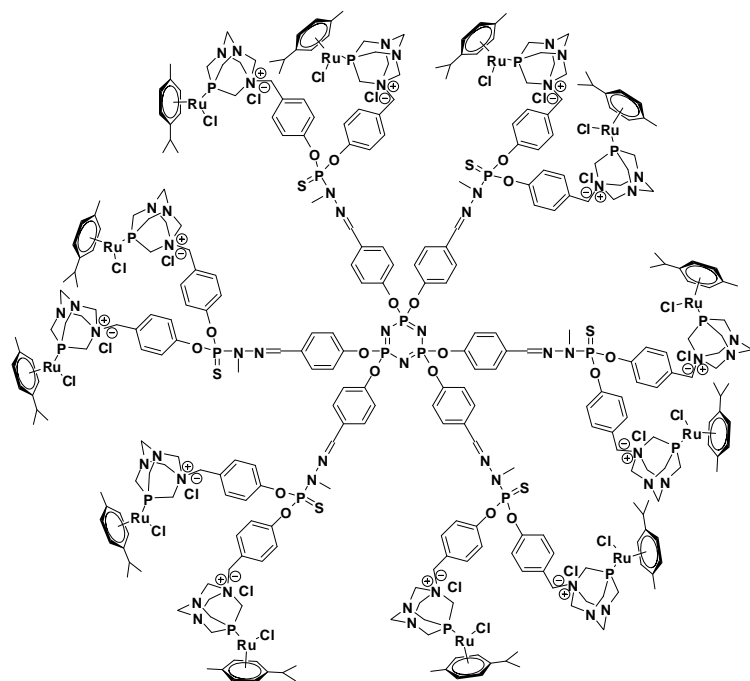
The phosphorus-containing dendrimers we synthesize possess at each step of the synthesis either $P(S)Cl_2$ or aldehyde end groups,[5] which can be easily modified for further functionalizations.[6] In particular, we have found that it is possible to graft PTA directly to phosphorus dendrimers yielding water-soluble dendrimers. These dendrimers can later on be reacted with metal complexes such as $[Ru(p\text{-cymene})Cl_2]_2$ to yield organometallic dendrimers (so called metallodendrimers) decorated with 6, 12 (see figure 1), 24 or 48 ruthenium atoms on the surface. Alcohol isomerization and alkyne hydration in the presence of water have been studied using the different synthesised generations (sizes) of dendrimers as well as a monomer (used for comparison) derived from p-methoxybenzyl-chloride.

The effect of the local density of ligands on the surface, using a variation of a highly functionalized[7] dendrimer has also been studied.

Figure 1. A first generation phosphorus dendrimer with Ru(II)-complex.

1   Cornils B., Herrmann W. A., Eckl R. W. *J. Mol. Cat. A: Chem.*, **1997**, *116*, 27
2   Daigle D. J., in: Darensbourg M. Y. (Ed.) *Inorg. Synth.*, **1998**, *32*, 40
3   Phillips A. D., Gonsalvi L., Romerosa A., Vizza F., Peruzzini M. *Coord. Chem. Rev.*, **2004**, *248*, 955
4   Ouali A., Laurent R., Caminade A. M., Majoral J. P., Taillefer M. *J. Am. Chem. Soc.*, **2006**, *128*, 15990; Gissibl A., Padié C., Hager M., Jaroschick F., Rasappan R., Cuevas-Yanez E., Turrin C.O., Caminade A.M., Majoral J.P., Reiser O. *Org. Lett.* **2007**, *9*, 2895
5   Launay N., Caminade A.M., Majoral J.P. *J. Am. Chem. Soc.* **1995**, *117*, 3282
6   Krishna T.R., Parent M., Werts M.H.V., Moreaux L., Gmouh S., Charpak S., Caminade A.M., Majoral J.P., Blanchard-Desce M. *Angew. Chem. Int. Ed.* **2006**, *45*, 4645
7   Servin P., Rebout C., Laurent R., Peruzzini M., Caminade A. M., Majoral J. P., *Tetrahedron Lett.*, **2007**, *48*, 579

Synthesis of dendrimers ended by bis(diphenylphosphinomethyl)amino ligands and their use in Palladium catalyzed C-C cross-coupling reactions in the presence of water

Paul Servin,[a] Régis Laurent,[a] Antonio Romerosa,[b] Maurizio Peruzzini,[c] Jean-Pierre Majoral,[a] and Anne-Marie Caminade[a]

[a] Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France. Fax: + 33 5 61 55 30 03; Tel: + 33 5 61 33 31 25; E-mails: majoral@lcc-toulouse.fr, caminade@lcc-toulouse.fr
[b] Área de Química Inorgánica, Facultad de Ciencias Experimentales, Universidad de Almería, 04071 Almería, Spain
[c] ICCOM CNR, Istituto di Chimica dei Composti Organo Metallici, Via Madonna del Piano, 10 Polo Scientifico di Sesto Fiorentino 50019 Sesto Fiorentino, Italy

A very special class of polymers named dendrimers is at the forefront of polymer researches since almost two decades, because of their very exceptional characteristics compared with conventional polymers. In particular, they possess a large number of terminal groups, the nature of which governs the interactions of the dendrimer with its environment and most of its properties. These unique features of dendritic macromolecules have led to the design of functional dendrimers for specific applications, amongst which catalysis occupies an important place since the first example in 1994.[1]

One of the major successes of catalysis in general concerns C-C couplings, especially when one (or both) reagent is an aromatic. For such purpose, three major reactions have been proposed, using palladium complexes as catalysts, namely Suzuki,[2] Sonogashira,[3] and Heck[4] reactions. On many occasions, such reactions have proved to afford important building block in pharmaceutical and materials science. In this area as well as for molecular catalysis in general, efforts are currently directed towards the discovery or optimization of catalysts having an improved efficiency, longer lifetimes, tolerance of air and moisture, and/or easier separation, recovery and recycling.
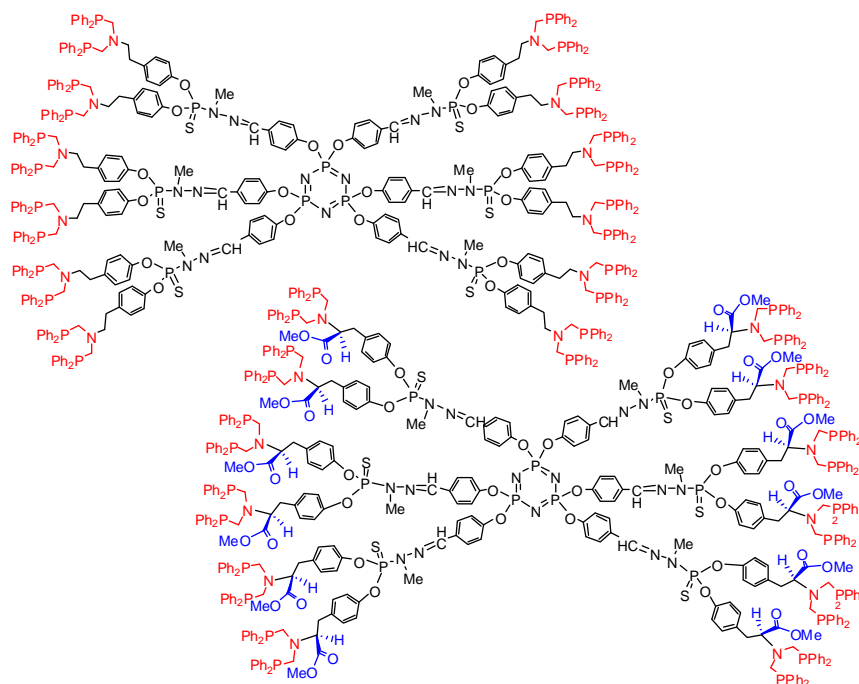
Scheme. Two first generation dendrimers capped by bis(phosphino)amino end groups issued form tyramine or L-tyrosine methyl ester.

We will describe the synthesis of two new series of phosphorus-containing dendrimers[5] having two types of bis(diphenylphosphinomethyl) amino end groups from generation zero (6 diphosphino end group) to generation 3 (48 diphosphino end groups) (See generations 1 in the Scheme).

These dendrimers are synthesized in only one step starting from the $P(S)Cl_2$ end groups of the dendrimers, contrarily to another series we previously described,[6] which necessitated 3 steps.

The diphenylphosphino groups are first grafted either to tyramine or L-tyrosine methyl ester, and the phenol groups are reacted in basic conditions to the $P(S)Cl_2$ groups. The use of L-tyrosine give birth to chiral dendrimers,[7] and induces a certain steric hindrance at the level of the diphosphino groups.

Both new series of these dendrimers appear as surprisingly stable towards oxygen and water.

The corresponding palladium complexes (obtained in situ from Pd(OAc)$_2$) are used to catalyse Suzuki, Sonogashira and Heck reactions in mixtures water/acetonitrile (1/3 to 2/3 of water), with 1% loading of Pd. Moderate (Suzuki) to good (Heck) and even very good (Sonogashira) results have been obtained, concerning the catalytic efficiency. The influence of the generation (the size) of the dendrimer, as well as the local steric hindrance will be discussed.

1 Van Koten, G.; Grove, D.M.; Wijkens, P.; van Leeuwen, P.W.; de Wilde, J.C.; van der Made, A.W.; Knapen, J.W.C. *Nature*, **1994**, *372*, 659.
2 Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419.
3 Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.
4 Heck, F.R.; Nolley, J.P. *J. Org. Chem.* **1972**, *37*, 2320.
5 Launay, N.; Caminade, A.M.; Lahana, R.; Majoral, J.P. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1589.
6 Slany M., Bardají M., Casanove M.J., Caminade A.M., Majoral J.P., Chaudret B. *J. Am. Chem. Soc.* **1995**, *117*, 9764; Bardají, M.; Kustos, M.; Caminade, A.M.; Majoral, J.P.; Chaudret, B. *Organometallics* **1997**, *16*, 403.
7 Turrin C.O., Chiffre J., de Montauzon D., Balavoine G., Manoury E., Caminade A.M., Majoral J.P. *Organometallics* **2002**, *21*, 1891

Grafting of scorpionate and other N-ligands to the surface of dendrimers. Preliminary results on the use of their Palladium complexes as catalyts in the presence of water

Paul Servin,[a] **Régis Laurent,**[a] **Riccardo Wanke,**[b] **Armando Pombeiro,**[b] **Jean-Pierre Majoral,**[a] **and Anne-Marie Caminade**[a]

[a] *Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France. Fax: + 33 5 61 55 30 03; Tel: + 33 5 61 33 31 25; E-mails:* majoral@lcc-toulouse.fr, caminade@lcc-toulouse.fr

[b] *Centro de Química Estrutural, Complexo I, Instutito Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal*

Besides phosphino ligands, nitrogen ligands can also be used for the complexation of metals. We have previously shown that iminopyridine derivatives are very efficient ligands for the copper catalysed arylation of nucleophiles,[1] and that azabis(oxazolines) allows the asymmetric benzoylation of diols in the presence of copper.[2] In both cases, these ligands were garfted to the surface of phosphorus-containing dendrimers.[3]

We report here the grafting of several new types of nitrogen ligands to the surface of small phosphorus-containing dendrimers (generations 0 and 1). These potential ligands are either monodentate (pyridine), bidentate (dipyridine), or tridentate (scorpionate[4]). 4-hydroxypyridine is directly reacted with the P(S)Cl$_2$ end groups of dendrimers, and dipyridine acetone is first reacted with tyramine, then the resulting phenol imine is reacted with P(S)Cl$_2$ end groups.
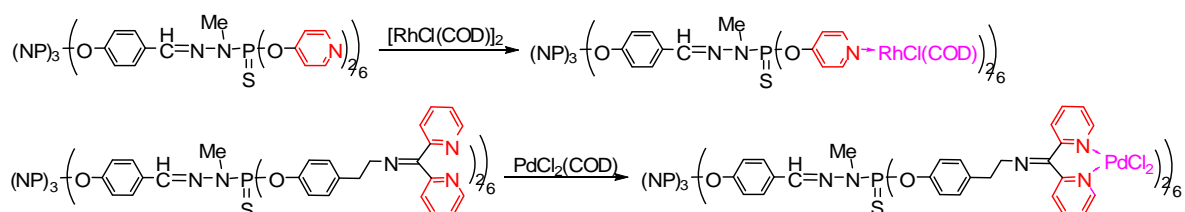
In the case of the scorpionate derivative, the starting point is an alcohol derivative, to which a phenol is grafted, to be reacted also with the P(S)Cl$_2$ end groups.
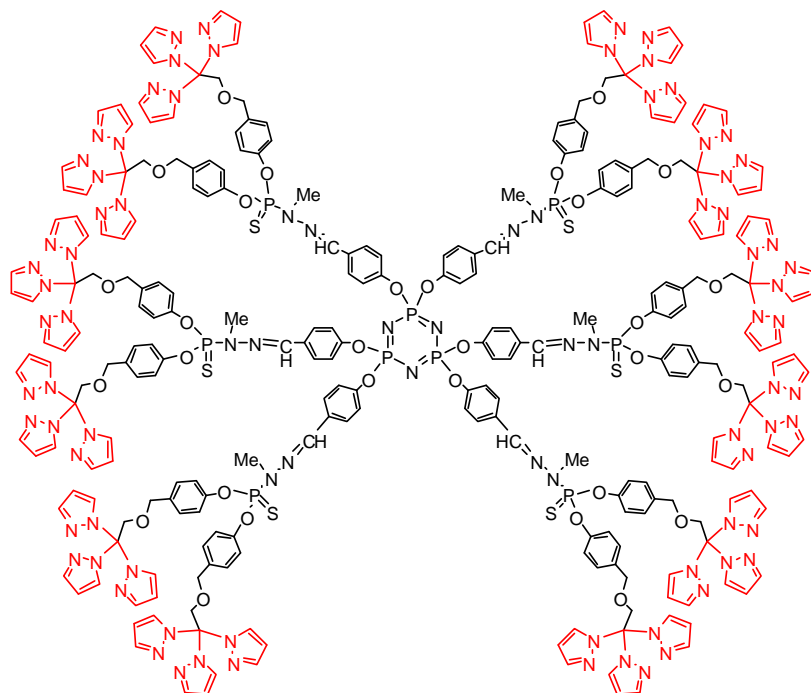
The complexing ability of some of these ligands was first tested. The monopyridine end groups were used for the complexation of rhodium; the dipyridine is able to complex palladium.

First catalytic tests were then performed using the dipyridine and the scorpionate ligands in Heck reactions (styrene + phenyliodide) with Pd(OAc)$_2$ as metallic derivative (in situ complexation) and in the presence of water (water/acetonitrile 1/2).

The first generation (G1) of the dipyridine derivative is the most efficient (80% of conversion with G1-dipyridine, 63% with G1-scorpionate) .

1   Ouali A., Laurent R., Caminade A. M., Majoral J. P., Taillefer M. *J. Am. Chem. Soc.*, **2006**, *128*, 15990.
2   Gissibl A., Padié C., Hager M., Jaroschick F., Rasappan R., Cuevas-Yanez E., Turrin C.O., Caminade A.M., Majoral J.P., Reiser O. *Org. Lett.* **2007**, *9*, 2895
3   Launay, N.; Caminade, A.M.; Lahana, R.; Majoral, J.P. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1589. Launay N., Caminade A.M., Majoral J.P. *J. Am. Chem. Soc.* **1995**, *117*, 3282.
4   Reger, D.L.; Grattan, T.C.; Brown, K.J.; Little, C.A.; Lamba, J.J.S.; Rheingold, A.L.; Sommer, R. D. *J. Organomet. Chem.* **2000**, *607*, 120. Alegria, E.C.B.; Martins, L.M.D.R.S.; Haukka, M.; Pombeiro, A.J.L.; *Dalton Trans*, **2006**, 4954.

Towards Janus-type and other types of bifunctional water-soluble dendritic catalysts

Mar Tristany,[a] **Régis Laurent,**[a] **Jean-Pierre Majoral,**[a] **and Anne-Marie Caminade**[a]

[a] *Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France. Fax: + 33 5 61 55 30 03; Tel: + 33 5 61 33 31 25; E-mails: majoral@lcc-toulouse.fr, caminade@lcc-toulouse.fr*

Besides classical bowl-shaped dendrimers, which are hyperbranched (tree-like) and perfectly defined macromolecules, due to their step-by-step synthesis, there exists special dendritic architectures, which enable the presence of at least two types of functional groups in a single macromolecules. The ratio and the location of both types of functional groups can be varied at will, provided the method of synthesis of the dendritic framework is perfectly mastered.

The method of synthesis of phosphorus-containing dendrimers that we develop since 1994[1] is extremely tolerant to various types of structural modifications, and we have already shown the possibility to apply this method for the design of macromolecules having two types of end groups located either on each branching point of the surface,[2] or in two different areas of the surface affording Janus-type dendrimers[3] or inside the structure and on the surface.[4] All these experiments pose the problem of compatibility between both types of functional groups. One particularly attractive type of bifunctional dendrimers is those in which one type of function ensures the solubility in water, whereas the other type of function affords another property.[5] The solubility in water of phosphorus-containing dendrimers is generally due to the presence of charges, either positive[6] or negative.[7]

One of the most interesting applications of dendrimers is in the field of catalysis, because they can generally be recovered and reused, thanks to their large size. Dendritic catalysts are generally obtained by grafting organometallic functional groups on the surface of dendrimers. Being interested in developping a catalytic activity in water, we though that it could be interesting to have simultaneously charged groups ensuring water-solubility, and organometallic groups able to afford catalytic properties in a single macromolecule.

We will present our efforts towards the synthesis of the very special dendritic architectures shown in the scheme below, in which the solubility in water will be ensured by ammonium groups, and the organometallic groups will be phosphines complexed by palladium.
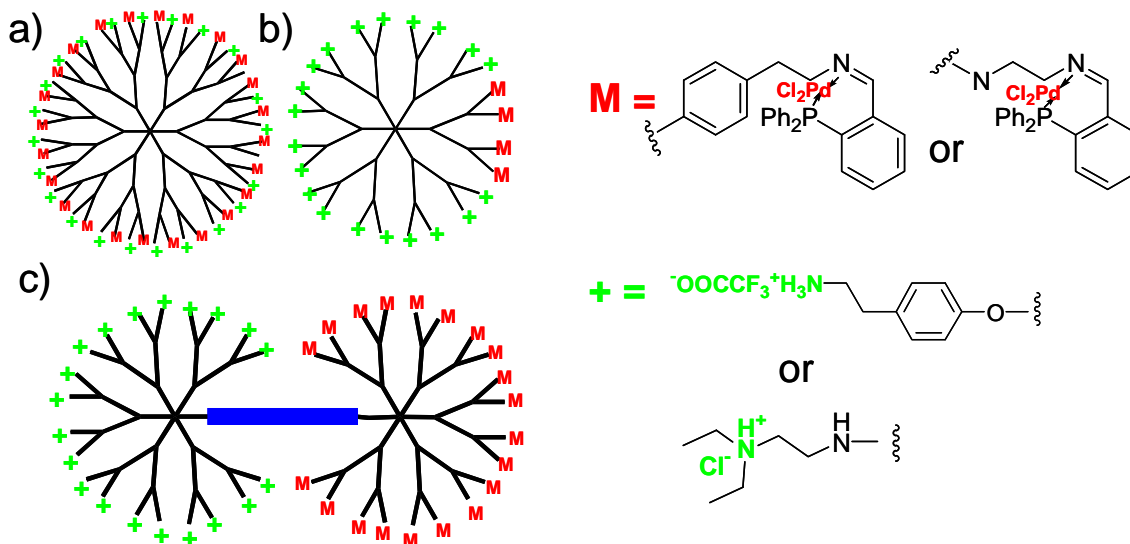
1   Launay N., Caminade A.M., Lahana R., Majoral J.P. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1589
2   Lartigue M.L., Slany M., Caminade A.M., Majoral J.P. *Chem. Eur. J.* **1996**, *2*, 1417
3   Maraval V., Laurent R., Donnadieu B., Mauzac M., Caminade A.M., Majoral J.P. *J. Am. Chem. Soc.* **2000**, *122*, 2499
4   Galliot C., Larré C., Caminade A.M., Majoral J.P. *Science* **1997**, *277*, 1981
5   Maraval V., Maraval A., Spataro G., Caminade A.M., Majoral J.P., Kim D.H., Knoll W. *New J. Chem.* **2006**, *30*, 1731
6   Leclaire J., Coppel Y., Caminade A.M., Majoral J.P. *J. Am. Chem. Soc.* **2004**, *126*, 2304
7   Griffe L., Poupot M., Marchand P., Maraval A., Turrin C.O., Rolland O., Métivier P., Bacquet G., Fournié J.J., Caminade A.M., Poupot R., Majoral J.P. *Angew. Chem. Int. Ed.* **2007**, *46*, 2523

Synthesis of new water soluble gold (I) alkynyl complexes

Elena Vergara[a] , Elena Cerrada[a], Fabian Mohr[b,d] and Mariano Laguna[a]
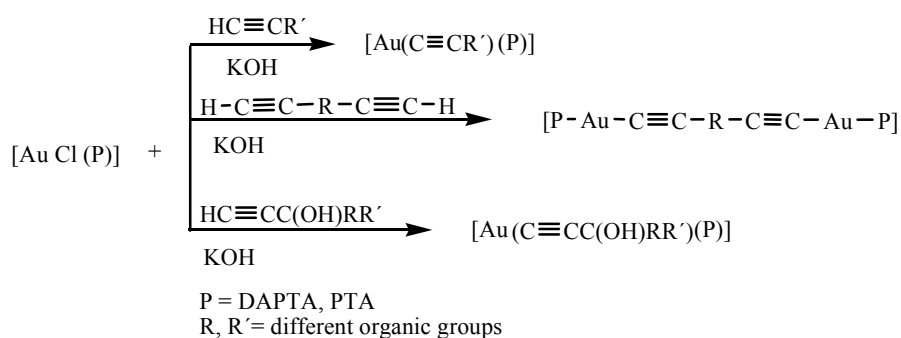
[a]Department of Inorganic Chemistry, Institute of Materials Science of Aragon, University of Zaragoza-CSIC, 50009 Zaragoza, Spain. Fax: 34 976 76 11 87; Tel: 34 976 76 11 81; E-mail: *evergara@unizar.es*

[b]*Department of Chemistry, Faculty of Sciences, University of Burgos, Burgos, Spain*

[d]*Bergische Universität Wuppertal, Fachbereich C Anorganische Chemie, 42119 Wuppertal, Germany*

The environmental problems related with the use of organic solvents have made scientists, specially chemists explore new water - based and water soluble catalytic reactions. Industries are interested in the design of new processes for greener alternatives avoiding the use of organic solvents, so these are the reasons why water "role" is acquiring new strength in Inorganic and Organometallic world[1].

A method for the synthesis of water soluble inorganic and organometallic compounds is the use of water soluble phosphines ligands as 1,3,5-triaza-7-phosphaadamantane (PTA)[3,4,5] or 3,7-diacetyl-1,3,7, triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA)[2,5]. Gold Alkynyl complexes containing these water soluble phospines were prepared by reaction of the phosphine gold(I) chlorides with different alkynes and propargyl alcohol derivates in the presence of a base. However, the solubility of these complexes varies considerably. Amongst the alkynylgold(I) complexes only the propargyl alcohols complexes are soluble in water. However, some compounds are completely insoluble in common organic solvents, some are poorly soluble in dmso or dmf, whilst others are soluble in halogenated solvents and acetone.

$$[AuCl(P)] \quad + \quad \begin{cases} HC\equiv CR' \xrightarrow{\quad} [Au(C\equiv CR')(P)] \\ KOH \\ H-C\equiv C-R-C\equiv C-H \xrightarrow{\quad} [P-Au-C\equiv C-R-C\equiv C-Au-P] \\ KOH \\ HC\equiv CC(OH)RR' \xrightarrow{\quad} [Au(C\equiv CC(OH)RR')(P)] \\ KOH \end{cases}$$

P = DAPTA, PTA
R, R´= different organic groups

All of these complexes were fully characterised by spectroscopic techniques including NMR and IR spectroscopy, mass spectrometry, and in the case of [Au{C≡CC(Et)(Me)OH}(PTA)], by X-Ray crystallography **(Figure1).**
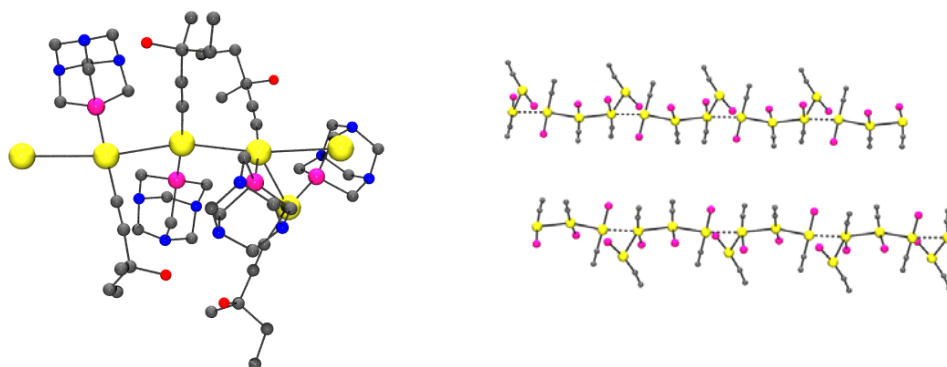
Figure 1

[1] See for example (a) B.Cornils and W.A. Herrmann, in *Aqueous-phase organometallic catalysis concepts and applications, Wiley-VCH, Weinheim,* **1998.** (b) F. Joó, in *Aqueous organometallic catalysis*, Kluwer Academic Publishers, Dordrecht, **2001**.

[2] D. J. Darensbourg, C. G. Ortiz, and J. W. Kamplain, *Organometallics,* **2004** 23, 1747.

[3]*D. J. Daigle, A. B. Peppermann Jr., and S. L. Vail,* J. Heterocyclic Chem.,***1974, 11, 407.***

[4] F. Mohr, E. Cerrada, M. Laguna, *Organometallics* **2006** 25, 645, **2007** 26, 952-957.

[5] E. Vergara, S. Miranda, F. Mohr, E. Cerrada, E. Tiekink, M. P. Romero, A. Mendía, M. Laguna. *Eur. J. Inorg. Chem.* **2007,** 18, 2926-2933.

Microemulsions for hydroformylation of 1-octene

Kristin Voiges, Jörg Kupka and Adrian Schumpe

Braunschweig University of Technology, Institute of Technical Chemistry, Hans-Sommer-Str. 10, 38106 Braunschweig, Germany.
Fax: +49 531 3915357; Tel: +49 531 3915356; E-mail: k.voiges@tu-bs.de

The hydroformylation of propene to butanal via the Rhône-Poulenc-Ruhrchemie-process employs a liquid/liquid-system with a rhodium-catalyst-complex dissolved in the aqueous phase. This combines the advantages of homogeneous and heterogeneous catalysis like mild conditions, high selectivity and activity as well as easy separation and recycling of the catalyst[1]. However, the technique fails for higher olefins ($> C_5$) since increasing chain length leads to lower solubility in the aqueous phase. Then the reaction occurs only in the film at the interface, mass transfer becomes rate-determining and the space-time-yield decreases to an uneconomic level[2].

A possible workaround is the use of surfactants forming a micro-emulsion with much larger interfacial area. Such micro-emulsions have a manifold micro-structure and temperature-dependent phase behaviour[3] (**Figure 1**). The principal sketch shows the phase number in dependence of the temperature T and the surfactant mass fraction γ in the micro-emulsion. The reaction rate reaches an optimum near to the phase-inversion-temperature (PIT) where the interfacial tension shows a minimum and the system consists of three or one phases. With decreasing temperature the surfactant water solubility in the aqueous phase raises, so that the three or one phased micro-emulsion turns into a biphasic system. It consists of an oil-in-water-micro-emulsion and an organic excess-phase. Therefore cooling after reaction enables the separation of the product and the catalyst-phase.
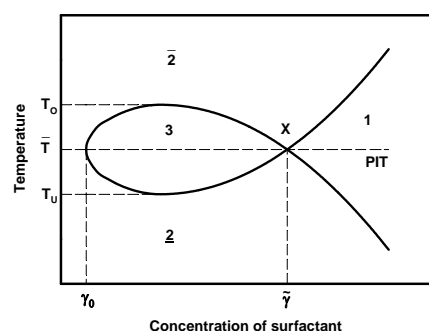
Figure 1: Schematic phase
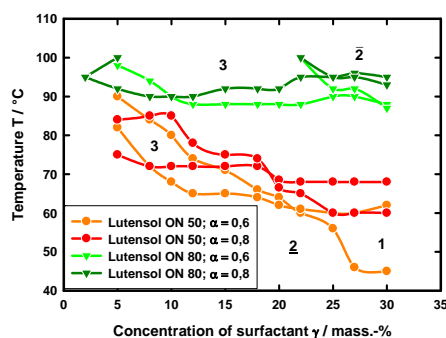
Figure 2: Messured phase

In our experiments, commercially available non-ionic surfactants of technical purity were used. No co-surfactant was necessary for the formation of micro-emulsions. As test-system we applied 1-octene and rhodium-catalyst with the industrially well established tri-phenylphosphine trisulfonate ligand (Rh/TPPTS). Herewith the influences of the oil mass fraction α (referred to the surfactant-free oil/water mixture), the kind of surfactant, the kind of oil and the influence of the reaction progress on the temperature-dependence of the phase behaviour were determined. Generally, an increasing oil-to-water-ratio α causes an increasing PIT. The nodal point X between the one- and three-phased state (inversion point) shows up at a maximum γ value when α is about 0.5. Increasing hydrophilicity of the surfactant leads also to a higher PIT and involves a shift of the inversion point X to higher γ (**Figure 2**). Considering these results, the hydroformylation was carried out near the PIT, usually, at 90 °C with Lutensol ON 70[4].

Darkening of the aqueous phase from light yellow to dark brown indicates the formation of Rhodium clusters; this can be counteracted by using higher TPPTS concentration. Also the loss of the noble metal to the organic phase is reduced when a higher TPPTS-concentration is applied but the turn-over frequency is decreased. Based on the temperature dependent phase behaviour, it was tried to recycle the catalyst, the ligand and the tenside. Phase separation in a temperature-controlled separator funnel was carried out at 60°C; only in the last step the liquid was cooled down to 20°C. Interfacial tension measurements showed that all of the surfactant was located in the aqueous phase and a viscous layer covering it while no surfactant was detectable in the organic liquid, above. Therefore the surfactant-rich layer was recycled together with the aqueous phase und used again up to five times for hydroformylation of 1-octene. Due to the small reactor volume used, the results suffer from liquid losses but still demonstrate the principal feasibility.

1   B. Cornils, E. Wiebus, *Chemie Ingenieur Technik*, **1994**, *66*, 916.
2   B. Fell, *Tenside Surfactants Detergents*, **1998**, *35*, 326.
3   R. Schomäcker, Nachrichten aus Chemie, Technik und Laboratorium, **1992**, 40, 1344.
4   J. Kupka, *Hydroformylierung von 1-Octen in Mikroemulsion*, **2006**, Thesis, TU Braunschweig.

Hydrogenation of Carbon Dioxide to Formic Acid Catalyzed by Water-Soluble Rh and Ru Phosphine Complexes

Guoying Zhao[a,b], Ferenc Joó[a,c]

[a] *Address, Institute of Physical Chemistry, University of Debrecen, H-4010 Debrecen, Hungary. Fax: +36-(52) 512-915; Tel:+36-(52) 512-900/22382*

[b] *Address, Department of Physical, Inorganic and Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91, Stockholm, Sweden. Fax: +46-(0)8-152187; Tel: +46-(0)8161260;E-mail: guayingz@ inorg.su.se*

[c] *Address, Research Group of Homogeneous Catalysis, Hungarian Academy of Sciences, H-4010, Debrecen, P.O. Box 7, Hungary; Fax:(52) 512-915; Tel:(52) 512-900/22382;Ee-mail: fjoo@delfin.unideb.hu*

Hydrogenation of carbon dioxide to formic acid is an attractive approach to utilize CO2 as an economical and ecological C1 building block for obtaining commercially important products(1). The reported processes to produce pure formic acid from carbon dioxide and hydrogen are complex, and time- and energy–consuming. They mainly include the generation of formate salts, the recovery and separation of solvent, catalyst and the unspent reactant, an exchange reaction to generate a thermally decomposable formate salt of an appropriate nitrogen base, finally the decomposition of this salt to formic acid(2). Extensive studies have been dedicated to the hydrogenation of CO2 in alcohols, supercritical CO2 and aqueous solutions with amines or carbonates as additives, which produced formate salt or formamides(3). But rarely was work devoted to hydrogenation of carbon dioxide directly to formic acid or to a decomposable formate salt, which would finally simplify and optimize the whole process to produce formic acid(4).

Here we describe two possible routes to simplify the process to generate formic acid or a decomposable formate salt directly from hydrogen and carbon dioxide, and report the corresponding results. One way is the hydrogenation of carbon dioxide in a task-specific ionic liquid (TSIL) to generate formate salt of TSIL, which can be further decomposed to formic acid and TSIL (see Scheme below)(5). The second is the hydrogenation of carbon dioxide in biphase systems consisting of supercritical carbon dioxide and water with sodium formate as additive, in which formic acid can be collected from the aqueous solution by distillation and the catalyst and sodium formate can be recovered and reused.
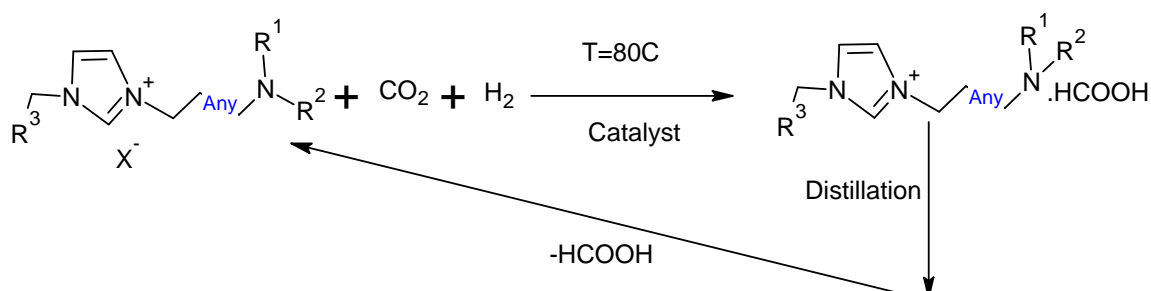
1   A. Xu, S. Indala, T. A. Hertwig, R. W. Pike, F. C.Knopf, C. L. Yaws, J. R. Hopper, *Clean Techn. Environ. Policy* , **2005**, 7, 97
2   J.J.A. Sproatley, D.J.D. Strawberry Hill, J.E.H. Hull, A.C.K. Beverley, *United States Patent*, 4855496, **1989**
3   P.G. Jessop, F. Joó, C. Tai, *Coordination Chemistry Reviews*, **2004**, 248, 2425; F. Joo, G.Laurenczy, L.Nadasdi, J. Elek, *Chemical Communications*, **1999**,11,971; Y. Himeda, N. Onozawa-Komatsuzaki, H.Sugihara, K.Kasuga, *J.Am.Chem.Soc.*,**2005**, 127,13118
4   H.Hayashi, S.Ogo, S. Fukuzumi, *Chemical Communications*, **2004**, 23,2714
5   G. Zhao, F. Joó, Abstr. *3rd Annual Aquachem Meeting*, Jan 12-14, **2007**, Debrecen, Hungary.

Application of Dynamic Combinatorial Chemistry in Catalysis

Tomasz Zieliński, Fabien Cougnon, Enda Bergin, Sijbren Otto

[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK; E-mail:
so230@cam.ac.uk

Rational development of an efficient homogenous catalyst is still a serious challenge due to our limited knowledge and understanding of processes that take place during chemical reactions. Therefore, the application of Dynamic Combinatorial Chemistry (DCC)[1] is an attractive, alternative approach to the discovery of new catalysts. In principle, if a Dynamic Combinatorial Library (DCL) is exposed to a template that resembles the transition state of a reaction, the most catalytically active member of the library should be amplified and selected. This idea was proven by the application of DCC to find catalysts for a Diels-Alder reaction and for acetal hydrolysis.[2]
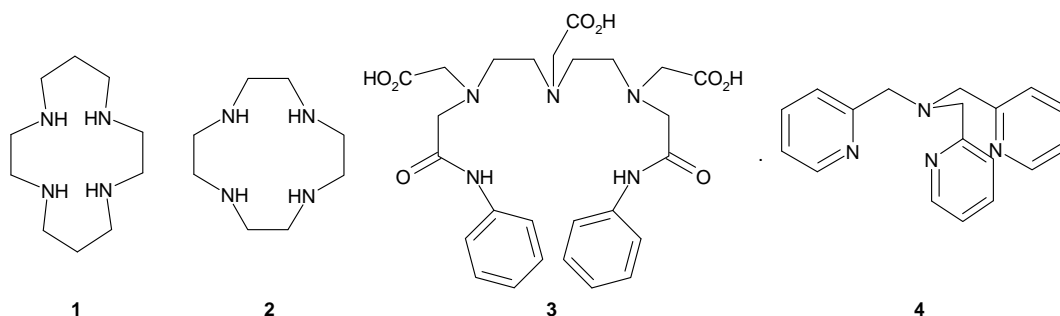
In those studies, only moderate catalytic activity was observed, so we decided to introduce building blocks capable of binding metals ions, in the expectation that this will produce more active catalysts. In this communication we present our studies of DCLs containing common ligands (**1-4**) for metal ions.

1   Corbett, P. T.; Leclaire, J.; Vial, L.; West K. R.; Wietor, J.; Sanders, J. K. M.; Otto, S. *Chem. Rev.* **2006**, *106*, 3652; Lehn, J. M., *Chem. Soc. Rev.*, **2007**, *36*, 151.
2   Brisig, B.; Sanders, J. K. M.; Otto, S., *Angew. Chem. Int. Ed.* **2003**, *42*, 1270; Vial, L.; Sanders, J. K. M.; Otto, S., *New J. Chem.* **2005**, *29*, 1001.

Rhenium Complexes as Catalysts for the Baeyer-Villiger Oxidation

Gonçalo Lopes,[a] **Elisabete C.B. Alegria,**[ab] **Luísa M.D.R.S. Martins**[ab] **and** <u>**Armando J.L. Pombeiro**</u>[b]

[a] *Departamento de Engenharia Química, ISEL, R. Conselheiro Emídio Navarro, 1950-062 Lisboa, Portugal*
[b] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. pombeiro@ist.utl.pt*

In spite of the expanded coordination chemistry for rhenium [1,2], the use of rhenium complexes as catalysts is still an underdeveloped field of research. However, the wide application of $[(Me)ReO_3]$ (MTO) in oxidation catalysis [3] clearly demonstrates the ability of this metal to form highly active catalysts for oxidation reactions of olefins and other unsaturated substrates. Hence, a contribution towards widening the use of Re complexes in catalysis is an objective of this work.

Recently we have found that some rhenium complexes with "scorpionate" nitrogen donor ligands, in particular the N_3 tripodal neutral hydrotris(1-pyrazolyl)methane $(HC(pz)_3$, Tpm) and the water soluble C-substituted sulfonate derivative tris(pyrazolyl)methanesulfonate $(SO_3C(pz)_3^-$ Tpms), can catalyse, in homogeneous systems, alkane functionalization reactions under mild or moderate conditions [4] .

In pursuit of our interest on the catalytic activity of rhenium compounds we now report that the complexes $[ReCl_2\{N_2C(O)Ph\}(Hpz)(PPh_3)_2]$ **1** (Hpz = pyrazole) [5], $[ReCl_3(HCpz_3)]$ **2** or $[ReO_3(SO_3Cpz_3)]$ **3** [6],
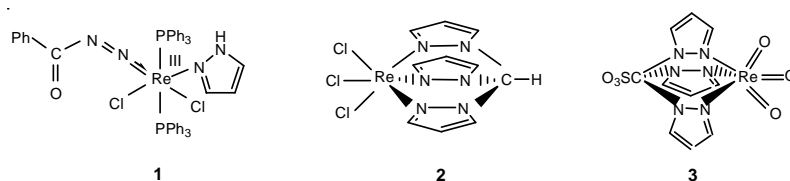
as well as their precursors, $[ReCl_2\{\eta^2\text{-}N,O\text{-}N_2C(O)Ph\}(PPh_3)_2]$ and $[ReOCl_3(PPh_3)_2]$, can act as catalysts (or catalyst precursors) for the Baeyer-Villiger oxidation of cyclic and acyclic ketones to the corresponding lactones or esters, by an aqueous diluted solution of H_2O_2, a green oxidant, under mild conditions:
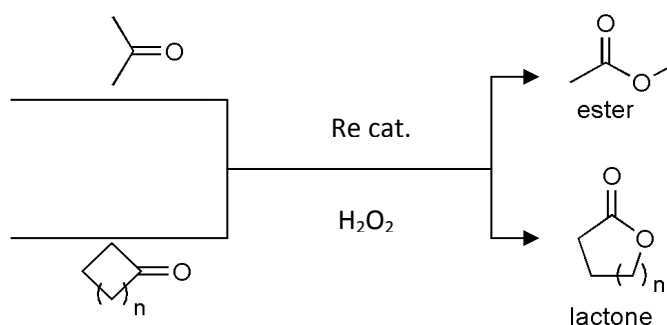

The effects of a variety of factors, such as the type of catalyst, solvent, reaction time or temperature, were studied towards the optimization of the processes.

Acknowledgments

1   A.J.L. Pombeiro, M.F.C.G. da Silva, R.H. Crabtree, in: R.B. King (Ed.), Encyclopedia Inorganic Chemistry, Vol. IX, Wiley, 2005, pp. 5499–5515.
2   C. Pettinari, C. Santini, in: J.A. McCleverty, T.J. Meyer (Eds.), Compreh. Coordination Chemistry II, Vol. I, Elsevier, Oxford, 2004, pp. 159–210.
3   C.C. Romão, F.E. Kühn, W.A. Herrmann, Chem. Rev. 97 (1997) 213.
4   E.C.B.A. Alegria, M.V. Kirillova, L.M.D.R.S. Martins, A. J. L. Pombeiro, *J. Appl. Catal. A: Gen.*, 317, **2007**, 43.
5   E.C.B.A. Alegria, L.M.D.R.S. Martins, M.F.C.G. da Silva and A.J.L. Pombeiro, *J. Organomet. Chem.*, **2005**
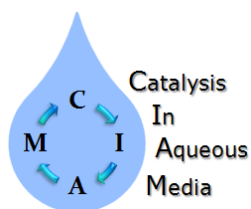
CATALYTIC HYDROGENATIONS IN WATER PHASE USING RUTHENIUM(II) COMPLEXES BEARING SULFONATED PHOSPHINES AND DIAMINES

**Inocenta Mery Mallqui Ayala[a,b], Luca Gonsalvi[a], Maurizio Peruzzini[a], Antonio Romerosa[b]
and Manuel Serrano Ruiz[b]**

[a] *ICCOM CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino (Italy)*
[b] *Area de Quimica Inorganica, Universidad de Almería, 04071, Almería (Spain)*

The replacement of present catalytic technology with "greener" protocols using water as solvent is still a matter of research interest for both academia and industry. In this field, the cage-like water soluble monodentate phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) has received renewed interest in the recent literature due to its properties to solubilize transition metal complexes in aqueous phase[1].

In the past few year we have investigated many aspect of this class of ligands, from the donor capacities of the potentially multidentate triaza phosphaadamantane moiety[2-8], mainly bearing cyclopentadienyl coligands. We are now revisiting the chemistry of other water soluble phosphines such as dppEts, 1,2-(bis[di-*m*-sodiumsulfato]-phenylphosphino)ethane with Ru(II) precursors in view of their application as hydrogenation catalysts in neat water.

We report here the latest results on the synthesis of complexes of general formula $[Ru(dppEts)(NN)Cl_2]$ (NN = (chiral) diamine) and catalytic data for saturated ketones and the selective hydrogenations of unsaturated ketones in water, both via transfer hydrogenation and under hydrogen atmosphere.

[1] A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.* **2004**, 248, 955.

[2] Chaker Lidrissi, Antonio Romerosa, Mustapha Saoud, Manuel Serrano-Ruiz, Luca Gonsalvi y Maurizio Peruzzini., *Angew. Chem. Int.* Ed. **2005**, 44, 2568-2572.

[3] S. Bolaño, A. Albinati, J. Bravo, L. Gonsalvi, and M. Perizzini, *Inorg. Chem. Comm.* **2006**, 9, 360

[4] D. N Akbayeva., L. Gonsalvi, W.Oberhauser, M. Peruzzini, F.Vizza, P.Bruggeller, A.Romerosa, G.Savad, A.Bergamo, *Chem. Comm.* **2003**, 264-265.

[5] S. Bolaño, L. Gonsalvi, F. Zanobini, F. Vizza, V. Bertolasi, A. Romerosa, M. Peruzzini. *Journal of Molecular Catalysis* **2004,** 224, 61-70.

[6] Romerosa A., Campos-Malpartida T., Lidrissi Ch., Saoud M., Serrano Ruiz M., Peruzzini M., Garrrido-Cárdenas J. A., Garcia-Maroto F., *Inorganic Chemistry*, **2006**, 45, 1289.

[7] S. Bolaño, L. Gonsalvi, P. Barbaro, A. Albinati, S. Rizzato, E. Gutsul, N. Belkova, L. Epstein, E. Shubina, M. Peruzzini, *J. Organomet. Chem. 2006*, 691, 629.

[8] A. Dorcier, W. H. Ang, S. Bolaño, L. Gonsalvi, L. Juillerat-Jeannerat, G Laurenczy, M. Peruzzini, A. D. Phillips, F. Zanobini, P. J. Dyson, Oragnometallics 2006, 25,4090.