

## 4<sup>TH</sup> YEAR AND FINAL REPORT

**Full Title:** *Transition Metal Chemistry and Catalysis in Aqueous Media*

**Acronym:** AQUACHEM (<http://www.iccom.cnr.it/aquachem>)

**Contract No.:** MRTN-CT-2003-503864

**Commencement Date:** December 23, 2003

**Duration of the Contract:** 48 months

**Period Covered by the Report:** Months 37-48

**Network Coordinator:**

**Dr. Maurizio Peruzzini**

Office: ICCOM CNR

Istituto di Chimica dei Composti Organo Metallici

Consiglio Nazionale delle Ricerche

Via Madonna del Piano 10

50019 Sesto Fiorentino (Florence), Italy

phone (Q) +39 055 5225 289

mobile +39 328 8163836

fax +39 055 5225 203

e-mail: [mperuzzini@iccom.cnr.it](mailto:mperuzzini@iccom.cnr.it)

web page: <http://www.iccom.cnr.it/peruzzini/>

**Network Manager:**

**Dr. Luca Gonsalvi**

Office: ICCOM CNR

Istituto di Chimica dei Composti Organo Metallici

Consiglio Nazionale delle Ricerche

Via Madonna del Piano 10

50019 Sesto Fiorentino (Florence), Italy

phone +39 055 5225 251

fax +39 055 5225 203

e-mail: [l.gonsalvi@iccom.cnr.it](mailto:l.gonsalvi@iccom.cnr.it)

web page: <http://www.iccom.cnr.it/gonsalvi/>

## Part A - Research Results

### A.1 Scientific Highlights 2007

#### Task 1 - Hydrosoluble ligands and their complexes

(YoK, CNR, UD, UAL, CNRS-LCC/a-b, UAB, IST, HUJI; Task Coordinator YoK)

**T1a)** Water soluble ruthenium complexes stabilised by PTA and TPPMS ligand (PTA = 1,3,5-triaza-7-phosphaadamantane, TPPMS = monosulfonated triphenylphosphine) (CNR, UAL). The collaborative work on this topic has been part of the shared PhD project of Mrs I. Mallqui, who spent 10 months at CNR in 2007. The main results dealing with the Ru coordination chemistry of the cyclopentadienyl ligand {Cp-1,3-(CONC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>} have been presented to international workshops and conferences [B10]. The new water soluble ruthenium(II) complexes Na<sub>2</sub>[RuCpX(mTPPMS)<sub>2</sub>] [X = Cl (1), I (2)] and Na<sub>x</sub>[RuCp(mTPPMS)(PR<sup>1</sup><sub>3</sub>)(PR<sup>2</sup><sub>3</sub>)](OTf)<sub>y</sub> [PR<sup>1</sup><sub>3</sub> = PR<sup>2</sup><sub>3</sub> = PPh<sub>3</sub> (3), PTA (4), x = y = 0. PR<sup>1</sup><sub>3</sub> = mTPPMS, PR<sup>2</sup><sub>3</sub> = PTA (5), x = 1, y = 0. PR<sup>1</sup><sub>3</sub> = mTPPMS, PR<sup>2</sup><sub>3</sub> = mPTA (6), x = y = 0. PR<sup>1</sup><sub>3</sub> = PR<sup>2</sup><sub>3</sub> = mTPPMS (7), x = 2, y = 0. PR<sup>1</sup><sub>3</sub> = PPh<sub>3</sub>, PR<sup>2</sup><sub>3</sub> = PTA (8), x = y = 0. PR<sup>1</sup><sub>3</sub> = mPTA, PR<sup>2</sup><sub>3</sub> = PPh<sub>3</sub> (9), x = 0, y = 1] (mTPPMS = Ph<sub>2</sub>P(3-OS(O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sup>-</sup>; PTA = 1,3,5-triaza-7-phosphaadamantane; mPTA = N-methyl-1,3,5-triaza-7-phosphaadamantane) have been synthesized and characterised by elemental analysis, NMR and IR spectroscopy and crystallographic methods. Noticeably, the X ray crystal structure determination of [RuCp(mTPPMS)(PPh<sub>3</sub>)(PTA)]·2H<sub>2</sub>O (8·2 H<sub>2</sub>O), the first half-sandwich ruthenium complex bearing three different phosphines, has been determined [A6].

**T1b)** Synthesis of water soluble vinylidenes and allenylidenes stabilised by hydrosoluble phosphines. (CNR, UAL) Water soluble vinylidene and allenylidene complexes such as [Ru{Cp-1,3-(CONC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>} (=C=C=CPh<sub>2</sub>)(L)(L')] (L = PPh<sub>3</sub>; L' = PTA, PTAMe<sup>+</sup>) were prepared by I. Mallqui and the x-ray crystal structures determined. The complexes showed an interesting reactivity towards nucleophiles and electrophiles. A joint manuscript is in preparation and the work has been presented to conferences as poster communication and oral contribution to workshops. [B36]

**T1c)** Synthesis of water-soluble N-heterocyclic carbene complexes of Ru (UD). Ru(II) complexes containing the 1-butyl-3-methyl-imidazol-2-ylidene ligand were synthesized and characterized at UD. New water-soluble N-heterocyclic carbene complexes were synthesized and characterized in the second year starting with [Rh<sub>2</sub>(OH)<sub>2</sub>] and [Ir<sub>2</sub>(OMe)<sub>2</sub>] precursors. Preliminary data on this subject have been disclosed at conferences [D38], [D40]. A (partially) COST-sponsored visit of M. Fekete from UD to UAL in 2006 resulted in the synthesis of several new vinylidene- and allenylidene-Ru(II) complexes containing also an N-heterocyclic carbene ligand. These were also used in Year 4 as catalysts for hydrogen transfer (see T6e). The results were communicated at conferences [D80], [D84], [D87], [D89], [D95]. New water-soluble 1,3-disubstituted imidazolium-derivatives containing sulfoalkyl- or sulfoaryl groups were synthesized in 2007 which served as ligand precursors in the synthesis of Ag(I)- and Au(I)-complexes. Four of these complexes were also characterized by single crystal X-ray diffraction. The Au(I)-compounds were studied as catalysts of alkyne hydration (see T6v). The results were presented at conferences [D84], [D86], [D87], [D92].

**T1d)** Synthesis of water soluble phosphines containing amino acid residues. (CNR-UAL then UAL-UAB-CNR) The initial collaborative work was carried on by a ESR fellow at UAL. The previous results on the synthesis of a new class of enantiomerically enriched multifunctional phosphines derived from ring opening of amino epoxides obtained from naturally occurring amino acids with Li-diphenylphosphido borane have been published as joint paper [A18]. DFT calculations were carried out on these systems as a novel collaborative project UAL-UAB-CNR and presented to a workshop [B38]

**T1e)** Synthesis of free dendritic ligands (CNRSLCC/a). After the synthesis of a series of dendrimers bearing PTA derivatives as end groups last year, the synthesis of several series of new symmetrical dendritic ligands (same end groups in all parts of the surface) has been carried out, generally up to the third generation. The first series possesses scorpionate ligands grafted to their surface (with IST). The second series possesses PNP ligands of type R<sub>2</sub>P-CH<sub>2</sub>-N-CH<sub>2</sub>-PR<sub>2</sub>, in which the N atom is connected to the dendrimer (with UAL, CNR); a third series has N,N ligands of type bipyridine grafted to the surface. In addition, the density of ligand end groups has been increased by increasing the density of branches in a totally new family of dendrimers ("super dense" dendrimers) (with CNR) [A11]. PTA ligands have been grafted to these new dendrimers through the alkylation of one N of PTA. Besides these symmetrical series of dendritic ligands, the synthesis of dendrimers bearing two types of functions (water-solubilizing entities and ligands) either linked to each branching point of the surface, or linked to two different areas of the surface and in variable proportion has been attempted. Such methodology was successfully applied to dendrons (1 protonable amine at the core, and 2 to 8 ligand end groups) [C34].

**T1f) Synthesis of dendritic complexes (CNRS/LCC/a with CNR, UAL, IST).** Several organometallic complexes derived from some of the dendritic ligands elaborated in **T1e)** have been synthesized, and isolated. Ru complexes of dendritic PTA derivatives (up to generation 3) were first obtained; then complexes of dendrons derived from  $[\text{RuCl}_2(\text{p-cymene})]_2$  and  $[\text{RhClcod}]_2$  (first and second generations) have been isolated [C34], as well as some examples of  $\text{PdCl}_2$  complexes of unsymmetrical dendrimers. Dendrimers ended by PTA were used to complex iridium, dendrimers ended by pyridine were used to complex rhodium, and dendrimers ended by pincer dipyridine ligands were used to complex palladium. In addition to these isolated complexes, a lot of other complexes were synthesized *in situ* for catalytic purposes (see tasks 6)

**T1g) Synthesis of water-soluble luminescence sensors for polyoxoanions (YoK).** The YoK group has conducted studies of the rhenium carbonyl complex linked to catecholate that serves as a sensor for oxometallate ions. Starting with  $[\text{Re}(\text{CO})_3(\text{bipyridyl})\text{L1}]\text{PF}_6$ , **S1PF<sub>6</sub>**, where L1 = 2,3-dihydroxy-*N*-pyridin-4-yl-benzamide, several derivatives were prepared in order to improve the solubility of the luminescent Re-compound in aqueous solution. Different counter ions have been introduced in order to make the sensor more hydrophilic (e.g.  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  or  $\text{CF}_3\text{SO}_3^-$ ) than the hexafluorophosphate salt. All compounds are characterised by standard spectroscopic methods like NMR, IR, UV/Vis, and ESI-MS. Crystals suitable for single crystal X-ray diffraction were grown of the benzyl protected compound  $[\text{Re}(\text{CO})_3(\text{bispyridyl})\text{L1}]\text{ClO}_4$  (**S1ClO<sub>4</sub>**). While for the starting sensor, **S1PF<sub>6</sub>**, the maximum amount of water tolerated in an acetonitrile solution is 20%, the exchange of the counter ion to  $\text{ClO}_4^-$  improves the solubility so we can employ a 2:1 water/acetonitrile mixture. The YoK team has succeeded in crystallising the product of the reaction of the sensor with molybdate as a  $[\text{MoO}_2(\text{sensor})_2]$  complex and have determined its crystal structure. This serves as an excellent demonstration of the coordination mode. Studies by mass spectrometry demonstrate that the same  $\text{Re}_2\text{Mo}$  species is present in solution. The photochemistry of the sensor has been studied by time-resolved IR spectroscopy in water/DMF mixtures on two visits to the Rutherford-Appleton Laboratory in which excellent data were collected (compare **T5f**). Two excited electronic states are observed (MLCT and ILCT) and electron transfer between them occurs at a rate that is dependent on pH. Time-resolved UV/vis data have also been collected. The spectroscopy of the free ligand has been studied for comparison.

**T1h) Synthesis of bis-hydroxyaminotriazines (BHTs) siderophores (HUJI):** A new, highly versatile group of tridentate iron(III) chelating agents exhibiting higher affinity to iron(III) than other tridentate iron(III) chelators and superior iron(III) over iron(II) selectivity compared to desferrioxamine-B (DFO), EDTA and other tridentate ligands was synthesised in collaboration with Dr. A. Melman from our department.. The ligands and their iron complexes were characterized by X-ray crystallography, acid-base titrimetry, spectrophotometry, electrochemical measurements, and electrospray mass spectrometry. Electrochemical measurements, and electrospray mass spectrometry. Electrochemical and electrocatalytic techniques for iron ion identification were devised based on these siderophores and commercially available ones.

**T1i) Syntheses of platinum(II) and copper(I) complexes with PTA and other water soluble phosphines. (IST)** The Pt reactions were performed by an ESR, Mr P. Sgarbossa. The syntheses of various Pt(II) complexes with water soluble phosphines have been carried out by reactions of  $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$  with PTA, MPTA, DAPTA or 1,2-bis(di-4-sulfonatophenylphosphino)benzene (dtsppb) yielding products such as  $[\text{PtCl}(\text{C}_6\text{F}_5)(\text{PTA})_2]$ ,  $[\text{PtCl}(\text{C}_6\text{F}_5)(\text{MPTA})_2]$ ,  $[\text{PtCl}(\text{C}_6\text{F}_5)(\text{DAPTA})_2]$  and  $[\text{PtCl}(\text{C}_6\text{F}_5)(\text{dtsppb})]$ . The electrochemical behaviour of some Pt(II) complexes of the type  $[\text{Pt}(\mu\text{-OH})(\text{nFdpppe})]_2(\text{BF}_4)_2$ , where nFdpppe is 1,2-bis(diphenylphosphino)ethane (dpppe), 1,2-bis(bis-2,4-difluorophenylphosphino)ethane (2Fdpppe), 1,2-bis(bis-2,3,4,5-tetrafluorophenylphosphino)ethane (4Fdpppe) and 1,2-bis(dipentafluorophenylphosphino)ethane (dfppe), respectively (prepared by Prof. R. Michelin's group) was also investigated. [D72] The complexes undergo reduction processes.  $[\text{Cu}(\text{Hpta})_4](\text{NO}_3)_5$  {Hpta = *N*-protonated form of 1,3,5-triaza-7-phosphaadamantane (pta)} has been easily prepared by reacting  $\text{Cu}(\text{NO}_3)_2$  and pta in aqueous acidic solution at room temperature [C53]. The unprotonated pta derivative  $[\text{Cu}(\text{pta})_4](\text{NO}_3)$  was obtained by further treatment with sodium hydroxide in water. Both compounds are water-soluble and stable in air, and represent the first examples of Cu complexes bearing pta or any derived ligand with a cage-like pta core, and expand the restricted family of aqua-soluble copper phosphine complexes.

**T1j) Syntheses of complexes with water soluble tris(pyrazolyl)methanesulfonate and related scorpionate ligands (IST, CNRS/LCC/b).** A series of complexes with the water soluble tris(1-pyrazolyl)methanesulfonate species ( $\text{SO}_3\text{Cpz}_3^-$ ) or related scorpionate ligands e.g. hydrotris(1-pyrazolyl)methane ( $\text{HCpz}_3$ ) have continued to be synthesized and characterized for various transition metals. In particular, the Re pyrazole complexes  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2]$  (Hpz = pyrazole),  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$  and  $[\text{ReClF}\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ , and the tris(pyrazolyl)methane compounds  $[\text{ReCl}_2(\text{HCpz}_3)(\text{PPh}_3)][\text{BF}_4]$

(pz = pyrazolyl), [ReCl<sub>3</sub>{HC(pz)<sub>3</sub>}], [ReOCl<sub>2</sub>{SO<sub>3</sub>C(pz)<sub>3</sub>}(PPh<sub>3</sub>)] and [ReO<sub>3</sub>{SO<sub>3</sub>C(pz)<sub>3</sub>}] were obtained and fully characterized (IST). Mo complexes with the tris(pyrazolyl)methanesulfonate ligand (Tpms) have also been obtained by Ms. Chiara Dinoi, an ESR from CNRSLCC/b, during her secondment at the IST. The series include Li[TpmsMo(CO)<sub>3</sub>] which, upon oxidation by iodine or protonation affords the iodo and hydride complexes [TpmsMo(I)(CO)<sub>3</sub>] and [TpmsMo(H)(CO)<sub>3</sub>] that can convert into [TpmsMoOCl]<sub>2</sub>O and [TpmsMoO<sub>2</sub>]<sub>2</sub>. Both these dinuclear complexes are the first reported oxomolybdenum(V) compounds bearing the tris(pyrazolyl)methanesulfonate ligand. The [TpmsMoO<sub>2</sub>]<sub>2</sub> system constitutes the first example of a structurally characterised Mo complex containing the Tpms ligand co-ordinated in the unusual N,N,O fashion.

The new scorpionate derivative tris(3-phenylpyrazolyl)methanesulphonate (Tpms<sup>Ph</sup>) was synthesized and its coordination behaviour investigated towards Cu(I) centres, with formation of [Cu(Tpms<sup>Ph</sup>)(CH<sub>3</sub>CN)] which is a precursor for mixed complexes bearing also PTA, [Me-PTA](BPh<sub>4</sub>) or urotropine (hexamethylenetetramine, HMA), such as [Cu(Tpms<sup>Ph</sup>)(PTA)], [Cu(Tpms<sup>Ph</sup>)(Me-PTA)](BPh<sub>4</sub>) and [Cu(Tpms<sup>Ph</sup>)(HMA)], respectively. The scorpionate ligand can exhibit the rare N,N,O chelating mode, involving the sulfonate moiety. This work was undertaken by the ESR Riccardo Wanke.

**T1k) Self-assembly synthesis of water soluble cobalt, nickel, copper and zinc complexes (IST).** The synthesis of 3d metal(II) complexes with N,O-polydentate ligands was continued, usually by self-assembly. Of particular interest was the preparation and full characterization of the heteronuclear water-soluble and air-stable compounds [M(H<sub>2</sub>O)<sub>5</sub>M'(dipic)<sub>2</sub>].mH<sub>2</sub>O (M/M' = Cu/Co, Cu/Ni, Cu/Zn, Zn/Co, Ni/Co, m = 2–3; H<sub>2</sub>dipic = dipicolinic acid) in aqueous solution at room temperature. They represent the first examples of heteronuclear dipicolinate compounds with 3d metals. Extensive H-bonding interactions involving all aqua ligands, dipicolinate oxygens and lattice water molecules further stabilize the dimetallic units by linking them to form three-dimensional polymeric networks.

The new aminopolyalcohol mono- and multicentered Cu(II) complexes [Cu{H<sub>3</sub>en}(NCS)], [Cu{Bu-Hdea}<sub>2</sub>].C<sub>6</sub>H<sub>3</sub>(3,5-NO<sub>2</sub>)<sub>2</sub>(COOH), [Cu<sub>2</sub>{Bu-Hdea}<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>], [Cu<sub>2</sub>{Bu-Hdea}<sub>2</sub>(4-Me-C<sub>6</sub>H<sub>4</sub>COO)<sub>2</sub>].2H<sub>2</sub>O and [Cu<sub>2</sub>{Bu-Hdea}<sub>2</sub>{C<sub>6</sub>H<sub>4</sub>(1,4-COO)<sub>2</sub>}]<sub>n</sub>.2nH<sub>2</sub>O have also been prepared and found to catalyse the mild peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone. This work was undertaken by the ESR Katrin Grunwald.

**T1l) Synthesis of (asymmetric) Ru(II) complexes of highly water soluble sulfonated chelating diphosphines for applications in (enantioselective) hydrogenations in water (UAL, CNR).** As part of the joint PhD project of ESR at CNR and UAL, the synthesis of highly water soluble complexes of general formula [Ru(dppets)(NN)Cl<sub>2</sub>] (dppets = 1,2-bis[di-*m*-sodiumsulfato]-phenylphosphino)ethane; NN = chiral or racemic diamine) bearing C<sub>2</sub>-symmetry has been carried out at CNR, albeit with slow progress, in racemic form. In the fourth year the catalytic performance of such complexes will be tested at first in the racemic form towards the reduction of aryl alkyl ketones and then extended to the chiral version using water or biphasic conditions. The work has been presented to conferences as poster communication and oral contribution to workshops. [B35, B37] A manuscript is in preparation [A26]

**T1m) Syntheses of the first PTA complexes with dinitrogen ligand (IST).** The first dinitrogen complexes with the hydrosoluble PTA ligand, or its protonated form PTA-H, *trans*-[ReCl(N<sub>2</sub>)(PTA-H)<sub>n</sub>(PTA)<sub>4-n</sub>]<sup>1+</sup> (n = 0-4), were prepared, shown to be soluble and stable in water, interconvertible by stepwise protonation /deprotonation and to form, upon N<sub>2</sub> loss, the corresponding penta-coordinate compounds. Dinitrogen displacement by CO affords *trans*-[ReCl(CO)(PTA)<sub>4</sub>].

**T1n) Syntheses of the first PTA complexes of copper (IST).**

The CuI compound [Cu(PTAH)<sub>4</sub>](NO<sub>3</sub>)<sub>5</sub> **1** {PTAH = *N*-protonated form of 1,3,5-triaza-7-phosphaadamantane (PTA)} was easily prepared by reacting hydrated Cu(NO<sub>3</sub>)<sub>2</sub> and PTA in aqueous acidic solution at room temperature. Further treatment of **1** with sodium hydroxide in water led to an unprotonated PTA derivative [Cu(PTA)<sub>4</sub>](NO<sub>3</sub>) **(2)**. Both compounds are water-soluble and air-stable, and were fully characterized by spectroscopic methods and single-crystal X-ray diffraction structural analyses. They represent the first examples of Cu complexes bearing PTA or any derived ligand with a cagelike PTA core and expand the restricted family of aqua-soluble copper phosphane complexes. Other Cu-PTA complexes also bearing a scorpionate ligand have been prepared by the ESR Riccardo Wanke (see above).

**T1o) Syntheses of salicylamide N<sub>x</sub>O<sub>y</sub>-type compounds and their chelates (IST).** We have designed, synthesised and characterised a series of novel salicylamide-type pro-ligands which provide (in their fully deprotonated forms) multiple negative charges and various coordination environments to transition metal ions. Thus, the newly designed pro-ligands <sup>R</sup>L<sup>1</sup>H<sub>3</sub> (R = H = <sup>R</sup>L<sup>1</sup>H<sub>3</sub>; 2-hydroxy-N-(2-hydroxyethyl)benzamide; R = <sup>t</sup>Bu, <sup>t</sup>BuL<sup>1</sup>H<sub>3</sub> = 3,5-di-tert-butyl-2-hydroxy-N-(2-hydroxyethyl)benzamide); L<sup>2</sup>H<sub>3</sub> (2-hydroxy-N-(2-(4-(2-hydroxybenzoyl)

piperazin-1-yl)ethyl)benzamide);  $L^3H_4$  (N,N'-(ethane-1,2-diyl)bis(2-hydroxybenzamide)) and  $L^4H_4$  (N-(2-(bis(2-hydroxyethyl)amino)ethyl)-2-hydroxybenzamide)) provide planar  $NO_2^{3-}$ ,  $N_3O_2^{3-}$ ,  $N_2O_2^{4-}$ , and  $N_2O_3^{4-}$  chelating units, respectively in their fully deprotonated forms. They have been reacted with various metal salts such as Cu(II), Ni(II), Fe(III), Mn(III) and V(V), in the presence of a strong base, affording *e.g.* the dinuclear di-anionic Cu(II) and Ni(II) complexes  $[Cu_2(L^1)_2][NBu_4]_2$  and  $[Ni_2(L^1)_2][NBu_4]_2$ , and the dinuclear copper complex  $[Cu_2(L^2)(Na)_2](THF)_2$ . Preliminary investigations indicate that they can act as catalyst for the peroxide oxidation of cyclohexane. These studies provide a starting point for the future development of new catalysts using polyanionic salicylamidate-type ligands. They were performed by Dr. Laurent Benisvy, an ER of the Network.

**T1p) Hydrosoluble tris(pyrazolyl)borate ruthenium(II) complexes of PTA (CNR, IST).** A series of Ru(II) chloro complexes bearing the tripodal ligand tris-(pyrazolyl)borate (Tp), the water soluble cage phosphane 1,3,5-triaza-7-phosphaadamantane (PTA) and its *N*-boranyl adduct, PTA(BH<sub>3</sub>), together with PPh<sub>3</sub> were synthesised, in cooperation with Prof. J.Bravo's group (Univ. Vigo). The corresponding monohydrido complexes were obtained by reaction of the chlorides with NaOMe. The X-ray crystal structures of  $[TpRuCl(PTA)(PPh_3)]$  (**2**) and  $[TpRuCl(PTA)_2]$  (**3**) are also described. Cyclic voltammetry (CV) studies in MeCN and DMSO generally show reversible Ru(II/III) oxidation waves and the values of  $E_{1/2}^{ox}$  reflect the electron-donor character of the ligands, Tp (each arm) > PTA > PTA(BH<sub>3</sub>), whose Lever electrochemical  $E_L$  parameter was estimated for the first time. A joint paper was published in 2007 [A19]

**T1q) Bimetallic Ru-Co containing the water soluble ligand dmoPTA (UAL).** The dinuclear complex  $[RuClCp(PPh_3)(dmoPTA-\kappa P)(\mu_2-N,N'-dmoPTA)Co(acac)_2] \cdot H_2O$  (**2**) (dmoPTA = 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1] nonane, [C46]) has been synthesized by reaction of  $[RuClCp(HdmoPTA)(PPh_3)](OSO_2CF_3)$  (**1**) with  $Co(acac)_2$  in acetone (HdmoPTA = 3,7-H-3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane; acac = acetylacetonate). The new complex has been characterized by NMR, IR, elemental analysis and monocrystal X-ray structure determination. This complex is active for the catalytic isomerization of but-1-en-3-ol in acetone.

**T1r) Molybdenum Complexes containing the water-soluble tris(pyrazolyl)methanesulfonate ligand, Tpms. (IST, CNRSLCC/b).** The ligand  $Li[(O_3S)C(pz)_3]$ , Tpms, has been used to make a variety of molybdenum complexes. Reaction with  $Mo(CO)_6$  produces  $Li[(Tpms)Mo(CO)_3]$ , the X-ray structure of which has been determined. Oxidation of this compound yields neutral 17-electron  $[(Tpms)Mo(CO)_3]$ , a zwitterionic compound, which is stable against dimerization. Protonation, on the other hand, affords the hydride complex  $[(Tpms)Mo(CO)_3H]$ , while oxidation with I<sub>2</sub> yields  $[(Tpms)Mo(CO)_3I]$ . These compounds are water soluble. Further oxidation of these materials in the presence of air has led to the isolation and structural characterization of  $[TpmsMoO_2]_2$ ,  $[TpmsMoOCl]_2(\mu-O)$ , and  $[TpmsMoO_2]_2(\mu-O)$ . A joint manuscript on this work will be published after the termination of the contract.

**T1s) Structural modifications of the water soluble phosphine PTA towards diastereomeric enrichment (CNR).** In 2007 at CNR it was started a new research line based on the chemistry of PTA devoted to the quest for synthetic protocols to enable diastereomeric enrichment of this phosphine, to be followed by resolution and finally to the application in water phase asymmetric catalytic processes. The first results included the synthesis of the water soluble PTA derivative phenyl-(1,3,5-triaza-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]dec-6-yl)methanol (PZA) as a mixture of two diastereoisomers. PZA derivatives phenyl-(1,3,5-triaza-7-phospha-tricyclo[3.3.1.1<sup>3,7</sup>]dec-6-yl)methanol sulfide PZA(S) and oxide PZA(O) were also synthesized, together with the first Ir(III) complex of PZA. The results were published as fast communication [C64]

## Task 2 - High oxidation state organometallic aqua ions

(CNRS-LCC/a, CNRS-LCC/b, UAB, UEN, INEOS, IST; Task Coordinator CNRS-LCC/b)

**T2a) Studies of the  $Cp^*Mo^{VI}$  aquated complexes (UEN, CNRSLCC/b, UAB, HUJI).** Following on the first year studies on the formation of aquated complexes of the type  $(Cp^*)MoO_2^+$ ,  $(Cp^*)MoO_2(OH)$ ,  $(Cp^*)MoO_3^-$  and  $(Cp^*)MoO_3H_2^+$  from  $(Cp^*)_2Mo_2O_5$ , kinetic studies on the formation process of  $[Cp^*MoO_2(H_2O)_x]^+$  by protonation of  $[Cp^*MoO_3^-]$  have been carried out at variable temperature and variable pressure at UEN, on a sample provided by CNRSLCC/b. The kinetic data allowed the calculation of the first acid dissociation constant of the oxo dihydroxo complex  $[(Cp^*)MoO(OH)_2]^+$  to be  $pK_{a1} = -0.56$ . The presence of a water dissociation equilibrium is invoked to account for the unusually low acidity of the  $[(Cp^*)MoO_2(H_2O)]^+$  ion, which is in agreement with the <sup>17</sup>O-NMR exchange experiments performed under such conditions (see below). The temperature dependence for the combined protonation/isomerization process of  $[(Cp^*)MoO_2(OH)]$  to  $[(Cp^*)MoO_2(H_2O)]^+$  gives a very negative activation entropy (-150 J/Kmol), whereas the pressure dependence gives a negative activation volume (-9 cm<sup>3</sup>/mol). These results are unexpected and ascribed to a reversible rapid protonation process followed by a slow internal rearrangement from  $[Cp^*MoO(OH)_2]^+$  to

$[\text{Cp}^*\text{MoO}_2(\text{H}_2\text{O})]^+$ , which is followed by a rapid release of coordinated water. A theoretical study (by DFT at **UAB**) of the  $\text{Cp}^*\text{Mo}^{\text{VI}}$  system in aqueous media has been completed. This work has elucidated the acid dissociation anomaly for the system  $[\text{Cp}^*\text{MoO}_2(\text{H}_2\text{O})]^+$  (the first acid dissociation is weaker than the second one) as resulting from a water dissociation equilibrium. Therefore, although complex  $[\text{Cp}^*\text{MoO}_2(\text{H}_2\text{O})]^+$  is intrinsically very acidic, its effective acidity is reduced by averaging with the much lower acidity of free water. Water exchange reactions on  $[(\text{Cp}^*)\text{MoO}_3]^-$  were followed by  $^{17}\text{O}$ -NMR in Erlangen (partly during a secondment of Ms. Chiara Dinoi to **UEN**) and Toulouse as a function of pH in the range 6.8 to 7.4. The reaction shows a linear dependence on the  $\text{H}^+$  concentration which is ascribed to the formation of  $(\text{Cp}^*)\text{MoO}_2(\text{OH})$  that exchanges oxygen much faster than  $[(\text{Cp}^*)\text{MoO}_3]^-$ . At lower pH the exchange reaction becomes too fast to be studied by  $^{17}\text{O}$  labelling. Thus the  $[\text{Cp}^*\text{MoO}_2(\text{H}_2\text{O})]^+$  complex exchanges orders of magnitude faster than  $[(\text{Cp}^*)\text{MoO}_2(\text{OH})]$  which in turn exchanges orders of magnitude faster than  $[(\text{Cp}^*)\text{MoO}_3]^-$ . This is in good agreement with the tendency expected for the lability of  $\text{Mo}=\text{O} \ll \text{Mo}-\text{OH} \ll \text{Mo}-\text{OH}_2$  under the *trans* effect of  $\text{Cp}^*$ . The joint studies on this system, described in detail in last year's report, have been published in 2007 [A14]. They have involved theoretical work by the **UAB** group and joint speciation studies, including the use of stopped-flow kinetics, by the **UEN** team on compounds prepared by the **CNRS/LCC/b** partners. Part of this work was carried out during a secondment of Ms. Chiara Dinoi to **UEN**.

**T2b) Improved syntheses and mass spectrometric investigations of  $\text{Cp}^*_2\text{M}_2\text{O}_5$  ( $M = \text{Mo}, \text{W}$ )** (**CNRS/LCC/b, HUJ**). The studies mentioned in last-year's report have been completed and published [A17]. Two-step, one-pot procedures for the rapid preparation of complexes  $\text{Cp}^*_2\text{M}_2\text{O}_5$  ( $M = \text{Mo}$  and  $\text{W}$ ) from  $\text{M}(\text{CO})_6$  have been optimized using only  $\text{Cp}^*\text{Na}$  and other inexpensive and environmentally friendly reagents (*t*BuOOH or  $\text{H}_2\text{O}_2$  as oxidant, water as solvent).

**T2c) Aqueous reduction of  $\text{Cp}^*_2\text{W}_2\text{O}_5$**  (**CNRS/LCC/b**). The chemical reduction studies of  $\text{Cp}^*_2\text{W}_2\text{O}_5$  in  $\text{MeOH}:\text{H}_2\text{O}$  acidified by  $\text{CF}_3\text{COOH}$  or by  $\text{CF}_3\text{SO}_3\text{H}$  yields have yielded the air-sensitive green  $[\text{Cp}^*_3\text{W}_3\text{O}_4(\text{OH})_2]^{2+}$  cation ( $\text{W}^{\text{V}}$ ), which is then cleanly reoxidized in air to the air stable  $[\text{Cp}^*_3\text{W}_3\text{O}_6]^+$  cation (a mixed-valence  $\text{W}_3^{\text{V},\text{V},\text{VI}}$  cluster). Both clusters have been fully characterized spectroscopically and their electronic structure analyzed by DFT calculations. An electrospray mass spectrometric investigation has been carried out during the secondment of Chiara Dinoi at **HUJ**. A joint publication has appeared in 2007 [A17].

### Task 3 - Solvent-complex interactions

(**UAB, INEOS, CNRS-LCC/a, YoK, UEN, CNRS-LCC/b**; Task coordinator: **UAB**)

**T3a) Hydrogen bonding between transition metal hydrides and bases.** (**INEOS, UAB**). Solvent effect on the position of hydrogen bonding and proton transfer equilibria between water soluble hydrides  $\text{CpM}(\text{CO})_3\text{H}$  ( $M = \text{Mo}, \text{W}$ ) and organic bases (pyridine,  $\text{Et}_3\text{N}$ ,  $(\text{Me}_2\text{N})_3\text{PO}$ ) was studied both theoretically and experimentally. Formation of the  $\text{M}-\text{H}\cdots\text{Base}$  hydrogen bond is the first step of proton transfer from the hydride to organic base. Theoretical single point SCRF calculations taking into account solvent effect within CPCM model show that passing from gas phase to higher polarity solvents practically does not affect the energy of transition state ( $\Delta\Delta E = 0.1$  kcal/mol), whereas the energies of  $\text{M}-\text{H}\cdots\text{B}$  complex decrease, and the energies of proton transfer product –  $\text{M}\cdots\text{HB}$  ion pair – increase. As the result the proton transfer is encumbered by H-bond weakening in the media of higher polarity. Experimental study shows that the proton transfer is low temperature assisted mainly due to the right shift of the H-bonding equilibrium. Protic solvent such as  $\text{CH}_2\text{Cl}_2$  compete with  $\text{CpM}(\text{CO})_3\text{H}$  for binding a base, whereas in basic solvent such as THF solvent competes with the added base for binding the hydride. As the result in both cases proton transfer occurs only at high base excess (in comparison to hexane). The results have been reported at the international conferences. The results have been reported at international conferences and joint **INEOS/UAB** paper has been published [A9], another is in preparation [A24].

**T3b) Solvent influence on hydrogen bonding to transition metal hydrides.** (**INEOS, CNR**). The results have been reported in an international conference [B23], a joint **CNR/INEOS** paper was published in a special issue of *J. Mol. Structure* [A16]

**T3c) Solvent effect on dihydrogen bonding to main group hydrides** (**INEOS, UAB**). Solvent effect on dihydrogen bonding was studied for  $\text{AlH}_4^-\text{CF}_3\text{OH}$  and  $[\text{B}_{10}\text{H}_{10}]^{2-}\text{CH}_3\text{OH}$  complexes by DFT/B3LYP and second order Møller–Plesset (MP2) methods changing the media from gas phase to heptane and then to water (13 solvents were considered). Non-specific interactions were taken into account by PCM calculations whereas to for specific solvation the solvent molecules were introduced into the system optimized. 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  $\text{H}\cdots\text{H}$  bond and lowering interaction energy. In acidic solvents like  $\text{CHCl}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  specific solvation of both hydride and alcohol significantly changes DHB

complex properties. Analysis of the computed interaction energies in different solvents shows that the enthalpy values are well described by PCM correction, whereas special approach is needed for the calculation of Gibbs free energy in solution. Among the several approaches probed one, which takes into account chemical nature of a solute-solvent interaction, is proved to be sufficiently accurate for the estimation of Gibbs free energy in solution. A joint paper by INEOS and UAB has been published [A7] and another is in preparation [A25]. This study has been communicated in international workshop [B41]

**T3d) Water exchange reactions on Fe, Co and Mn complexes (UEN).** Water exchange reactions on a series of seven-coordinate Fe(II), Fe(III), and Mn(II) complexes were studied with the use of  $^{17}\text{O}$ -NMR. These complexes show interesting catalytic effects in the activation of NO and as superoxide dismutase (SOD) catalysts. In most cases substrate activation is controlled by water displacement reactions from the first coordination sphere. The water exchange reactions were studied as a function of temperature and pressure in order to determine all activation parameters ( $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta V^\ddagger$ ) of which the latter is the mechanistic decisive one. Thus, a detailed understanding of the water exchange mechanism enables further insight into the mechanism of the catalytic cycle. Work recently published in this area included water exchange reactions on Fe(III) porphyrin complexes in which the spin state of the metal centre could be tuned by the introduction of negatively and positively charged substituents on the porphyrin ring, and by the pH of the solution. The spin state of the Fe(III) centre in turn controls the coordination number by going from a spin admixed, six-coordinate state at low pH to a high-spin, five-coordinate state at high pH. The water exchange rate and mechanism controls the binding of small molecules such as NO and  $\text{H}_2\text{O}_2$  at low pH, whereas the spin crossover controls the binding of small molecules at high pH. A series of papers on these studies have been published [C66, 68, 70, 75] In addition, we started quantum mechanical calculations on solvent exchange reactions of solvated metal ions using DFT techniques. We have completed mechanistic profiles for water exchange on aquated Fe(III) and Al(III) complexes and solvent exchange on  $\text{Li}^+$  and  $\text{Be}^{2+}$  complexes in different solvents. The water exchange mechanism depends strongly on the pH of the solution, which controls the speciation in terms of aqua and hydroxo complex ions. In all cases the transition state clearly depicts the intimate nature of the exchange mechanism in terms of A,  $\text{I}_a$ ,  $\text{I}_d$  and D mechanisms, and supports the mechanisms suggested on the basis of experimental data. A papers has been published [C67].

**T3e) Study of the solubility of dendritic complexes (CNRS/LCC/a).** The interior of the dendrimers we synthesize is hydrophobic, thus the end groups must be chosen to ensure the solubility in water, to perform catalytic experiments in water. The solubility in water of many dendritic ligands that were synthesized is good, but the solubility of the corresponding complexes, either isolated or generated *in situ* is in some cases relatively poor. These studies about the solubility in water have led us to the conclusion that the complexes we have obtained would be more suitable to be used as catalysts in biphasic conditions (water/organic solvent) than in pure water, or in mixtures of water with miscible organic solvents.

**T3f) The effect of the solvent (water) on the catalytic H/D exchange in aqueous solutions. (UD)** The results were published as a journal article [C16] and also communicated as a poster. *Task completed in 2006.*

**T3g) Detailed theoretical studies were started to discover the effects of the solvent water on the selectivity of hydrogenations of unsaturated aldehydes catalyzed by  $[\{\text{RuCl}_2(\text{mtppms})_2\}_2]$  (UD-UAB).** The results were presented at four conferences [B6 – B8], [B15-17] and published in three journal articles [A5], [A8], [A13] *Task completed in 2006.*

#### **Task 4 - Speciation studies**

(HUJI, UD, UEN, CNRS-LCC/b, YoK, IST; Task coordinator: HUJI)

**T4a) Speciation of poly-anionic and poly-cationic Fe(III) porphyrin complexes (UEN).** In collaboration with Norbert Jux of the Institute for Organic Chemistry, University of Erlangen-Nürnberg, two highly negatively and positively charged Fe(III) porphyrin systems were prepared to improve the water solubility of porphyrin complexes in general. These complexes are present in solution either in the diaqua, aqua-hydroxo or dihydroxo forms depending on the selected pH. Detailed potentiometric titrations enabled the determination of the acid dissociation constants and the speciation of the porphyrin systems. This has now been done for several differently charged Fe(III) porphyrin complexes, viz.  $\text{P}^{8+}$ ,  $\text{P}^{4+}$ ,  $\text{P}^{8-}$  and  $\text{P}^{16-}$ . Systematic NMR studies indicated that the investigated complexes undergo a change in the spin state of the metal on going from low to high pH which results in a change in coordination sphere from six-coordinate at low pH to five-coordinate at high pH. This information is of fundamental importance in studies dealing with the activation of NO,  $\text{H}_2\text{O}_2$  and organic peroxides (see T5d and T5e, respectively).

**T4b)** *pH-potentiometric characterization of [RhCl(OAc)(TPPMS)<sub>2</sub>].* (UD) Following first year results on [Rh(CO)(OAc)(TPPMS)<sub>2</sub>] which was chosen as a model compound of the complexes formed during the pretreatment with syngas of the aqueous solution of rhodium acetate and TPPTS in the Rhone Poulenc-Ruhrchemie industrial hydroformylation process, pH-potentiometric titrations were carried out and the results were published as a journal article [C17]. *Task completed in 2006.*

**T4c)** *Time-resolved Infra Red Spectroscopy Studies* (YoK). We have studied the photochemistry of the compounds described in T1k by time-resolved IR spectroscopy on a visit to the Rutherford-Appleton Laboratory in which we collected excellent data. The measurements were conducted in an aqueous mixed solvent system of DMF + 5% D<sub>2</sub>O and involved (a) the protected sensor, (b) the deprotected sensor at a range of pHs, (c) the deprotected sensor in the presence of molybdate, vanadate and tungstate. Spectra were collected in the CO-stretching region of the IR spectrum over two different time ranges: 1-1000 ps and 1-1000 ns. They show clearly the formation of two different types of excited state. The metal-to-bpy charge-transfer (MLCT) excited state is formed by the protected sensor and by the deprotected sensor at low pH. Its lifetime is typically 70 ns. The catecholate intra-ligand charge transfer excited state (ILCT) is formed by the deprotected sensor in basic solution. It is also observed in the presence of molybdate or tungstate in acid solution. The ILCT state is formed both by direct excitation and indirectly via the MLCT state. The rate of transfer between states is approx 10<sup>10</sup> s<sup>-1</sup>, but varies with pH. It decays with complex kinetics: some forms are highly reactive decaying in a few ps while others last ca 20 ns. Direct speciation studies have established the presence of the Re<sub>2</sub>Mo species at pH 4 and higher. However, evidence for a 1:1 complex has been found at pH 2.

**T4d)** *Speciation of Cp\*<sub>3</sub>W<sub>3</sub><sup>12+</sup> (Cp\*W<sup>VI</sup>) and Cp\*<sub>3</sub>W<sub>3</sub><sup>13+</sup> (Cp\*<sub>3</sub>W<sub>3</sub><sup>V,V,VI</sup>)* (CNRS/LCC/b). As shown in Task 1, reduction of Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub> yields clusters Cp\*<sub>3</sub>W<sub>3</sub>O<sub>4</sub>(OH)<sub>2</sub><sup>2+</sup> and Cp\*<sub>3</sub>W<sub>3</sub>O<sub>6</sub><sup>+</sup> under low pH (<1) conditions. The two compounds are related to each other by a coupled one-electron-two-proton redox process. Electrochemical investigations of this process at various pH values (Pourbaix diagram) have been initiated in Year 4, but have not yet been completed. They will be pursued beyond the termination of this Contract.

**T4e)** *Speciation of polysulfide ligands: A new method* (HUJI). A new approach based on rapid, chemical derivatization in a single phase, was used to determine the disproportionation constants and the underlying thermodynamics of inorganic polysulfides, a class of important ligation agent and promoters of natural reactions. in aqueous solutions. This method resolves the dispute over the existence of hexasulfide in aqueous solutions and establishes the presence of even higher polysulfide chains in water. The Gibbs free energies of formation, enthalpy of formation and entropy under standard conditions were also resolved. The approach is based on single phase, fast methylation of polysulfides with methyl trifluoromethanesulfonate (methyl triflate), and subsequent determination of the dimethylpolysulfides by HPLC. Kinetic studies and isotope dilution studies were used in order to confirm quantitative equivalence between the observed distribution of dimethylpolysulfides and the polysulfide distribution in the water. A new analytical method based on this concept was derived and it was used to decipher polysulfide distribution in a number of water wells in Israel. ESI-MS methods were used to resolve speciation in molybdenum polysulfide system.

## **Task 5 - Substrate activation and mechanistic studies**

(CNR, UD, UAB, YoK, CNRS-LCC/b, IST, UAL, INEOS, UEN; Task coordinator: UEN)

**T5a)** *Chemical reduction studies of Cp\*Mo<sup>VI</sup> by sulfur compounds* (CNRS/LCC/b, HUJI). The investigation of the activation of mercaptopyruvic acid, HSCH<sub>2</sub>CH<sub>2</sub>COOH, by compound Cp\*<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>, described in last year's report, has been completed and published [A15]. Surprisingly, an oxo-bridged product, Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>, has been obtained instead. The reaction has been studied by ESI MS during a secondment period of Ms. Chiara Dinoi in Jerusalem. On the basis of this work, a mechanism of the complex-substrate interaction and substrate activation has been proposed.

**T5b)** *Activation of NO by Fe(III) porphyrin complexes* (UEN). The highly water soluble poly-anionic and poly-cationic Fe(III) porphyrin complexes synthesized and characterized under T4a were used to study reactions with NO as a function of pH, temperature and pressure. The kinetics of both the "on" and "off" reactions were studied using flash photolysis and stopped-flow techniques. For all complexes studied the product is formally Fe(II)-NO<sup>+</sup>. Work recently published in this area concerns the activation of NO by Fe(III) porphyrin complexes in which the spin state of the metal centre can be tuned by the introduction of negatively and positively charged substituents on the porphyrin ring, and the pH of the solution. The spin state of the Fe(III) centre in turn controls the coordination number by going from a spin admixed, six-coordinate state at low pH to a high-spin, five-coordinate state at high pH. The water exchange rate and mechanism controls the binding of NO at low pH, whereas the spin crossover controls the binding of NO at high pH. The coordinated nitrosyl ligand in Fe(II)-NO<sup>+</sup>



subsequently undergoes a reductive nitrosylation reaction that is catalyzed by nitrite and hydroxide to form Fe(II)-NO as final product in the presence of NO. A detailed study on the nitrite catalyzed reductive nitrosylation process was performed as a function of pH, temperature and pressure. An inner-sphere electron transfer process is suggested to account for the observed kinetic data. In addition, the work was extended to the activation of NO by Co(III) model porphyrin complexes and cobalamin (Vitamin B<sub>12</sub>), in which case the observed reactions are induced by traces of nitrite in solution. A series of papers have been published or are presently in press.

**T5c) Activation of H<sub>2</sub>O<sub>2</sub> and organic peroxides by Fe(III) complexes (UEN).** Rapid-scan techniques were employed to study the activation of H<sub>2</sub>O<sub>2</sub> and organic peroxides by a series of Fe(III) complexes including porphyrin and non-porphyrin chelate systems. In all studied systems coordination of the peroxide to the Fe(III) centre is rapid and controlled by the water-exchange process. Coordinated hydrogen peroxide is stabilized via deprotonation to form an intermediate hydroperoxo species, whereas the organic peroxides also undergo deprotonation on binding to the Fe(III) centre. These reactions are followed by the rate-determining homolysis or heterolysis of the O-O bond, which in turn is controlled by the nature of the spectator ligand and the ability of the metal centre to form higher oxidation state species like Fe(IV)-P<sup>+</sup>. A detailed study on the pH dependence of the activation of organic peroxides and peroxy acids by several Fe(III) porphyrin complexes was also undertaken. The catalytic activity of the activation process was studied in the presence of typical substrate molecules that can undergo hydroxylation or epoxidation reactions. Kinetic studies on the catalytic cycle were also performed as a function of pH, substrate, peroxide and catalyst concentration, temperature and pressure. Important mechanistic information was obtained from low temperature rapid-scan measurements at -40 °C. This enabled us to observe the complete catalytic cycle for the oxidation of *cis*-stilbene by *m*-chloroperoxybenzoic acid catalyzed by a functional model complex for cytochrome P450. Kinetic data could be obtained for all the individual reaction steps which could be used to simulate the kinetic traces observed for the overall catalytic cycle. Several papers have been published or are presently in press [C67, 69, 71]

**T5d) Mechanistic studies in ionic liquids (UEN).** We recently initiated a series of experimental and theoretical studies on the mechanistic behaviour of Pt(II) complexes in ionic liquids involving ligand substitution and hydroformylation reactions in order to determine the role of the solvent in controlling the nature of the transition state. The revealed mechanistic information allows a more complete understanding of the role of electrostriction in such reactions when performed in aqueous and non-aqueous solvents. Activation parameters for typical ligand substitution reactions in ionic liquids were determined from systematic temperature and pressure dependence studies. The results demonstrate that ionic liquids are indeed very suitable solvents to gain further mechanistic insight especially in terms of electrostriction effects in the transition state. Following completion of this work we focussed our attention on extending these studies to fast reactions using stopped-flow techniques. For that reason we looked into a series of ionic liquids of low viscosity that will allow rapid mixing of the reactant solutions. This development has been successful and we are presently able to investigate reactions in ionic liquids on the millisecond time scale at pressures up to 150 MPa. Several papers have been published or are presently in press [C76].

**T5e) Aqueous activity of tetrathiomolybdate (HUJI - CNRSLCC/b):** Aqueous dehalogenation activity of tetrathiomolybdate for a large number of haloorganic compounds was discovered for the first time. Tetrathiomolybdate is a potent cleansing agent able to detoxify fumigants (CH<sub>3</sub>Br, ethylene dibromide), pest control agents (DDT, alachlor), herbicides (simazine and atrazine) and other haloorganic compounds (haloalkanes). The catalytic activity of tetrathiomolybdate was studied in collaboration with Poli's group (CNRSLCC/b) revealing that it can catalyse the dehalogenation ethylene dibromide by hydrogen sulfide in aqueous solutions. This is the first record of catalytic dehalogenation by hydrogen sulfide in aqueous solutions

**T5f) Activation of nitriles. Imidoamidate Ni(II) complexes derived from a novel oxime-mediated single-pot reaction of nitriles, and 3D H-bonded supramolecular assemblies (IST).** A series of unsymmetrical neutral bisimidoamidate (or 1,3,5-triazapentadiene) Ni(II) complexes, bearing an iminoisoindolinone moiety, have been generated by a novel 2-propanone oxime-mediated single-pot reaction of phthalonitrile and nickel(II) acetate in solution of the corresponding alkylnitrile (RCN). The synthesised compounds represent rare specimens of genuine unsymmetrical imidoamidate complexes as well as their first examples generated from nitriles in a single-pot reaction.

Two structurally related compounds {Ni{HN=C(3-py)NC(3-py)=NH}2}·H<sub>2</sub>O·MeOH (**1**) and [Ni{HN=C(3-py)N(H)C(3-py)=NH}2]Cl<sub>2</sub> (**2**) with symmetrical 3-pyridyl (3-py) substituents have been prepared by direct 2-butanone oxime mediated transformation of 3-cyanopyridine in the presence of Ni(MeCO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O or NiCl<sub>2</sub>·2H<sub>2</sub>O, respectively. Their slow recrystallization in air from organic solvents revealed a high affinity for water and resulted in the formation of the derived compounds [Ni{HN=C(3-py)NC(3-py)=NH}2]·6H<sub>2</sub>O (**1'**) and [Ni{HN=C(3-py)N(H)0.5C(3-py)=NH}2]Cl·2H<sub>2</sub>O (**2'**). Single-crystal X-ray diffraction analyses allowed the identification of discrete hexameric water or hybrid water-chloride clusters hosted by the crystal matrixes of **1'** and **2'**, respectively. Both the (H<sub>2</sub>O)<sub>6</sub> and [(H<sub>2</sub>O)<sub>4</sub>(Cl)<sub>2</sub>]<sub>2</sub>- clusters possess similar geometries and consist of

cyclic planar tetranuclear (H<sub>2</sub>O)<sub>4</sub> or [(H<sub>2</sub>O)<sub>2</sub>(Cl)<sub>2</sub>]<sub>2</sub>-cores with two dangling water molecules. These water associates occupy voids in the crystal cells and display extensive H-bonding interactions with monomeric nickel-organic units, thus playing a key role in the formation of 3D hydrogen-bonded supramolecular assemblies.

**T5g) Activation of hydrogen peroxide in the catalyzed epoxidation of olefins (CNRS/LCC/b, UAB).** A theoretical mechanistic study has been conducted on the high-oxidation state Mo-catalyzed epoxidation of olefins. This study was inspired by three considerations: (i) experimental studies (see Task 6, T6j) show that compound Cp\*<sub>2</sub>M<sub>2</sub>O<sub>5</sub> (M = Mo, W) are good catalysts for the oxidation of thiophene derivatives with H<sub>2</sub>O<sub>2</sub>, and preliminary work shows that they also catalyze olefin epoxidation with TBHP; (ii) three complexes are known to speciate in aqueous conditions to yield [Cp\*MO<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup> at low pH; (iii) there is confusion in the literature on the mechanism of olefin epoxidation by H<sub>2</sub>O<sub>2</sub> (and hydroperoxides). Thus, a theoretical study has analyzed the mechanism of H<sub>2</sub>O<sub>2</sub> activation and oxygen transfer to ethylene (as a model olefin), finding a previously unreported, low-energy pathway that rationalizes the catalytic action of these compounds. A joint paper is in preparation and will be submitted very shortly [A23].

### **Task 6 - Catalysis, photocatalysis and electrocatalysis in water and biphasic media** (UD, IST, CNR, YoK, UAL, CNRS-LCC/a, HUJI; Task coordinator: UD)

**T6a) Asymmetric allylic alkylations catalyzed by Pd-dendrimers (CNRS/LCC/a).** Task completed in 2005.

**T6b) Isomerization of allyl alcohols in biphasic medium catalyzed by a Ru-dendrimer (CNRS/LCC/a).** A model complex, and the series of dendrimers bearing PTA-Ru-*p*-cymene end groups, from generation 1 (12 end groups) to generation 3 (48 end groups) have been used to catalyze the isomerization of 1-octen-3-ol to 3-octanone in a biphasic heptane/water medium, under vigorous stirring. An increase of the percentage of conversion is observed from the monomer (38% to the third generation (98%). There is clearly a relatively rare positive dendritic effect, and the first example using an organometallic dendrimer as catalyst in water. We have shown (with CNR) that even the first generation (but not the monomer) can be recycled and reused up to six times. A dropping of efficiency was observed only for runs 5 and 6.

**T6c) Hydration of alkynes in H<sub>2</sub>O/*i*PrOH catalyzed by a Ru-dendrimer (CNRS/LCC/a).** Comparison of the efficiency of the “classical” PTA complex, of a model compound and of dendrimers from generation 1 to generation 3 bearing PTA-Ru complexes as end groups has shown that the highest percentage of conversion of the alkyne is obtained with generation 1 (58 %, only 32% with the “classical” PTA complex). In all cases we have shown (with CNR) that there is a high selectivity for the ketone over the aldehyde form, from 91% with the model compound, to 98% with PTA as well as with the second and third generations of the dendritic catalyst.

**T6d) Water soluble ruthenium PTA complexes as catalysts for selective hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds. (PTA = 1,3,5-triaza-7-phosphaadamantane) (CNR, UAL).** Following preliminary work carried out in the second year during the secondment activity of Mrs Mallqui at CNR, regarding Ru catalyzed transfer hydrogenations of ketones, the tests were repeated showing complete conversion of benzylidene acetone to the saturated ketone. More interesting results were obtained using the water soluble Ru complexes containing sulfonated diphosphines, hence the focus of the research was shifted in this direction. A joint paper is in preparation [A26]

**T6e) Water-soluble Ru-N-heterocyclic carbene complexes as catalysts of hydrogenation, transfer hydrogenation and redox isomerization processes. (UD)** The newly synthesized Ru(II)-NHC complexes (**T1f**) such as [RuCl(H<sub>2</sub>O)(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)]<sup>+</sup> were applied in the redox isomerization of a variety of allylic alcohols (**UD**). A very pronounced effect of the pH of the aqueous phase on the total conversions and product distributions of the transposition reactions was observed. Also, it was found, that addition of NaCl increase the conversion and favoured isomerization over hydrogenation. These effects could be rationalized on basis of the previously studied complex equilibria. The results were summarized in a paper [C18] and were presented at three conferences [D38], [D40], [D44]. The moderately air-stable [RuCl(H<sub>2</sub>O)(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)]<sup>+</sup> was also successfully applied for the hydrogenation of allylic alcohol in aqueous solution using a microfluidics-based flow-through reactor at 90 °C and 2 bar H<sub>2</sub> pressure. Under such conditions, unexpectedly high turnover frequencies (>12000 h<sup>-1</sup>) were observed. The newly synthesized Ru(II)-, Rh(I)-, and Ir(I)-NHC complexes (see **T1c**) were studied in detail as catalysts for the redox isomerization and hydrogenation of allylic alcohols in homogeneous aqueous solution and in biphasic systems. It was established that [RhCl(cod)(bmim)][BF<sub>4</sub>] catalyzed the reaction under an argon atmosphere with no need of prior “activation” by H<sub>2</sub>; hence there was no hydrogenation of the substrate as a side-reaction. The mixed carbene/phosphine complexes of Ir(I), [Ir(cod)(bmim)(tppms)] and Na<sub>2</sub>[Ir(cod)(bmim)(tppts)] proved moderately selective catalysts of the hydrogenation of phenylacetylene. Both [RuCl(H<sub>2</sub>O)(1-butyl-3-methylimidazol-2-

ylidene)(*p*-cymene)]<sup>+</sup> and [RhCl(cod)(bmim)][BF<sub>4</sub>] were active catalysts of the reduction of benzylideneacetone and acetophenone by hydrogen transfer from isopropanol. In all cases the reaction rates showed a sharp maximum as the function of the pH. These results were communicated in a journal article [C43] and at conferences [D80], [D84], [D87], [D89], [D95], and form the basis of the PhD Thesis of Ms. M. Fekete. A visit of F. Joó, Á. Kathó and M. Fekete to UAL as well as of A. Romerosa and A. Mena to UD (all funded by a Hungarian-Spanish bilateral intergovernmental agreement) as well as the secondment of W. Wojtków (AquaChem ER) in Almería resulted in a joint publication [A20] on the redox isomerization and transfer hydrogenation of allylic alcohols catalyzed by various Ru(II)-phosphine and -carbene complexes.

**T6f) Catalytic hydrogenation of carbon dioxide, bicarbonates and carbonates. (CNR, UAL, UD).** Catalytic CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> reduction by H<sub>2</sub> in water was studied in a multilateral project including AQUACHEM members (UAL, UD, CNR) and a Swiss laboratory (EPFL) as part of the COST Chemistry Action D29. The catalytic hydrogenation of bicarbonate by [RuCl<sub>2</sub>(TPPMS)<sub>2</sub>]<sub>2</sub> was further investigated at UD using DFT (B3LYP) calculations. The results are summarized in a paper [C19]. The hydrogenation of bicarbonates and aqueous suspensions of CaCO<sub>3</sub> and MgCO<sub>3</sub> under CO<sub>2</sub>/H<sub>2</sub> pressure was studied at UD – the results form part of the PhD Thesis of Mr. I. Józsa and were published in 2007 [C44]. Two STSMs within COST Action D29 were carried out by M. Erlandsson from CNR at EPFL, to investigate the catalytic reduction of CO<sub>2</sub> and bicarbonate in the presence of Ru(II), Rh(III) and Ir(III) cyclopentadienyl PTA complexes. The results have been presented at conferences [D131, 132] and published in 2008 [C62-63].

**T6g) Selective hydrogenations on heterogenized ruthenium complexes. (UD)** The UD team has started a comprehensive study of the selective hydrogenation of (disubstituted) alkynes both in aqueous/organic biphasic systems and on heterogenized complex catalysts. It has been observed, that the selectivity of the hydrogenation of disubstituted alkynes catalyzed in aqueous/organic biphasic systems by [RuCl<sub>2</sub>(TPPMS)<sub>2</sub>]<sub>2</sub> is strongly dependent on the pH of the aqueous phase. New heterogenized catalysts with cationic ligands have also been prepared and applied to the hydrogenation of acetylenes. Studies in 2007 revealed that Ru(II) complexes of methyl- and benzyl-pta catalyzed the C=O hydrogenation of cinnamaldehyde, while Rh(I) complexes with these ligands were selective of the C=C hydrogenation of the same substrate. The catalysts could be applied both in homogeneous aqueous solutions and in heterogenized form on ion-exchange supports. The results form part of the PhD Thesis of Ms. Henrietta H. Horváth (UD), were presented at a conference [D81] and their publication is underway.

**T6h) pH-dependent regioselective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with Ru(II) water-soluble complexes. (UAB, UD)** Detailed theoretical studies have been performed in collaboration by the UAB and UD teams to unravel the mechanism and the factors governing the pH-dependent regioselectivity of hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes catalyzed by [RuCl<sub>2</sub>(mtppps)<sub>2</sub>]<sub>2</sub>. Three conference presentations and two UAB-UD joint publications [A5,A8] came out from this work. The reaction was also further studied experimentally and the effect of NaI was clarified by way of kinetic and NMR experiments. It was established that iodide promotes the formation of [Ru(H)(H)(mtppps)<sub>3</sub>] already in slightly acidic media which influences the regioselectivity of the process [D39]. In 2007, the hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds (cinnamaldehyde, benzylideneacetone) was further studied using Ru(II)- and Rh(I)-N-heterocyclic carbene complexes (see also T1c). The rate of these reactions also showed a pronounced maximum as a function of the pH. The results were presented at conferences [D80], [D87] and in a journal article [C43].

**T6i) Catalysis of the H/D exchange by [RhCl(TPPMS)<sub>3</sub>]. (UD) Task completed in 2006 (see also T3f).**

**T6j) Catalytic oxidations of thiophene derivatives using green oxidants. (CNR, CNRSLCC/b)** During year 4, the investigation of the [Cp\*<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>]- and [Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub>]-catalyzed oxidation of thiophene derivatives by H<sub>2</sub>O<sub>2</sub> has been pursued. The activity varies in the order DMBT (4,6-dipethylthiophene) ~ DBT (dibenzothiophene) > BT (benzothiophene) and W >> Mo. The tungsten system is extremely efficient, a complete oxidation being achieved in less than 2h with a 1% catalyst loading at 15 °C for the DBT substrate! The rate law has been established (first order in thiophene substrate and catalyst, zero order in oxidant). The activation parameters from a variable temperature study indicate a highly ordered transition state for the rate limiting step ( $\Delta S^\ddagger = -30$  eu). The study is not yet completely finished, but a joint paper has been accepted for publication after the termination of the contract [A21]. The initial part of this study was carried out during a secondment of Ms. C. Dinoi at CNR.

**T6k) Photoinduced redox reactions (YoK)** The experiments described in T4b will be used in order to develop redox active species for use in water-DMF mixtures. A series of new water-soluble metalloporphyrins have been synthesised for attachment to redox-active centres such as Re(CO)<sub>3</sub>(bpy). These metalloporphyrins include methylpyridinium units to ensure water solubility and an arm with amide linked substituents ready for binding to another metal.

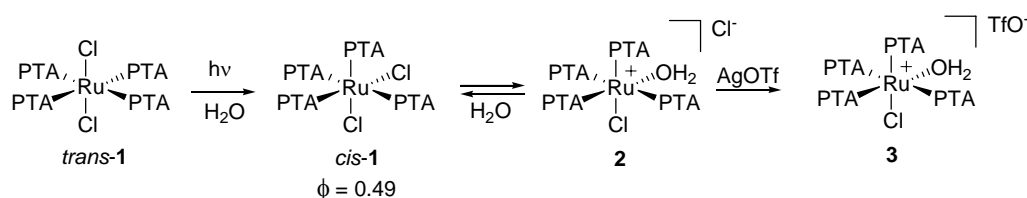
**T6l) Synthesis of new water soluble visible light active ruthenium complex (UAL).** The complex [RuCl<sub>2</sub>(mPTA)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub> (**1**) is a new water soluble complex that is transformed by the visible light in D<sub>2</sub>O

into the complex  $[\text{RuCl}_2(\text{mPTA})_3](\text{OTf})_2$  (**2**) only under visible light irradiation. This is an irreversible reaction that leads to a new water-soluble complex active in photocatalysis.

**T6m) Electrochemical activity of Ruthenium complexes (HUJI, CNR, UAL).** The electrooxidation of Ruthenium cyclopentadienyl PTA complexes was studied by ESI-MS, cyclic voltammetry and on-line electrochemistry/ESI-MS techniques, resulting in a three-way joint publication, authored by ER at HUJI [A10].

**T6n) Ru-N-heterocyclic carbene complexes as catalysts of alkyne oligomerization processes. (UD)** The results were summarized in a journal article [C22]. Task completed in 2006.

**T6o) Assessment under visible light of water-soluble complexes containing PTA and PTA derivatives (UAL).** The influence of visible light on the published water-soluble complexes containing PTA and PTA derivatives has been investigated mainly through a secondment activity of ER R. Girotti at YoK [B39]. It was found that visible light induces the photoisomerization of the well-known *trans*- $[\text{RuCl}_2(\text{PTA})_4]$  (*trans*-**1**) to *cis*-**1** in chloroform at various wavelengths (Scheme 1, Figure 1), and in this case a reversible equilibrium has been observed. 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.



**T6p) Photochemical isomerization of allylic alcohols under mild conditions mediated by water-soluble ruthenium-complexes (UAL).** As part of UAL's interest in the synthesis and reactivity of new water-soluble metal complexes, the 2007 research has been focused on ruthenium complexes containing PTA (1,3,5-triaza-7-phosphaadamantane) and its methylated derivatives. This family of complexes could represent active catalysts for allylic isomerization in mild conditions. Particularly, attention was recently paid to the new water-soluble complexes  $[\text{RuCl}_2(\text{mPTA})_4](\text{OTf})_4$  (mPTA = N-methyl-1,3,5-triaza-7-phosphaadamantane) and  $[\text{RuCl}_2(\text{mPTA})_3](\text{OTf})_3$ , which are active catalysts for allylic isomerization at room temperature under photochemical conditions.

**T6q) Catalytic peroxidative oxidation of cycloalkanes by polynuclear copper complexes (IST).** The synthesis of copper complexes with N,O-ligands (some of which acting as models of particulate methane monooxygenase, pMMO) and their application as catalysts or catalyst precursors on the peroxidative oxidation of cycloalkanes have continued. They include various Cu(II) complexes with aminopolyalcohol or salicylaminate ligands (studies done by the ESR Katrin Grunwald and the ER Laurent Benisvy, see task 1) and the trinuclear triangular copper derivatives  $[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{EtCOO})_2(\text{H}_2\text{O})]$  (Hpz = pyrazole) and  $[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{EtCOO})_2(\text{H}_2\text{O})]$ , with intra- and intermolecular H-bonds, generating complex supramolecular 2-D MOFs, which have been synthesized by the groups of Profs. L. Pandolfo (Univ. Padova) and C. Pettinari (Univ. Camerino). They act as selective catalysts or catalyst precursors for liquid biphasic (MeCN/ $\text{H}_2\text{O}$ ) peroxidative oxidation of cyclohexane and cyclopentane to the corresponding alcohols and ketones.

**T6r) Catalytic single-pot oxidation of ethane and cyclohexane by scorpionate and pyrazole complexes (IST)** The study of the complexes  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2]$  (Hpz = pyrazole),  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ ,  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ ,  $[\text{ReCl}_2\{\text{HC}(\text{pz})_3\}(\text{PPh}_3)]$ ,  $[\text{ReCl}_2\{\text{HC}(\text{pz})_3\}(\text{PPh}_3)]$ ,  $[\text{ReCl}_2\{\text{HC}(\text{pz})_3\}(\text{PPh}_3)]$ ,  $[\text{ReOCl}_2\{\text{SO}_3\text{C}(\text{pz})_3\}(\text{PPh}_3)]$  and  $[\text{ReO}_3\{\text{SO}_3\text{C}(\text{pz})_3\}]$ , and their precursors  $[\text{ReCl}_2\{\eta^2\text{-N}_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$  and  $[\text{ReOCl}_3(\text{PPh}_3)_2]$ , was pursued. They catalyze, in a single-pot process, the oxidation of ethane, in the presence of potassium peroxodisulfate  $\text{K}_2\text{S}_2\text{O}_8$ , in trifluoroacetic acid (TFA), to give acetic acid, in a remarkable yield and under mild conditions (in some cases carboxylation can also occur to give propionic acid, but in a much lower yield). The catalytic peroxidative oxidation of ethane to acetaldehyde and of cyclohexane to cyclohexanone and cyclohexanol by an aqueous solution of  $\text{H}_2\text{O}_2$  at room temperature is also achieved by using most of those catalyst precursors. The effects of a variety of factors were studied towards the optimization of the processes which are shown to proceed via both C-centered and O-centered radical mechanisms.

**T6s) Catalytic Baeyer-Villiger oxidation of cyclic ketones by rhenium complexes (IST).** This task, initially performed by an ESR, Paolo Sgarbossa, was pursued. Various rhenium complexes have been tested successfully

as catalysts or catalysts precursors for the aqueous peroxidative Baeyer-Villiger oxidation of 2-methylcyclohexanone to the corresponding lactones.

**T6t)** *Mechanism of the stereoselective hydrogenation of phenyl-substituted alkynes with Ru(II) water-soluble complexes. (UAB, UD)* DFT calculations including solvent effects by means of the explicit description of a cluster of water molecules in addition to a continuum model have been performed to describe the reaction mechanism of the stereoselective hydrogenation of 1,2-diphenylacetylene catalyzed by the water soluble  $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$  in acidic aqueous solutions. It was shown that the reaction takes place in two steps; one hydrogen comes from the hydrido complex, whereas the second hydrogen is transferred from the hydroxonium ions present in solution. A joint UAB/UD article has been published in 2007 [A13] and the results have been presented at two international conferences [B13, B16].

**T6u)** *Ru-N-heterocyclic carbene complexes as catalysts of alkyne hydration. (UD)* The new water-soluble Au(I)-N-heterocyclic carbene complexes (see **T1c**) were studied in the hydration of various alkynes. These complexes contained 1,3-bis(sufloalkyl)- or 1,3-bis(sulfoaryl)imidazolium ligands and the biphasic reaction mixtures separated with no problem of emulsification. Terminal alkynes were smoothly hydrated to the corresponding carbonyl compounds (e.g. phenylacetylene to acetophenone) under reasonably mild conditions. Hydration of p-ethynylmethoxybenzene in a MeOH:H<sub>2</sub>O=5:1 mixture at reflux temperature on the action of an  $[\text{AuCl}(\text{Na}_2\text{BetSI})]$  catalyst proceeded rapidly with an excellent TOF of 400 h<sup>-1</sup>. The reaction rate was studied as the function of the water content of the solvent; it was established that highly aqueous (80%) solvents are suitable as reaction media for these hydration processes. The results were communicated at several conferences [D86], [D87], [D90], [D92] and a manuscript of a journal article is in preparation. Further synthetic, structural and catalytic studies are underway and will continue even after termination of the Aquachem project.

**T6v)** *Group 5-7 transition metal oxides as efficient catalysts for the oxidative functionalization of alkanes (IST).* Oxides of group 5–7 metals are convenient and efficient catalysts for the single-pot carboxylation of gaseous (methane, ethane, propane) and liquid alkanes to carboxylic acids, as well as for the aqueous peroxidative hydroxylation/oxygenation of liquid alkanes to alcohols and ketones. The reactions occur under mild conditions, and the carboxylations proceed with unprecedented remarkably high turnover numbers. The diagonal metals commonly provide the most active oxide catalysts in the order V > Re > Mo.

**T6w)** *Supported vanadium complexes as catalysts for the proxidative oxidation of benzene and alkanes (IST).* The bis(maltolato)oxo complexes of vanadium(V) and vanadium(IV) both in a soluble form and anchored to chemically modified silica gel, when used in combination with pyrazine-2-carboxylic acid (PCA), catalyze the oxidation of benzene to phenol and alkanes to the corresponding alkyl hydroperoxides with H<sub>2</sub>O<sub>2</sub> at 40–50 °C. Heterogenizing the complexes leads to changes in regioselectivity and bond selectivity parameters of the alkane oxidation, and this opens new routes to the enhancement of the selectivity in oxidation processes.

**T6x)** *Catalytic activity of dendrimers ended by N-ligands (pyridine, bipyridine, scorpionate) (CNRS/LCC/a with IST).*

All experiments in this field were carried out in water/acetonitrile homogeneous mixtures using dendritic complexes generated *in situ* from the corresponding free ligands and Pd(OAc)<sub>2</sub>. The first generation of the dendrimer ended by pyridine and the first generation of the dendrimer ended by scorpionate, as well as its monomer, were used in Sonogashira reactions at 40 and 60°C. In both cases, the scorpionate compounds are most efficient than the pyridine ones. Heck reactions on styrene were attempted with the first generations of dendrimers ended by pyridine, dipyridine, and scorpionate end groups, as well as the corresponding monomers at 70°C. The best results are obtained with the dipyridine series. A joint paper is in preparation.

**T6y)** *Catalytic activity of dendrimers ended by PNP-ligands (CNRS/LCC/a with UAL and CNR).*

All experiments in this field were carried out in water/acetonitrile homogeneous mixtures using dendritic complexes generated *in situ* from the corresponding free ligands and Pd(OAc)<sub>2</sub>. Sonogashira reactions at 40°C were carried out with the generations 0, 1, and 3 of the dendrimers ended by diphosphino tyramine end groups and the corresponding monomer. The best efficiency was observed with generation 3. Another series of dendritic PNP ligands built from L-tyrosine (monomer, generations 1 and 3) was tested in the same conditions. In this case the first generation is the best, but it is slightly less efficient than the tyramine series. Suzuki experiments were carried out only with the tyramine series, at 120°C, using the monomer and the first (which afforded the best results) and third generations of the dendrimer. Two types of Heck reactions were tested. In the case of styrene, in the tyramine series (monomer, generations 0, 1, and 3) the best results were obtained with generation zero at 40°C, and generation one at 70°C; in the L-tyrosine series the best results were also obtained with the first generation at 70°C. In the case of Heck reactions with ethyl acrylate at 40°C, the best results were obtained with generation one in the L-tyrosine series, and with generation zero in the tyramine series. Recycling experiments were successfully carried out with the later series. In general, we observed that the dendritic ligands issued from

the tyramine series are more efficient than the dendrimers issued from the L-tyrosine series. A paper including members the 3 teams is accepted for publication to *Organometallics*. [A22]

## A.2 Joint Publications in Refereed journals (from the beginning of the project)

- [A1] (CNR-UAL) C. Ciardi, G. Reginato, L. Gonsalvi, I. de los Rios, A. Romerosa, M. Peruzzini "Ruthenium(II)  $\pi$ -Alkyne and Vinylidene Complexes Derived from Glycoynitols: New Precursors for Water-Soluble Unsaturated Carbenes" *Organometallics* **2004**, *23*, 2020 (Article)
- [A2] (CNR-UAL) S. Bolaño, L. Gonsalvi, F. Zanobini, F. Vizza, V. Bertolasi, A. Romerosa, M. Peruzzini "Water soluble ruthenium cyclopentadienyl and aminocyclopentadienyl PTA complexes as catalysts for selective hydrogenation of  $\alpha,\beta$ -unsaturated olefins. (PTA = 1,3,5-triaza-7-phosphaadamantane) *J. Mol. Catal. A: Chem.* **2004**, *224*, 61 (Article)
- [A3] (CNRSLCC/b-IST) A. M. Martins, C. C. Romão, M. Abrantes, M. C. Azevedo, J. Cui, A. R. Dias, M. T. Duarte, M. A. Lemos, T. Lourenço, R. Poli: "Molybdenum and Tungsten Cyclopentadienyl Oxo Monomers and Dimers: Syntheses and Applications in Olefin Epoxidation Catalysis" *Organometallics* **2005**, *24*, 2582-2589. (Article)
- [A4] (UAL-CNR) C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano Ruiz, L. Gonsalvi, M. Peruzzini, "Stable, water soluble PTA based Ru-Ag organometallic polymers" *Angew. Chem. Int. Ed.* **2005**, *44*, 2568 (Article)
- [A5] (UD-UAB) G. Kovács, G. Ujaque, A. Lledós, F. Joó: "Theoretical investigation of the selective C=C hydrogenation of unsaturated aldehydes catalyzed by  $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$  in acidic media.", *Organometallics* **2006**, *25*, 862-872 (Article)
- [A6] (UAL-CNR) A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J.A. Garrido-Cárdenas, F. García-Maroto: "Synthesis, Characterization and DNA Activity of New Water Soluble Cyclopentadienyl Ruthenium(II) Complexes Incorporating Phosphines." *Inorg. Chem.* **2006**, *45*, 1289 - 1298 (Article)
- [A7] (INEOS-UAB) O.A. Filippov, A.M. Filin, V.N. Tsupreva, N.V. Belkova, A. Lledós, G. Ujaque, L.M. Epstein, E.S. Shubina, "Proton Transfer and H<sub>2</sub> Elimination Reaction of Main Group Hydrides  $\text{EH}_4^-$  (E = B, Al, Ga) with Alcohols", *Inorg. Chem.* **2006**, *45*, 3086-3096 (Article)
- [A8] (UAB-UD) A. Rossin, G. Kovács, G. Ujaque, A. Lledós, F. Joó: "Regioselective C=O hydrogenation of trans-cinnamaldehyde to cinnamyl alcohol with the water-soluble complexes  $[\text{RuH}_2(\text{mtppps})_x]$  ( $x=3,4$ ;  $\text{mtppps}=(\text{meta-sulphonatophenyl})\text{diphenylphosphine}$ ). A theoretical study of the reaction mechanism and selectivity." *Organometallics* **2006**, *25*, 5010 - 5023. (Article)
- [A9] (INEOS-UAB) N.V. Belkova, E.I. Gutsul, O.A. Filippov, V.A. Levina, D.A. Valyaev, L.M. Epstein, A. Lledós, E.S. Shubina, "Intermolecular Hydrogen Bonding Between Neutral Transition Metal Hydrides  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$  (M = Mo, W) and Bases" *J. Am. Chem. Soc.* **2006**, *128*, 3486-3487 (Communication)
- [A10] (HUJI-CNR-UAL) Gutkin, V.; Gun, J.; Prikhodchenko, P. V.; Lev, O.; Gonsalvi, L.; Peruzzini, M.; Romerosa, A.; Campos Malpartida, T.; Lidrissi, C. "Electrooxidation of ruthenium cyclopentadienyl PTA complexes in DMF: ESI-MS, cyclic voltammetry and on-line electrochemistry/ESI-MS studies" *J. Electrochem Soc.* **2007**, *154*, F7-F15 (Article)
- [A11] (CNRSLCC/a-CNR) P. Servin, C. Rebout, R. Laurent, M. Peruzzini, A.M., Caminade, J.P. Majoral, "Reduced number of steps for the synthesis of dense and highly functionalized dendrimers". *Tetrahedron Lett.* **2007**, *48*, 579-583 (Article)
- [A12] (UAB-CNR) Rossin, A.; Gonsalvi, L.; Phillips, A. D.; Maresca, O.; Lledós, A.; Peruzzini, M. "Water-assisted H-H Bond Splitting Mediated by  $[\text{Cp}(\text{Ru})(\text{PTA})_2\text{Cl}]$  (PTA = 1,3,5-triaza-7-phosphaadamantane)" *Organometallics* **2007**, *26*, 3289-3296 (Article)

- [A13] (UAB-UD) **Kovács, G.**; Ujaque, G.; Lledós, A.; Joó, F. “The role of water in the stereoselective hydrogenation of 1,2-diphenylacetylene catalyzed by the water soluble  $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$ . A theoretical study” *Eur. J. Inorg. Chem.* **2007**, 2879-2889 (**Article**)
- [A14] (CNRS/LCC/b-UEN-UAB) J.-E. Jee, A. Comas-Vives, **C. Dinoi**, G. Ujaque, R. Van Eldik, A. Lledós, R. Poli: “Nature of  $\text{Cp}^*\text{MoO}_2^+$  in water and intramolecular proton transfer mechanism by stopped-flow kinetics and DFT calculations” *Inorg. Chem.* **2007**, 46, 4103-4113 (**Article**)
- [A15] (CNRS/LCC/b-HUJI) **C. Dinoi**, **P. Prihodchenko**, F. Demirhan, J. Gun, O. Lev, J.-C. Daran, R. Poli: “Reduction of  $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$  by mercaptopropionic acid in an aqueous medium. Isolation and characterization of a dinuclear oxo- and 3-sulfido-propionato(2-)-bridged molybdenum(IV) compound” *J. Organomet. Chem.* **2007**, 692, 2599-2605(**Article**).
- [A16] (INEOS-CNR) N. V. Belkova, T. N. Gribanova, E. I. Gutsul, R. M. Minyaev, C. Bianchini, M. Peruzzini, F. Zanobini, L. M. Epstein, E. S. Shubina “Specific and non-specific influence of the environment on dihydrogen bonding and proton transfer to  $[\text{RuH}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]$ ” *J. Mol. Structure* **2007**, 884-885, 115-131 (**Article upon invitation**)
- [A17] (CNRS/LCC/b-HUJI) **C. Dinoi**, P. Sözen, G. Taban, D. Demir, F. Demirhan, **P. Prihodchenko**, J. Gun, O. Lev, J.-C. Daran, R. Poli: “Aqueous reduction of  $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ : characterization of the triangular clusters  $[\text{Cp}^*_3\text{W}_3\text{O}_4(\text{OH})_2]^{2+}$  and  $[\text{Cp}^*_3\text{W}_3\text{O}_6]^+$ . Comparison with molybdenum” *Eur. J. Inorg. Chem.* **2007**, 4306-4316 (**Article**)
- [A18] (UAL-CNR) Ciardi, C.; Romerosa, A., Serrano-Ruiz, M.; Gonsalvi, L.; Peruzzini, M.; Reginato, G. “Synthesis of New Enantiomerically Enriched  $\beta$ -Hydroxy,  $\gamma$ -Amino Phosphines by Selective Transformation of Naturally Occurring Amino Acids” *J. Org. Chem.* **2007**, 72, 7787 – 7789 (**Note**)
- [A19] (CNR-IST) S. Bolaño, J. Bravo, J.A. Castro, M.M. Rodríguez-Rocha, M.F.C. Guedes da Silva, A.J.L. Pombeiro, L. Gonsalvi, M. Peruzzini, “Synthesis, Reactivity, X-ray Crystal Structures and Electrochemical Behaviour of Water-soluble [Tris-(pyrazolyl)borato]ruthenium(II) Complexes of 1,3,5-triaza-7-phosphaadamantane (PTA)”, *Eur. J. Inorg. Chem.* **2007**, 5523-5532 (**Article**)
- [A20] (UAL-UD) T. Campos-Malpartida, M. Fekete, F. Joó, Á. Kathó, A. Romerosa, M. Saoud, **W. Wojtków** “Redox Isomerization of Allylic Alcohols Catalysed by Water-soluble Ruthenium Complexes in Aqueous Systems” *J. Organometal. Chem.* **2008**, 693, 468-474 (**Article**)
- [A21] (CNRS/LCC/b-CNR) M. Ciclosi, **C. Dinoi**, L. Gonsalvi, M. Peruzzini, E. Manoury, R. Poli “Oxidation of thiophene derivatives with  $\text{H}_2\text{O}_2$  in acetonitrile catalyzed by  $[\text{Cp}^*_2\text{M}_2\text{O}_5]$  (M = Mo, W): a kinetic study” *Organometallics* **2008** accepted (**Article**).
- [A22] (CNRS/LCC/a-CNR-UAL) **P. Servin**, R. Laurent, A. Romerosa, M. Peruzzini, J.P. Majoral, A.M. Caminade “Synthesis of dendrimers ended by bis(diphenylphosphinomethyl) amino ligands and use of their Palladium complexes for catalyzing C-C cross-coupling reactions” *Organometallics* **2008** accepted (**Article**).
- [A23] (CNRS/LCC/b-UAB) A. Comas-Vives, G. Ujaque, A. Lledós, R. Poli “A computational study of the olefin epoxidation mechanism catalyzed by cyclopentadienyloxidomolybdenum(VI) complexes” in preparation.
- [A24] (INEOS-UAB) N.V. Belkova, V.A. Levina, O.A. Filippov, D.A. Valyaev, L.M. Epstein, A. Lledós, E.S. Shubina, “Solvent effect on the deprotonation of transition metal hydrides  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$  (M = Mo, W) by bases” in preparation
- [A25] (INEOS-UAB) O. Filippov, V. Tsupreva, E. Shubina, L. Epstein, A. Lledós, “Computational Analysis of Solvent Effects in Dihydrogen Bonding” in preparation
- [A26] (CNR-UAL) **Mallqui Ayala, I. M.**; Gonsalvi, L.; Peruzzini, M.; Romerosa, A.; Serrano Ruiz, M. “Water phase ketone hydrogenations with ruthenium(II) complexes bearing sulfonated phosphines and diamines” in preparation.

- [A27] (UAL-CNR) **Mallqui Ayala, I. M.**; Serrano Ruiz, M.; Romerosa, A.; Gonsalvi, L.; Peruzzini, M. "Synthesis and reactivity of water soluble allenylidene ruthenium complexes bearing Cp(CONC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> and phosphines" in preparation.
- [A28] (CNRSLCC/a-CNR) **P. Servin, M. Tristany**, R. Laurent, A.M. Caminade, J.P. Majoral, L. Gonsalvi, M. Peruzzini: "Ru(II)-PTA dendrimers as catalysts in Water phase", in preparation.

### A.3 Joint Publications in Conference Proceedings (from the beginning of the project)

- [B1] (CNR-UAL) Peruzzini M., Bolaño Garcia S., Bosquain S., Campos T., Gonsalvi L., Lidrissi C., Mañas Carpio S., Phillips A. D., Romerosa A., Saoud M., Serrano-Ruiz M. "Nuovi complessi metallici idrosolubili stabilizzati dalla fosfina PTA (PTA = 1,3,5-triaza-7-fosfadamantano)", *XXXII National Italian Conference of Inorganic Chemistry*, Roma, Italy, 20/25-09-2004 (oral presentation).
- [B2] (CNR-UAL) Romerosa A., Campos T., Lidrissi C., Saoud M., Serrano M., Gonsalvi L., Bolaño S., Peruzzini M. "New water soluble vinylidene and allenylidene ruthenium complexes containing hydrosoluble phosphines and cyclopentadiene derivatives" *Green Solvents For Synthesis*, Bruchsal, Germany, 3/6-10-2004 (Keynote lecture sponsored by COSTD29 Management Committee as "COST Awarded Lecture")
- [B3] (CNR-UAL) Bolaño S., Gonsalvi L., Zanobini F., Vizza F., Bertolasi V., Romerosa A., Peruzzini M. "Regioselective hydrogenation of benzylidene acetone and cinnamaldehyde catalysed by water soluble ruthenium complexes" - 7<sup>th</sup> Post-graduate Summer School on Green Chemistry; Venice, Italy, 5/21-09-2004 (poster presentation).
- [B4] (CNR-UAL) Ciardi, C.; Gonsalvi, L.; Peruzzini, M.; Reginato, G.; Romerosa, A.; Serrano, M. Synthesis of New Chiral Water Soluble Phosphines from Naturally Occurring Amino Acids *OMCOS 13 – IUPAC Symposium on Organometallic Chemistry directed towards Organic Synthesis*, Geneva, Switzerland, 17-21 July 2005 (poster presentation).
- [B5] (CNR-UAL) Ciardi C., Di Credico B., Gonsalvi L., Peruzzini M., Reginato G., Romerosa A., Serrano M. "Sintesi di Nuove Fosfine Chirali Solubili in Acqua Ottenute dalla Elaborazione Sintetica di Amminoacidi Naturali" *XXX CONGRESSO NAZIONALE DELLA DIVISIONE DI CHIMICA ORGANICA*, Siena, 19/23-9-2005, Atti del Congresso. Abstract P1 (poster presentation).
- [B6] (UAB-UD) **A.Rossin**, G.Ujaque, A.Lledós, G. Kovács, F.Jóo "Computational studies of selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with ruthenium(II) catalysts" XXXIII Congresso Nazionale della Divisione di Chimica Inorganica della Società Chimica Italiana; July 11-16<sup>th</sup> 2005, Siena (Italy) (oral presentation)
- [B7] (UAB-UD) **A.Rossin**, G.Ujaque, A.Lledós, G. Kovács, F.Jóo "Regioselective C=C/C=O hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with ruthenium(II) water-soluble complexes: a computational mechanistic study" ISHHC-XII; July 18-22<sup>nd</sup> 2005, Firenze (Italy) (oral communication)
- [B8] (UAB-UD) **A.Rossin**, G.Ujaque, A.Lledós, G. Kovács, F.Jóo "Regioselective C=O hydrogenation of trans-cinnamaldehyde to cinnamyl alcohol with the water-soluble complexes (H)<sub>2</sub>Ru(m-TPPMS)<sub>x</sub> [x=3,4; m-TPPMS=(meta-sulphonatophenyl)diphenylphosphine]. A theoretical study of the reaction mechanism and selectivity" Conference DFT2005; September 11-15<sup>th</sup> 2005, Genève (Switzerland) (poster presentation)
- [B9] (UAB-INEOS) V.A. Levina, N.V. Belkova, E.I. Gutsul, D.A. Valyaev, O.A. Filippov, L.M. Epstein, E.S. Shubina, A. Lledos "First instances of neutral hydride complexes as proton donors in the intermolecular hydrogen bonding" *International Conference "From molecules towards materials"*, Nizhny Novgorod, Russia, September 3-10, 2005
- [B10] (UAL-CNR) **Mallqui, M.**; Serrano-Ruiz, M.; Romerosa, A.; Gonsalvi, L.; Peruzzini, M. "Aqueosoluble ruthenium complexes with the Cp(CONC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> ligand and PPh<sub>3</sub>, PTA, mPTA and TPPMS" *XXIIInd ICOMC, 22nd International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July 2006 (poster presentation)



- [B11] (CNR-UAB) **Rossin, A.**; Gonsalvi, L.; Peruzzini, M.; Phillips, A. D.; Lledos, A., Maresca, O. “The active role of the water solvent in the dihydrogen activation in Ru(II) water soluble complexes bearing PTA ligands: a DFT analysis (PTA=1,3,5-triaza-7-phospha-adamantane)” *XXIInd ICOMC, 22nd International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July 2006 (**poster presentation**)
- [B12] (CNR-UAB) **Rossin, A.**; Gonsalvi, L.; Peruzzini, M.; Phillips, A. D.; Lledos, A. “Water-assisted dihydrogen activation in Ruthenium PTA complexes: a DFT study (PTA=1,3,5-triaza-7-phospha-adamantane)” *XXII CONGRESSO NAZIONALE DELLA SOCIETA' CHIMICA ITALIANA*, Firenze, Italy, 10-15 September 2006 (**oral presentation**)
- [B13] (UAB-UD) **Kovács, G.**; Ujaque, G.; Lledós, A.; Joó, F. “Theoretical investigation of the stereoselective reduction of diphenylacetylene in acidic aqueous solutions catalyzed by water-soluble phosphine complexes of ruthenium(II)” *Experiment & Theory in Transition Metal Chemistry: a meeting point*” Barcelona, Spain, 27-29 September, 2006, (**oral presentation**)
- [B14] (YoK- HUJI) Perutz, R. N.; Duhme-Klair, A.K; Reddig N.; Gunn, J.; Ovadia, L.; Excited State Switching & Photo-induced Electron Transfer in Catecholate-Rhenium Assemblies, COST D35 Lausanne, Sept 2006
- [B15] (UAB-UD) Lledós, A.; Rossin, A.; Kovács, G.; Ujaque, G.; Joó, F. “Computational modelling of aqueous organometallic catalysis” *XXXVII<sup>th</sup> ICCO, 37<sup>th</sup> International Conference on Coordination Chemistry*, Cape Town, South Africa, 13-18 August 2006 (**oral presentation**)
- [B16] (UAB-UD) **Kovács, G.**; Ujaque, G.; Lledós, A.; Joó, F. “Theoretical investigation of the stereoselective reduction of diphenylacetylene in aqueous acidic solutions catalyzed by water soluble Ru(II) phosphine complexes” *XXIInd ICOMC, 22nd International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July 2006 (**poster presentation**)
- [B17] (UAB-UD) **Kovács, G.**; Ujaque, G.; Lledós, A.; Joó, F. “Theoretical investigation of the stereoselective reduction of diphenylacetylene in acidic aqueous solutions, catalyzed by water soluble phosphine complexes of ruthenium(II)” *Workshop “Experiment & Theory in Transition Metal Chemistry: a meeting point*, Bellaterra, Spain, 27-29 September 2006 (**oral presentation**)
- [B18] (CNRSLCCb-UAB-UEN) Poli, R.; **Dinoi, C.**; Lledós, A.; Comas-Vives, A.; Ujaque, G.; van Eldik, R. Jee, J.-J. “Speciation and oxygen exchange mechanism of Cp\*MoV I oxo complexes in water” *Workshop “Experiment & Theory in Transition Metal Chemistry: a meeting point*, Bellaterra, Spain, 27-29 September 2006 (**plenary lecture**)
- [B19] (CNR-UAB) **Rossin, A.**; Gonsalvi, L.; Peruzzini, M.; Phillips, A. D.; Lledos, A.; Maresca, O. “H<sub>2</sub> activation mediated by Ru(II) PTA water-soluble complexes: how the water solvent takes an active part in the process (PTA=1,3,5-triaza-7-phosphaadamantane)” *Workshop “Experiment & Theory in Transition Metal Chemistry: a meeting point*, Bellaterra, Spain, 27-29 September 2006 (**oral presentation**)
- [B20] (CNRSLCC/b-UEN) **C. Dinoi**, R. Poli, J.-E. Jee, A. Zahl, R. van Eldik: “Acid-base chemistry of Cp\*2Mo2O5 and 17O NMR studies of water exchange in the Cp\*Mo(VI) oxo systems”, *Journées de la Chimie de Coordination*, Toulouse, France, 3-4 April 2006. (**poster presentation**)
- [B21] (CNRSLCC/b-UEN-UAB) R. Poli, **C. Dinoi**, A. Lledós, A. Comas-Vives, G. Ujaque, R. van Eldik, J.-E. Jee: “Speciation and oxygen exchange mechanism of Cp\*MoVI oxo complexes in water”, *Experiment and Theory in Transition Metal Chemistry: a meeting point*, Bellaterra, Spain, Sept 28-29, 2006 (**oral presentation**)
- [B22] (INEOS-UAB) O.A. Filippov, A.M. Filin, A. Lledós, G. Ujaque, V.N. Tsupreva, V.V. Gavrilenko, V.I. Bregadze, N.V. Belkova, E.S. Shubina “Dihydrogen bonding and proton transfer to anionic hydrides of the main group elements” *XXII International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July, 2006
- [B23] (INEOS-CNR) N. V. Belkova, E. I. Gutsul, T. N. Gribanova, R. M. Minyaev, C. Bianchini, M. Peruzzini, F. Zanobini, L. M. Epstein, E. S. Shubina “Solvent effect on dihydrogen bonding and proton transfer to transition metal hydrides” *XXII International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July, 2006
- [B24] (CNRSLCC/a-IST) **P. Servin**, R. Laurent, **R. Wanke**, A. Pombeiro, J.-P. Majoral, A.-M. Caminade, “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”, *Catalysis In Aqueous Media -CIAM workshop*, Toulouse, France, Nov 30-Dec 1, **2007**.
- [B25] (CNRS/SLCC/a-CNR) **P. Servin, M. Tristany**, R. Laurent, A.M. Caminade, J.P. Majoral, L. Gonsalvi, M. Peruzzini: “Water-soluble dendritic catalysts”, *Figipas07*, Vienna (Austria), 4-7 July **2007** (**Poster presentation**)
- [B26] (CNRS/SLCC/a-CNR) **P. Servin, M. Tristany**, R. Laurent, A.M. Caminade, J.P. Majoral, L. Gonsalvi, M. Peruzzini: “Ru(II) Catalysis in the Presence of Water with a PTA Dendritic Ligand”, *IDS5 International dendrimer symposium, Toulouse (France)*, 28 August-1 September **2007** (**Poster presentation**)
- [B27] (CNRS/SLCC/a-CNR) **P. Servin**, C. Rebout, R. Laurent, M. Peruzzini, A.M. Caminade, J.P. Majoral: “Reduced number of steps for the synthesis of dense and highly functionalized dendrimers”, *IDS5 International dendrimer symposium, Toulouse (France)*, 28 August-1 September **2007** (**Poster presentation**)
- [B28] (CNRS/SLCC/a-CNR) **P. Servin**, R. Laurent, L. Gonsalvi, M. Peruzzini, J.P. Majoral, A.M. Caminade: “PTA ligands as end groups of water-soluble phosphorus dendrimers. Use of their Ru(II) complexes as catalysts” *Catalysis In Aqueous Media-CIAM workshop*, Toulouse, France, Nov 30-Dec 1, **2007** (**Poster presentation**)
- [B29] (CNRS/SLCC/a-CNR-UAL) **P. Servin**, R. Laurent, A. Romerosa, M. Peruzzini, J.P. Majoral, A.M. Caminade: “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.” *Catalysis In Aqueous Media -CIAM workshop*, Toulouse, France, Nov 30-Dec 1, **2007** (**Poster presentation**)
- [B30] (CNRS/SLCC/b-CNR) **C. Dinoi**, L. Gonsalvi, M. Peruzzini, R. Poli: “Binuclear cyclopentadienyl oxo molybdenum and tungsten complexes as catalysts for aryl thiophenes oxidation using H<sub>2</sub>O<sub>2</sub>”, *3rd International Conference on Green and Sustainable Chemistry*, Delft, The Netherlands, 1-5 July **2007** (poster)
- [B31] (CNRS/SLCC/b-UEN-UAB) A. Comas-Vives, J.-E. Jee, **C. Dinoi**, G. Ujaque, A. Lledós, R. van Eldik, R. Poli: “A Theoretical Study of the Cp\*MoO<sub>2</sub><sup>+</sup> Complex in Water and on its Use as Epoxidation Catalyst”, *Symposium on Relations between Homogeneous and Heterogeneous Catalysis*, San Francisco, CA, USA, July 16-20, **2007**. (**Poster presentation**)
- [B32] (CNRS/SLCC/b-CNR) **C. Dinoi**, M. Ciclosi, S. Vincendeau, R. Poli, L. Gonsalvi, M. Peruzzini: “Efficient oxidation of thiophene derivatives catalyzed by organomolybdenum and –tungsten oxido complexes”, *Catalysis in Aqueous Media Workshop*, Toulouse, France, November 30- December 1, **2007**.
- [B33] (CNRS/SLCC/b-CNR) **C. Dinoi**, M. Ciclosi, S. Vincendeau, R. Poli, L. Gonsalvi, M. Peruzzini: “Efficient oxidation of thiophene derivatives catalyzed by organomolybdenum and –tungsten oxido complexes”, *235th ACS National Meeting, Cotton Memorial Symposium*, New Orleans, LA, April 6-10, **2008** (poster).
- [B34] (UAB-UD) **Kovács, G.**; Ujaque, G.; Lledós, A.; Joó, F.: „Modelització de la reactivitat organometàlica en aigua: hidrogenació de molècules insaturades”, *XIIIena Reunió de la Xarxa de Química Teòrica de Catalunya*, Tarragona, Spain, 4-5 July **2007** (Oral presentation)
- [B35] (CNR-UAL) **Mallqui Ayala, I. M.**; Gonsalvi, L.; Peruzzini, M.; Romerosa, A.; Serrano Ruiz, M. “Water phase catalytic hydrogenations with ruthenium(II) complexes bearing sulfonated phosphines and diamines” *9<sup>th</sup> FIGIPAS Meeting in Inorganic Chemistry* Vienna, Austria, 4-7 July 2007.
- [B36] (CNR-UAL) **Mallqui Ayala, I. M.**; Serrano Ruiz, M.; Romerosa, A.; Gonsalvi, L.; Peruzzini, M. “Synthesis and reactivity of water soluble allenylidene ruthenium complexes bearing Cp(CONC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> ligand and PPh<sub>3</sub>, PTA, mPTA and TPPMS” *6<sup>th</sup> ISOC International School of Organometallic Chemistry* Camerino, Italy, 8-12 September 2007
- [B37] (CNR-UAL) **Mallqui Ayala, I. M.**; Gonsalvi, L.; Peruzzini, M.; Romerosa, A.; Serrano-Ruiz, M. “Catalytic hydrogenations in water phase using ruthenium(II) complexes bearing sulfonated phosphines and diamines” *CIAM Workshop – Catalysis in Aqueous Media* Toulouse, France, 30 November-1 December 2007.
- [B38] (UAL-UAB-CNR) **Petersen, E.**; **Kovacs, G.**; Serrano, M.; Lledos, A.; Romerosa, A.; Ciardi, C.; Reginato, G.; Peruzzini, M. “Deboronation of phosphines containing amino acids. Theoretical and

experimental results” *CIAM Workshop – Catalysis in Aqueous Media* Toulouse, France, 30 November-1 December 2007.

- [B39] (UAL-YoK) A. Romerosa, **R. Girotti**, S. Mañas, R. Perutz “Photochemical behaviour of the water soluble complex  $[\text{RuCl}_2(\text{PTA})_4]$ , *CIAM Workshop – Catalysis in Aqueous Media* Toulouse, France, 30 November-1 December 2007.
- [B40] (INEOS-UAB) Levina V. A., Belkova N. V., Gutsul E. I., Filippov O. A., Valyaev D. A., Lledos A., Epstein L. M., Shubina E. S. “Neutral Metal Hydrides As Proton Donors In Hydrogen Bonding And Proton Transfer” *XVIII Mendeleev Congress on General and Applied Chemistry*, Moscow 23-28 September 2007.
- [B41] (INEOS-UAB) O. Filippov, V. Tsupreva, E. Shubina, L. Epstein, A. Lledos, “Solvent Effects in Dihydrogen Bonding: A Computational Analysis” *CIAM Workshop – Catalysis in Aqueous Media* Toulouse, France, 30 November-1 December 2007.

#### A.4 Joint Patents (from the beginning of the project)

(UAL-CNR) A. Romerosa, T. Campos Malpartida, C. Lidrissi, M. Peruzzini. “Nuevos catalizadores para la metátesis de olefinas en medio acuoso”. Spanish Patent Application P200502298 (2005)

#### A.5 Publications acknowledging RTN AQUACHEM in Refereed journals without joint coauthorships (from the beginning of the project)

- [C1] (CNRS/SLCC/a) R. Laurent, A.M. Caminade, J.P. Majoral: “A third generation chiral phosphorus-containing dendrimer as ligand in Pd-catalyzed asymmetric allylic alkylation” *Tetrahedron Lett.* **2005**, 46, 6503-6506.
- [C2] (CNRS/SLCC/b) F. Demirhan, B. Çagatay, D. Demir, M. Baya, J.-C. Daran, R. Poli: “Reduction of  $\text{Cp}^*_2\text{Mo}_2\text{O}_5$  in an aqueous medium. Structure and properties of a triangular mixed oxo-hydroxo-bridged product,  $[\text{Cp}^*_3\text{Mo}_3(\mu\text{-O})_2(\mu\text{-OH})_4](\text{X})_2$ , with  $\text{X} = \text{CF}_3\text{CO}_2$  or  $\text{CF}_3\text{SO}_3$ ” *Eur. J. Inorg. Chem.*, **2006**, 757.
- [C3] (CNRS/SLCC/b) F. Demirhan, G. Taban, M. Baya, **C. Dinoi**, J.-C. Daran, R. Poli: “Reduction of  $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$  by thioglycolic acid in an aqueous medium. Synthesis and structure of  $[\{\text{Cp}^*\text{Mo}(\mu\text{-SCH}_2\text{COO})\}_2(\mu\text{-S})]$ ”, *J. Organometal. Chem.*, **2006**, 691, 648.
- [C4] (IST) E. Reisner, V.B. Arion, A. Eichinger, N. Kandler, G. Geister, A.J.L. Pombeiro and B.K. Keppler, “Tuning of Redox Properties for the Design of Ruthenium Anticancer Drugs: Part 2 Syntheses, Crystal Structures and Electrochemistry of Potentially Antitumor  $[\text{Ru}^{\text{III/II}}\text{Cl}_{6-n}(\text{azole})_n]^z$  ( $n = 3,4,6$ ) Complexes”, *Inorg. Chem.*, **2005**, 44, 6704-6716.
- [C5] (IST) A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M.F.C. Guedes da Silva and A.J.L. Pombeiro, “Multinuclear Copper Triethanolamine Complexes as Selective Catalysts for the Peroxidative Oxidation of Alkanes under Mild Conditions”, *Angew. Chem., Int. Ed.*, **2005**, 44, 4345-4349.
- [C6] (IST) A.M. Kirillov, M. Haukka, M.F.C. Guedes da Silva and A.J.L. Pombeiro, “Preparation and Crystal Structures of Benzoylhydrazido- and -diazenidorhenium Complexes with N,O-Ligands and Their Catalytic Activity towards Peroxidative Oxidation of Cycloalkanes”, *Eur. J. Inorg. Chem.*, **2005**, 2071-2080.
- [C7] (IST) A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, **E. Yu. Karabach**, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, “Mild peroxidative oxidation of cyclohexane catalysed by mono-, di-, tri-, tetra- and polynuclear copper triethanolamine complexes”, *Adv. Synth. Cat.*, **2006**, 348, 159-174.
- [C8] (CNR) Di Vaira M., Frediani P., Seniori Costantini S., Peruzzini M., Stoppioni P., “Plane Hydrolysis of Ruthenium-Coordinated White Phosphorus Affording High Stable  $\text{PH}_3$  Complexes” *Dalton Trans.*, **2005**, 2234 – 2236.

- [C9] (CNR) D. N. Akbayeva, M. Peruzzini, L. Gonsalvi, A. Ienco, F. Vizza “On the Protonation of Ruthenium-PTA Complexes in Water. X-ray crystal structure of  $\text{RuCl}_4(\text{PTAH})_2 \cdot 4\text{H}_2\text{O}$  (PTA = 1,3,5-triaza-7-phosphaadamantane)” *Compt. Rend. Chimie.* **2005**, *8*, 1491 – 1496. (Article)
- [C10] (CNRS/LCC/b) E. Collange, L. Metteau, P. Richard, R. Poli “Synthesis and structure of a new organometallic polyoxomolybdate,  $\text{Cp}^*_2\text{Mo}_6\text{O}_{17}$ ”, *Polyhedron* **2004**, *23*, 2605-2610. (Article)
- [C11] (YoK) A. F. A. Peacock, H. D. Batey, C. Raendler, A. C. Whitwood, R. N. Perutz and A. K. Duhme-Klair “A metal-based lumophore tailored to sense biologically relevant oxometalates” *Angew Chem. Int. Ed.* **2005**, *44*, 1712-1714 (Article).
- [C12] (IST) E. Reisner, V.B. Arion, M.F.C. Guedes da Silva, R. Lichtenecker, A. Eichinger, B.K. Keppler, V. Yu. Kukushkin and A.J.L. Pombeiro “Tuning of Redox Potentials for the Design of Ruthenium Anticancer Drugs — an Electrochemical Study of  $[\text{trans-RuCl}_4\text{L}(\text{DMSO})]^-$  and  $[\text{trans-RuCl}_4\text{L}_2]$  Complexes, where L = Imidazole, 1,2,4-Triazole, Indazole” *Inorg. Chem.* **2004**, *43*, 7083. (Article)
- [C13] (IST) Q. Li, M.F.C. Guedes da Silva, Z. Jinghua and A.J.L. Pombeiro “Diorganotin(IV) Derivatives of Arylhydroxamic Acids. Synthesis, Properties and Antitumour Activity” *J. Organomet. Chem.* **2004**, *689*, 4584. (Article)
- [C14] (UAB) M. Viciano, M. Poyatos, M. Sanaú, E. Peris, A. Rossin, G. Ujaque, A. Lledós “C-H Oxidative Addition of Bisimidazolium Salts to Ir and Rh Complexes, and N-Heterocyclic Carbene Generation. A combined Experimental and Theoretical study” *Organometallics* **2006**, *25*, 1120-1134. (Article)
- [C15] (UD) G. Papp, H. Horváth, Á. Kathó, F. Joó: “Aqueous Organometallic Chemistry. Synthesis and Solution Equilibria of Trisodium Carbonylchlorotris[3-(diphenylphosphino-κP)benzenesulfonato]-hydridoruthenate(3-) ( $[\text{RuH}(\text{Cl})(\text{CO})\{m\text{-(Ph}_2\text{P)-C}_6\text{H}_4\text{-SO}_3\text{Na}\}_3]$ ) and Trisodium Aquacarbonyltris[3-(diphenylphosphino-κP)benzenesulfonato]-hydridoruthenate(2-) Tetrafluoroborate(1-) ( $\text{RuH}(\text{CO})(\text{H}_2\text{O})\text{-}\{m\text{-(Ph}_2\text{P)-C}_6\text{H}_4\text{-SO}_3\text{Na}\}_3$ )  $[\text{BF}_4]$ ”, *Helvetica Chimica Acta*, **2005**, *88*, 566 (Article)
- [C16] (UD) G. Kovács, G. Schubert, F. Joó, I. Pápai: “Theoretical Mechanistic Study of Rhodium(I) Phosphine-Catalyzed H/D Exchange Processes in Aqueous Solutions”, *Organometallics*, **2005**, *24*, 3059 (Article)
- [C17] (UD) J. Kovács, F. Joó, and C. D. Frohning: “Anion effects in the formation of the active catalyst in the Ruhrchemie-Rhône Poulenc aqueous biphasic hydroformylation process. Are there any?” *Canadian J. Chem.*, **2005**, *83*, 1033 (Article)
- [C18] (UD) M. Fekete, F. Joó: Redox isomerization of allylic alcohols in aqueous-organic biphasic systems catalyzed by water-soluble Ru(II)-N-heterocyclic carbene complexes.” *Catal. Commun.*, **2006**, *7*, 783-786 (Article)
- [C19] (UD) G. Kovács, G. Schubert, F. Joó, I. Pápai: “Theoretical investigation of catalytic  $\text{HCO}_3^-$  hydrogenation in aqueous solutions.” *Catalysis Today*, **2006**, *115*, 53-60 (Article)
- [C20] (UD) H. H. Horváth, F. Joó: “Stereoselective homogeneous catalytic hydrogenation of disubstituted alkynes in aqueous-organic biphasic media.” *React. Kinet. Catal. Lett.* **2005**, *85*, 355 (Article)
- [C21] (UD) H. H. Horváth, G. Papp, C. Csajági, F. Joó: “Selective catalytic hydrogenations in a microfluidics-based high throughput flow reactor on ion-exchange supported transition metal complexes. A modular approach to the heterogenization of soluble complex catalysts.” *Catal. Commun.*, **2007**, *8*, 442-446 (Article)
- [C22] (UD) P. Csabai, F. Joó, A. M. Trzeciak, J. J. Ziólkowski: “Catalytic activity of a half-sandwich Ru(II)-N-heterocyclic carbene complex in the oligomerization of alkynes.” *J. Organomet. Chem.*, **2006**, *691*, 3371-3376 (Article)
- [C23] (UEN) A. Theodoridis and R. van Eldik: “The role of positively charged meso-substituents on the kinetics of the reductive nitrosylation of iron(III)-porphyrins. The catalytic role of nitrite.” *J. Mol. Cat. A*, **2004**, *224*, 197-205 (Article)
- [C24] (UEN) P. Illner, A. Zahl, R. Puchta, N.J.R. van Eikema Hommes, P. Wasserscheid and R. van Eldik: “Mechanistic studies on the formation of Pt(II) hydroformylation catalysts in imidazolium-based ionic liquids.” *J. Organomet. Chem.*, **2005**, *690*, 3567-3576 (Article)
- [C25] (UEN) R. Puchta, N.J.R. van Eikema Hommes and R. van Eldik: “Evidence for interchange ligand-exchange processes on solvated beryllium cations.” *Helv. Chim. Acta*, **2005**, *88*, 911-922 (Article)

- [C26] (UEN) C.F. Weber, R. Puchta, N.J.R. van Eikema-Hommes, P. Wasserscheid and R. van Eldik: "Transition-state effects of ionic liquids in substitution reactions of Pt(II) complexes." *Angew. Chem. Int. Ed.*, **2005**, 44, 6033-6038 (Article)
- [C27] (HUJI) I. Gun J, Ekeltchik I, Lev O, Shelkov R, Melman A "Bis-(hydroxyamino) triazines: highly stable hydroxylamine-based ligands for iron(III) cations", *Chem Commun* **2005**, 5319-5321 (Communication)
- [C28] (HUJI) I. Ekeltchik, J. Gun, O. Lev, R. Shelkov and A. Melman, "Bis-hydroxyaminotriazines: Versatile and high-affinity hydroxylamine ligands for iron(III) chelation" *Dalton* 2006 1285-1293 (Article)
- [C29] (HUJI) A. Goifman, J. Gun, F. Gelman, I. Ekeltchik, E. Worch, and O. Lev "Catalytic oxidation of thiol compounds by novel fuel cell - inspired Co-porphyrin and Co-imidazole catalysts", *Israel J. Chem.* 2006, 46, 17-26 (Article)
- [C30] (CNR) Landaeta V., Peruzzini M., Herrera V., Bianchini C., Sánchez-Delgado R. A., Goeta, A. E., Zanobini F. "Synthesis, Characterization and Reactivity of Tribenzylphosphine Rhodium and Iridium Complexes" *J. Organomet. Chem.* **2006**, 691, 1039 - 1050.
- [C31] (CNR) Landaeta V., Muñoz B. K., Peruzzini M., Herrera V., Bianchini C., Sánchez-Delgado R. A. "Imine Hydrogenation by Tribenzylphosphine Rhodium and Iridium Complexes" *Organometallics*, **2006**, 25, 403 - 409.
- [C32] (CNR) Landaeta V., Gonsalvi, L., Peruzzini M. "Ruthenium catalyzed selective oxidation of aryl thiophenes using hydrogen peroxide" *J. Mol. Catal. A: Chem.* **2006**, 257, 112-117.
- [C33] (CNR) Dorcier, A.; Ang, W. H.; Bolaño, S.; Gonsalvi, L.; Juillerat-Jeannerat, L.; Laurency, G.; Peruzzini, M.; Phillips, A. D.; Zanobini, F.; Dyson, P. J. "In vitro evaluation of rhodium and osmium RAPTA analogues: the case for organometallic anticancer drugs not based on ruthenium" *Organometallics* **2006**, 25, 4090-4096.
- [C34] (CNRS/LCC/a) I. Angurell, C.O. Turrin, R. Laurent, V. Maraval, P. Servin, O. Rossell, M. Seco, A.M. Caminade, J.P. Majoral, "Decorating step-by-step and independently the surface and the core of dendrons". *J. Organomet. Chem.* **2007**, 692, 1928-1939 (Article)
- [C35] (UEN) J.-E. Jee and R van Eldik: "Mechanistic studies on the nitrite-catalyzed reductive nitrosylation of highly charged anionic and cationic Fe<sup>III</sup>-porphyrin complexes" *Inorg. Chem.*, **2006**, 45, 6523-6534 (Article)
- [C36] (HUJI) J. Gun, P. Salaüna and C.M.G. van den Berg "Advantages of using a mercury coated, micro-wire, electrode in adsorptive cathodic stripping voltammetry" *Anal. Chim. Acta*, **2006**, 71, 86-92.
- [C37] (HUJI) A. Amrani, A. Kamyshny, Jr., O. Lev, Z. Aizenshtat, "Sulfur stable isotopes distribution of polysulfide anions in (NH<sub>4</sub>)<sub>2</sub>S<sub>n</sub> aqueous solution" *Inorg. Chem.* **2006**, 45, 1427-1429.
- [C38] (HUJI) A. Kamyshny, Jr., I. Ekeltchik, J. Gun O. Lev, "A Method for the Determination of Inorganic Polysulfide Distribution in Aquatic Systems" *Anal. Chem.* **2006**, 78, 2631-2639.
- [C39] (IST) D.S. Nesterov, V. N. Kokozay, V.V. Dyakonenko, O. V. Shishkin, J. Jezierska, A. Ozarowski, A.M. Kirillov, M.N. Kopylovich, A.J.L. Pombeiro, "An Unprecedented Heterotrimetallic Fe/Cu/Co Core for Mild and Highly Efficient Catalytic Oxidation of Cycloalkanes by Hydrogen Peroxide", *Chem. Commun.*, **2006**, 4605-4607.
- [C40] (IST) Y.Yu. Karabach, A.M. Kirillov, M.F.C. Guedes da Silva, M.N. Kopylovich, A.J.L. Pombeiro, "An Aqua-soluble Copper(II) - sodium 2D Coordination Polymer with Intercalated Infinite Chains of Decameric Water Clusters", *Crystal Growth & Design*, **2006**, 6, 2200-2203.
- [C41] (IST) E.C.B. Alegria, L.M.D.R.S. Martins, M. Haukka, A.J.L. Pombeiro, "Rhenium Complexes of Tris(pyrazolyl)methanes and Sulfonate Derivative", *Dalton Trans.*, **2006**, 4954-4961.
- [C42] (IST) A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, E. Yu. Karabach, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, "Mild peroxidative oxidation of cyclohexane catalysed by mono-, di-, tri-, tetra- and polynuclear copper triethanolamine complexes", *Adv. Synth. Cat.*, **2006**, 348, 159-174.
- [C43] (UD) M. Fekete, F. Joó, "Transfer Hydrogenation of Carbonyl Compounds and Alkenes Catalyzed by Ruthenium(II)-N-Heterocycle Carbene Complexes." *Collect. Czech. Chem. Commun.* **2007**, 72, 1037-1045.

- [C44] (UD) I. Józszai, F. Joó, “Hydrogenation of Calcium Carbonate in Aqueous Systems Catalyzed by Rh(I)- and Ru(II)-Complexes using Poly(methylhydrosiloxane) or Hypophosphite as Hydrogen Sources.” *React. Kinet. Catal. Lett.* **2007**, *91*, 361-368.
- [C45] (UAL) P. Bergamini, V. Bertolasi, A. Canella, R. Gavioli, N. Mantovani, S. Mañas, A. Romerosa, “Phosphinic Platinum Complexes With 8-Thiotheophylline Derivatives: Synthesis, Characterization And Antiproliferative Activity”, *Inorg. Chem.* **2007**, *46*, 4267-4276.
- [C46] (UAL) A. Mena-Cruz, P. Lorenzo-Luis, A. Romerosa, M. Saoud, M. Serrano-Ruiz, “Synthesis Of The Water Soluble Ligands Dmpta, Dmopta And The Complex [Ruclep(Hdmopta)(Pph<sub>3</sub>)](Cf<sub>3</sub>so<sub>3</sub>) (Dmpta = N,N<sup>o</sup>-Dimethyl-1,3,5-Triaza-7-Phosphaadamantane; Dmopta = 3,7-Dimetyl-1,3,7-Triaza-5-Phosphabicyclo[3.3.1]Nonane; Hdmopta = 3,7-H-3,7-Dimetyl-1,3,7-Triaza-5-Phosphabicyclo[3.3.1]Nonane)”, *Inorg. Chem.* **2007**, *46*, 6120-6128.
- [C47] (IST) A.J.L.Pombeiro, “Vanadium-catalyzed Alkane Functionalization Reactions under Mild Conditions”, in “Vanadium: the Versatile Metal”, K.Kustin, J.C. Pessoa, D.C. Crans (eds.), American Chemical Society Symposium Series, No. 974, American Chemical Society, Oxford University Press, **2007**, Ch.4, pp.51-60.
- [C48] (IST) E.C.B. Alegria, M.V. Kirillova, L.M.D.R.S. Martins, A.J.L. Pombeiro, “Pyrazole and Trispyrazolymethane Rhenium Complexes as Catalysts for Ethane and Cyclohexane Oxidations”, *Appl. Cat. A: Gen.*, **2007**, *317*, 43-52.
- [C49] (IST) C. Di Nicola, Y. Yu. Karabach, A.M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari, A.J.L. Pombeiro, “Supramolecular Assemblies of Trinuclear Triangular Copper(II) Secondary Building Units through Hydrogen Bonds. Generation of Different Metal-Organic Frameworks, Valuable Catalysts for Peroxidative Oxidation of Alkanes”, *Inorg. Chem.*, **2007**, *46*, 221-230.
- [C50] (IST) M.N. Kopylovich, M. Haukka, A.M. Kirillov, V. Yu. Kukushkin, A.J.L. Pombeiro, “Unsymmetrical Ni<sup>II</sup>-Imidoylamidine Complexes Derived from a Novel Oxime-mediated Single-pot Reaction of Nitriles”, *Chem. Eur. J.*, **2007**, *13*, 786-791.
- [C51] (IST) M.V. Kirillova, M.F.C. Guedes da Silva, A.M. Kirillov, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, “3D Hydrogen Bonded Heteronuclear Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> Aqua Complexes Derived from Dipicolinic Acid”, *Inorg. Chim. Acta*, **2007**, *360*, 506-512.
- [C52] (IST) G.B. Shul’pin, G.S. Mishra, L.S. Spul’pina, T.V. Strelkova, A.J.L. Pombeiro, “Oxidation of Hydrocarbons with Hydrogen Peroxide Catalysed by Maltolato Vanadium Complexes Covalently Bonded to Silica Gel”, *Cat. Commun.*, **2007**, *8*, 1516-1520.
- [C53] (IST) A.M. Kirillov, P. Smolénski, M.F.C. Guedes da Silva, A.J.L. Pombeiro, “The First Copper Complexes Bearing the 1,3,5-Triaza-7-phosphaadamantane (PTA) Ligand”, *Eur. J. Inorg. Chem.*, **2007**, 2686-2692.
- [C54] (IST) M.V. Kirillova, A.M. Kirillov, P.M. Reis, J.A.L. Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, “Group 5-7 Transition Metal Oxides as Efficient Catalysts for Oxidative Functionalization of Alkanes under Mild Conditions”, *J. Catal.*, **2007**, *248*, 130-136.
- [C55] (IST) M.N. Kopylovich, E.A. Tronova, M. Haukka, A.M. Kirillov, V.Yu. Kukushkin, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, “Identification of Hexameric Water and Hybrid Water-Chloride Clusters Intercalated in the Crystal Hosts of (Imidoylamidine)nickel(II) Complexes”, *Eur. J. Inorg. Chem.*, **2007**, 4621-4627.
- [C56] (UEN) M. Brindell, D. Piotrowska, A.A. Shoukry, G. Stochel and R. van Eldik.: “Kinetics and mechanism of the reduction of (ImH)[*trans*-RuCl<sub>4</sub>(dmsO)(Im)] by ascorbic acid in acidic aqueous solution” *J. Biol. Inorg. Chem.*, **2007**, *12*, 809-818 (Article)
- [C57] (HUJI) Kamyshny A, Gun J, Rizkov D, Voitsekovski T, Lev O, “Equilibrium distribution of polysulfide ions in aqueous solutions at different temperatures by rapid single phase derivatization” *Environmental Science & Technology* **2007**, *41* (7), 2395-2400 (Article)
- [C58] (CNRS/LCC/a) Caminade A.M., Servin P., Laurent R., Majoral J.P. “Dendrimeric phosphines in asymmetric catalysis” *Chem. Soc. Rev.* **2008**, *37*, 56.
- [C59] (LCC/b) C. Dinói, G. Taban, P. Sözen, F. Demirhan, J.-C. Daran, R. Poli: “Improved syntheses of [Cp\*<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>] and [Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub>]. Structural characterization of Na[Cp\*MoO<sub>3</sub>].5H<sub>2</sub>O and [Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub>]”, *J. Organomet. Chem.* **2007**, *692*, 3743–3749. (Article)

- [C60] (LCC/b) R. Poli: "High Oxidation State Organomolybdenum and Organotungsten Chemistry in Protic Environments", *Coord. Chem. Rev.* submitted (invited review for a special issue).
- [C61] (UAB) Kovács, G.; Ujaque, G.; Lledós, A.: "Theoretical analysis of the gold(I) catalyzed hydroamination of 1,3-dienes" *J. Am. Chem. Soc.* **2008**, *130*, 853-864 (Article)
- [C62] (CNR) Bosquain, S. S.; Dorcier, A.; Dyson, P. J.; Erlandsson, M.; Gonsalvi, L.; Laurency, G.; Peruzzini, M. "Aqueous phase carbon dioxide and bicarbonate hydrogenation catalysed by cyclopentadienyl ruthenium complexes" *Appl. Organomet. Chem.* **2007**, *21*, 947-951 (Article)
- [C63] (CNR) Erlandsson, M.; Landaeta, V. R.; Gonsalvi, L.; Peruzzini, M.; Phillips, A. D.; Dyson, P.J.; Laurency, G. Methylcyclopentadienyl iridium PTA complexes and their application in catalytic water phase carbon dioxide hydrogenation (PTA = 1,3,5-triaza-7-phosphaadamantane) *Eur. J. Inorg. Chem.* **2008**, 620-627. (Article)
- [C64] (CNR) Erlandsson, M.; Gonsalvi, L.; Ienco, A.; Peruzzini, M. "Diastereomerically enriched analogues of the water soluble phosphine PTA. Synthesis of phenyl-(1,3,5-triaza-7-phosphatricyclo [3.3.1.1<sup>3,7</sup>]dec-6-yl)methanol (PZA) and the Sulfide PZA(S) and X-ray Crystal Structures of the Oxide PZA(O) and [Cp\*IrCl<sub>2</sub>(PZA)]" *Inorg. Chem.* **2008**, *47*, 8-10 (Communication)
- [C65] (HUJI) Kamyshny A, Gun J, Rizkov D, Voitsekovski T, Lev O, "Equilibrium distribution of polysulfide ions in aqueous solutions at different temperatures by rapid single phase derivatization" *Env. Sci. and Technol.* **2007**, *41*, 2395-2400.
- [C66] (UEN) M. Wolak and R. van Eldik, "Mechanistic studies on peroxide activation by a water-soluble iron(III) porphyrin. Implications for O-O bond activation in aqueous and non-aqueous solvents" *Chem. Eur. J.* **2007**, 4873-4883 (Article)
- [C67] (UEN) H. Hanauer, R. Puchta, T. Clark and R. van Eldik "Searching for stable five-coordinate, aquated Al(III) species. Water exchange mechanism and effect of pH" *Inorg. Chem.*, **2007**, *46*, 1112-1122 (Article)
- [C68] (UEN) A. Franke, F. Roncaroli and R. van Eldik "Mechanistic studies on the activation of NO by iron and cobalt complexes" *Eur. J. Inorg. Chem.*, **2007**, 773-798 (Microreview)
- [C69] (UEN) D. Chatterjee, A. Mitra and R. van Eldik "Reaction of [Ru<sup>III</sup>(edta)(H<sub>2</sub>O)]<sup>-</sup> with H<sub>2</sub>O<sub>2</sub> in aqueous solution. Kinetic and mechanistic investigation" *Dalton Trans.*, **2007**, 943-948 (Article)
- [C70] (UEN) J.-E. Jee, S. Eigler, N. Jux, A. Zahl and R. van Eldik "Influence of an extremely negatively charged porphyrin on the reversible binding kinetics of NO to Fe(III) and the subsequent reductive nitrosylation" *Inorg. Chem.*, **2007**, *46*, 3336-3352 (Article)
- [C71] (UEN) J. Maignut, R. Meier, A. Zahl and R. van Eldik „Elucidation of the solution structure and water-exchange mechanism of paramagnetic [Fe<sup>II</sup>(edta)(H<sub>2</sub>O)]<sup>2-</sup>" *Inorg. Chem.*, **2007**, *46*, 5361-5371 (Article)
- [C72] (UEN) N. Hessenauer-Ilicheva, A. Franke, D. Meyer, W.-D. Woggon and R. van Eldik „Low-temperature rapid-scan detection of reactive intermediates in epoxidation reactions catalyzed by a new enzyme mimic of cytochrome P450" *J. Am. Chem. Soc.*, **2007**, *129*, 12473-12479 (Article)
- [C73] (UEN) P. Illner, S. Kern, S. Begel and R. van Eldik „Rapid ligand substitution reactions in ionic liquids studied by stopped-flow technique" *Chem. Commun.*, **2007**, 4803-4805 (Communication)
- [C74] (UEN) T.D. Dolidze, D.E. Khoshtariya, P. Illner, L. Kulisiewicz, A. Delgado and R. van Eldik "High-pressure testing of heterogeneous charge transfer in a room-temperature ionic liquid: Evidence for solvent dynamic control" *J. Phys. Chem. B*, **2008**, *112*, 3085-3100 (Article)
- [C75] (UEN) A. Theodoridis, J. Maignut, R. Puchta, E.V. Kudrik and R. van Eldik "A novel iron(III)-porphyrin complex. Complex speciation and reactions with NO and H<sub>2</sub>O<sub>2</sub>" *Inorg. Chem.*, in press
- [C76] (UEN) T.D. Dolidze, D.E. Koshtariya, P. Illner and R. van Eldik "Heterogeneous electron transfer at Au/SAM junctions in a room-temperature ionic liquid under pressure" *Chem. Commun.*, in press
- [C77] (YoK) Batey, H. D.; Whitwood, A.C.; Duhme-Klair, A. K. "Synthesis, Characterization, Solid-State Structures, and Spectroscopic Properties of Two Catechol-Based Luminescent Chemosensors for Biologically Relevant Oxometalates" *Inorg. Chem.* **2007**, *46*, 6516-6528 (Article)

## A.6 Publications in Conference Proceedings without joint coauthorship (from the beginning of the project)

- [D1] (CNR) **Landaeta, V.**; Gonsalvi, L.; Peruzzini, M. "Ruthenium – Catalyzed Selective Oxidation of Aryl Thiophenes Using H<sub>2</sub>O<sub>2</sub>" (poster) ISHHC XII, *12<sup>th</sup> International Symposium on Relations between Homogeneous and Heterogeneous Catalysis* Fiesole, Italy, 18-22 July 2005.
- [D2] (CNRS/SLCC/a) R. Laurent, M. Zablocka, **P. Servin**, C. Padié, A.M. Caminade, J.P. Majoral: "Phosphorus dendrimers: complexation and catalysis" (poster) 1<sup>er</sup> colloque Maroc-Français de Chimie Moléculaire, Rabat, Morocco, 26/28-01-2005
- [D3] (CNRS/SLCC/a) **P. Servin**, R. Laurent, A.M. Caminade, J.P. Majoral: "Synthesis of PTA bearing phosphorus dendrimers" (oral) Journées Jeunes Chercheurs de la SFC, Toulouse, France, 7/8-04-2005
- [D4] (CNRS/SLCC/a) A.M. Caminade, R. Laurent, **P. Servin**, J.P. Majoral: "Organometallic phosphorus dendrimers and their use as catalysts" (oral) XVI FECEM Conference on Organometallic Chemistry, Budapest, Hungary, 3/8-09-2005
- [D5] (CNRS/SLCC/b) **C. Dinoi**, R. Poli, J.-C. Daran, M. Baya, F. Demirhan, G. Taban "Réactions des complexes hémimétallo-céniques de molybdène(VI) avec des composés souffrés" (poster) *GECOM-CONCOORD 2005*, Autrans, France, June 5-10, 2005
- [D6] (CNRS/SLCC/b) **C. Dinoi**, R. Poli, J.-C. Daran, M. Baya, F. Demirhan, G. Taban: "Reactions of Hemimetallo-cenic Molybdenum(VI) Complexes with Sulfur Compounds" (poster) *5<sup>th</sup> International School of Organometallic Chemistry (ISOC)*, Camerino, Italy, Sept 10-14, 2005
- [D7] (CNR) M. Peruzzini "Catalytic activation of white phosphorus: reality or fairy tale?" *5<sup>th</sup> International School on Molecular Catalysis (ISMC-5)*. Poznan, - Rosnowko, Poland, 12/16-08-2005. Book of Abstracts. L27. (Invited keynote lecture)
- [D8] (CNR) Di Vaira M., Frediani P., Seniori Costantini S., Peruzzini M., Stoppioni P. "From P<sub>4</sub> to PH<sub>3</sub> metal complexes by plane hydrolysis" (poster) *XX Congress of the International Union of Crystallography*, Florence, Italy, 23/31-08-2005. Acta Cryst. 2005, A61, C298 - P.07.01.14. (poster presentation)
- [D9] (CNR) M. Peruzzini "The Astonishing Organometallic Chemistry of Phosphorus: Achievements and Perspectives in the functionalization of Elemental Phosphorus" *5<sup>th</sup> International School of Organometallic Chemistry (ISOC)* Camerino, Italy, Sept 10-14, 2005 (Invited keynote lecture)
- [D10] (CNR) **Landaeta, V.**; Gonsalvi, L.; Peruzzini, M "Oxidación catalítica selectiva de aril tiofenos utilizando complejos de rutenio y H<sub>2</sub>O<sub>2</sub>" *VII Congreso Venezolano de Química* Merida, Venezuela, 6/10-11-2005, Abstract CA35. (oral communication)
- [D11] (CNR) Peruzzini M. "Organometallic chemistry of white phosphorus" *XXX Reunión Bienal de la Real Sociedad Española de Química* Lugo, Spain, 19/23-09-2005. Conferencias y Comunicaciones Resúmenes. Abstract GII-I7, p 169. (Invited session lecture)
- [D12] (IST) **E. Yu. Karabach**, A.M. Kirillov, M.N. Kopylovich, M.F.C. Guedes da Silva, M. Haukka, A.J.L. Pombeiro, "New Self-Assembled Copper 1D- and 2D-Coordination Polymers as Catalysts for Biphasic Peroxidative Oxidation of Cyclohexane under Mild Conditions", *Current and Future Trends in Polymeric Materials*, Prague, Czech Republic, 2005, PC 23.
- [D13] (IST) A.M. Kirillov, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, "Rhenium Benzoylhydrazido and -Diazenido Complexes with N,O-Ligands and Their Application in the Catalytic Peroxidative Oxidation of Cycloalkanes", *20<sup>th</sup> Intern. Conf. on Coordination and Bioinorganic Chemistry*, Smolenice, Bratislava, Slovakia 2005, 56.
- [D14] (UD) H. Horváth, G. Papp, Á. Kathó, F. Joó: "Metamorphosis of the [RuHCl(CO)(mtppps)<sub>3</sub>] catalyst during the hydrosilylation of alkynes in aqueous-organic biphasic systems." *Int. Conf. on Knowledge-*



*based Materials and Technologies for Sustainable Chemistry* (Tallinn, Estonia, 2005), Book of Abstracts, p. 56 (poster presentation)

- [D15] (UD) F. Joó, H. H. Horváth, G. Papp: „Hydrogenations on supported Ru(II)- and Rh(I)-complex catalyst using the H-Cube™ reactor.” *1<sup>st</sup> Int. Microfluidic-Based Hydrogenation Course*, Thales Nanotechnology Inc. (Budapest, Hungary, September 8, 2005) (invited oral presentation)
- [D16] (UAB) A. Lledós “New Approaches in the Activation of Unreactive Bonds : Interplay between Experiment and Computation” XVIth FEChem Conference on Organometallic Chemistry; September 3-8<sup>th</sup> 2005, Budapest (Hungary) (invited plenary lecture)
- [D17] (UEN) A. Brausam and R. van Eldik: “New mechanistic insight into the long known reaction between Fe<sup>III</sup>(edta) and hydrogen peroxide.” *Inorganic Reaction Mechanisms Meeting*, Athens (Greece), 2004 (Poster)
- [D18] (UEN) R. Meier, J. Maigut and R. van Eldik: “Ternary Fe<sup>III/II</sup>(edta)-fluoride complexes – Efforts to optimize NO uptake by Fe<sup>II</sup>(edta).” *Inorganic Reaction Mechanisms Meeting*, Athens (Greece), 2004 (Oral contribution)
- [D19] (UEN) A. Theodoridis and R. van Eldik: “The role of positively charged meso-substituents on the kinetics of the reductive nitrosylation of an iron(III)-porphyrine.” *Inorganic Reaction Mechanisms Meeting*, Athens (Greece), 2004 (Poster)
- [D20] (UEN) R. van Eldik; “Mechanistic details on the binding of NO to different metal centers.” *Inorganic Reaction Mechanisms Meeting*, Athens (Greece), 2004 (Plenary lecture)
- [D21] (UEN) R. van Eldik: “Mechanistic details of the interaction of NO with metal complexes in aqueous solution.” *5<sup>th</sup> Netherlands Catalysis and Chemistry Conference*, Noordwijkerhout (The Netherlands), 2004 (Plenary lecture)
- [D22] (UEN) R. van Eldik: “Mechanistic insight gained from volume profile analysis.” *National Meeting of the American Chemical Society*, Anaheim, Los Angeles (USA), 2004 (Invited lecture)
- [D23] (UEN) R. van Eldik: “Tuning the lability of Pt(II) complexes. Steric, electronic and medium effects.” *36<sup>th</sup> International Conference on Coordination Chemistry*, Merida (Mexico), 2004 (Invited lecture)
- [D24] (UEN) R. van Eldik: “Electronic tuning of the lability of inert Co(III) and Pt(II) complexes.” *228<sup>th</sup> National Meeting of the American Chemical Society*, Philadelphia (USA), 2004 (Invited lecture)
- [D25] (UEN) R. van Eldik: “Elucidation of inorganic reaction mechanisms from high pressure kinetics.” *42<sup>nd</sup> EHPRG Meeting on Advances in High Pressure Research*, Lausanne (Switzerland), 2004 (Plenary lecture)
- [D26] (UEN) R. van Eldik: “Pressure tuning of fast electron and charge transfer processes in inorganic and bioinorganic chemistry.” *Fast Reactions in Solution Discussion Group Meeting*, Burgos (Spain), 2004 (Plenary lecture)
- [D27] (UEN) R. van Eldik: “Mechanistic interpretation of activation volumes. Correlation with other activation parameters.” *Inorganic Reaction Mechanisms Meeting*, Liverpool (UK), 2005 (Plenary lecture)
- [D28] (UEN) P. Illner and R. van Eldik: “Mechanistic study on the formation of active species in a hydroformylation reaction in two imidazolium-based ionic liquids.” *Inorganic Reaction Mechanisms Meeting*, Liverpool (UK), 2005 (Poster)
- [D29] (UEN) C. Weber, R. Puchta and R. van Eldik: “The ionic liquid [BMIM]BTA as a fascinating solvent for substitution reactions on a Pt(II) complex.” *Inorganic Reaction Mechanisms Meeting*, Liverpool (UK), 2005 (Poster)

- [D30] (UEN) R. van Eldik: "To be or not to be NO? A mechanistic approach in coordination chemistry" *INORG 2005*, Pietermaritzburg (South Africa), 2005 (Plenary lecture)
- [D31] (UEN) R. van Eldik: "Elucidation of inorganic and bioinorganic reaction mechanisms from volume profile analysis." *Joint 20<sup>th</sup> AIRAPT - 43<sup>rd</sup> EHPRG Meeting*, Karlsruhe (Germany), 2005 (Plenary lecture)
- [D32] (UEN) C.F. Weber, P. Illner, R. Puchta and R. van Eldik: "Mechanistic studies on the reactivity of Pt(II) complexes in imidazolium-based ionic liquids." *First International Congress on Ionic Liquids*, Salzburg (Austria), 2005 (Poster)
- [D33] (UEN) A. Brausam and R. van Eldik: "Chasing intermediates: How do Fe(III)(TAML) complexes bleach dyes?" *9<sup>th</sup> International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidation*, Cologne (Germany), 2005 (Poster)
- [D34] (UEN) A. Theodoridis, M. Wolak and R. van Eldik: "Mechanistic studies on peroxo O-O bond activation by a model iron(III) porphyrin (TMPS)Fe(III) in aqueous solution." *9<sup>th</sup> International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidation*, Cologne (Germany), 2005 (Poster)
- [D35] (UEN) R. van Eldik: "Mechanistic studies on the reaction of NO with cytochrome P450 and model iron(III) complexes." *3<sup>rd</sup> International SFB Conference on Metal Mediated Reactions Modeled after Nature*, Jena (Germany), 2005 (Invited lecture)
- [D36] (CNRS/LCC/a) P. Servin, R. Laurent, A.M. Caminade, J.P. Majoral: "New dendritic water-soluble ruthenium(II) catalysts" *Journées Grand Sud-Ouest*, Montpellier, France, November 25<sup>th</sup>, 2005 (oral communication)
- [D37] (CNRS/LCC/a) I. Angurell, C.O. Turrin, R. Laurent, V. Maraval, P. Servin, O. Rossell, M. Seco, A.M. Caminade, J.P. Majoral, "Decorating step-by-step and independently the surface and the core of dendrons". *2<sup>èmes</sup> Journées Franco-Catalanes de Chimie Moléculaire*, Toulouse, France, February 1-2<sup>nd</sup>, 2007 (invited lecture)
- [D38] (UD) M. Fekete, F. Joó: „Synthesis of new Ru(II) and Rh(I) carbene complexes and their application for the catalysis of the redox isomerisation of allylic alcohols and in hydrogen transfer reactions" *42<sup>nd</sup> Colloquium on Metal Complex Chemistry*, Mátrafüred, Hungary, May 31-June 02, 2006 (oral presentation)
- [D39] (UD) Á. Kathó, J. Molnár, G. Papp, F. Joó: „Effect of NaI on the biphasic hydrogenation of cinnamaldehyde catalyzed by  $[RuCl_2(mtppps)_2]_2$ " *42<sup>nd</sup> Colloquium on Metal Complex Chemistry*, Mátrafüred, Hungary, May 31-June 02, 2006 (oral presentation)
- [D40] (UD) F. Joó, M. Fekete, H. Horváth, Á. Kathó, J. Elek: „Water-soluble N-heterocyclic complexes of rhodium and ruthenium", *Experiment & Theory in Transition Metal Chemistry: a meeting point*" Barcelona, Spain, 27-29 September, 2006 (oral presentation)
- [D41] (UD) H. Horváth, Á. Kathó, F. Joó, E. Sola, M. Martín: „Reactions of  $[RuCl(NCMe)_4(PiPr_3)](BF_4)$  in Aqueous and Organic Media: Synthetic, Equilibrium and Catalytic Studies", *XXI<sup>Ind</sup> ICOMC, 22<sup>nd</sup> International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July 2006 (poster presentation)
- [D42] (UD) R. Jones, Cs. Csajági, F. Joó, H. Horváth, G. Papp, J. Gerencsér, F. Darvas: „Fast optimization of chemo- and stereoselective reactions using a continuous-flow hydrogenation reactor" *231<sup>st</sup> ACS National Meeting*, Atlanta, GA, USA, March 26-30, 2006 (oral presentation)
- [D43] (UD) F. Joó, „Aqueous Organometallic Catalysis: new role for an ancient solvent", *Groh Seminarium - 2006*, Eötvös University, Budapest, Hungary, Dec 07, 2006 (oral presentation)

- [D44] (UD) Á. Kathó, M. Fekete, H. Horváth, H. H. Horváth, G. Papp, F. Joó: „Biphasic Organometallic Catalysis with water-Soluble Ruthenium(II) Complexes”, University of Rovira i Virgili, Tarragona, Spain, April 29, 2006 (invited lecture)
- [D45] (UD) F. Joó, „New trends in organometallic catalysis. Storm in a glass of water?” Hungarian Academy of Sciences, Budapest, Hungary November 7, 2006 (invited lecture)
- [D46] (UEN) Mechanistic studies on the reaction of NO with cytochrome P450 and model iron(III) complexes, R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Plenary lecture).
- [D47] (UEN) Chasing intermediates: How do Fe(TAML) complexes bleach dyes?, A. Brausam, R. Puchta, N. van Eikema Hommes and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D48] (UEN) Thermodynamic and kinetic studies on the binding of nitric oxide to the RSO<sub>3</sub><sup>-</sup>-substituted model complex for cytochrome P450, A. Franke, N. Hessenauer-Ilicheva, D. Meyer, G. Stochel, W.-D. Woggon and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D49] (UEN) From interchange to dissociative water exchange on aquated Al<sup>3+</sup> ions, Hans Hanauer, R. Puchta, T. Clark and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D50] (UEN) Experimental and theoretical studies on ion pair interaction in ionic liquids containing the [emim]<sup>+</sup>-cation, P. Illner, R. Puchta and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D51] (UEN) Comparative study of the interaction of NO with highly positively- and negatively-charged iron(III) porphyrins, J.-E. Jee, M. Wolak, N. Jux and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D52] (UEN) Reactivity of a novel low spin Fe(II) complex. Medium-induced spin-crossover behaviour and its ability to catalyze oxidation reactions, E.V. Kudrik, A. Theodoridis and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D53] (UEN) The mechanism of water exchange on a series of iron aminopolycarboxylate complexes, J. Maigut, R. Meier, A. Zahl and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D54] (UEN) High pressure <sup>7</sup>Li NMR kinetic study of Li<sup>+</sup> complexation by cryptands in gamma-butyrolactone, E.Pasgreta, R. Puchta, N. van Eikema Hommes, A. Zahl and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D55] (UEN) Exploring the mechanism of C-H activation of hydrocarbons through detailed mechanistic studies on Pt(II) and Pt(IV) complexes, J. Procelewska and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D56] (UEN) Substituent effects on the ligand exchange processes of solvated beryllium cations, R. Puchta, M. Galle, N. van Eikema Hommes and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D57] (UEN) Kinetic investigation of a series of multinuclear Pt(II) complexes with biological relevant nucleophiles, N. Summa, H. Ertürk and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D58] (UEN) Mechanistic studies on the activation of H<sub>2</sub>O<sub>2</sub> by a novel Fe<sup>III</sup>-porphyrazine complex, A. Theodoridis, E. Kudrik and R. van Eldik, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).

- [D59] (UEN) Kinetics and mechanism of the reduction of (ImH)[*trans*-RuCl<sub>4</sub>(dmsO)(Im)] by ascorbic acid in acidic aqueous solution, **M. Brindell**, D. Piotrowska, A. Szumlanska, R. van Eldik and G. Stochel, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D60] (UEN) Transmetallation of chlorophyll *a*. Effect of acetate on the kinetics of magnesium to copper(II) exchange, **L. Orzel**, M. Wolak, L. Fiedor, R. van Eldik and G. Stochel, 35<sup>th</sup> Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D61] (UEN) To be or not to be NO? A mechanistic approach in coordination chemistry, R. van Eldik, Biannual Conference on Chemistry, Cairo (Egypt), 2006 (Plenary lecture).
- [D62] (UEN) Activation of small molecules. Mechanistic insight from volume profiles, R. van Eldik, Bunsentagung, Erlangen (Germany), 2006 (Invited lecture).
- [D63] (UEN) Experimental and theoretical studies on the mechanistic behaviour of catalytic-relevant metal complexes in ionic liquids, P. Illner, C.F. Weber, R. Puchta, N. van Eikema Hommes and R. van Eldik, Bunsentagung, Erlangen (Germany), 2006 (Poster).
- [D64] (UEN) DFT-calculations on the water exchange mechanisms for aquated iron ions, R. Puchta, N. van Eikema Hommes and R. van Eldik, Bunsentagung, Erlangen (Germany), 2006 (Poster).
- [D65] (UEN) Fascinating inorganic and bioinorganic reaction mechanisms: From fundamental insight to edutainment, R. van Eldik, 37<sup>th</sup> International Conference on Coordination Chemistry, Cape Town (South Africa), 2006 (Plenary lecture).
- [D66] (YoK) Applications of Siderophore Analogues in Metallosupramolecular Chemistry, A. Mueller, **N. Reddig**, R. N. Perutz, A. J. Wilkinson, A.-K. Duhme-Klair, 37<sup>th</sup> International Conference on Coordination Chemistry, Cape Town, South Africa, August 2006.
- [D67] (YoK) Luminescent Sensors for Biologically Relevant Oxometallates, A.-K. Duhme-Klair, R. N. Perutz, H. D. Batey, **N. Reddig**, EU COST Working Group 35 Meeting, Lausanne, Switzerland, September 2006.
- [D68] (YoK) Luminescent Sensors Studied by Ultrafast Laser Spectroscopy, A.-K. Duhme-Klair, R. N. Perutz, H. D. Batey, **N. Reddig**, Laser for Sciences Facility User Meeting, Oxford, November 2006
- [D69] (IST) E. Alegria, **R. Wanke**, L. Martins, A. Pombeiro, "Synthesis and Electrochemical Behaviour of Scorpionate Iron Complexes", *XXII International Conference on Organometallic Chemistry*, (Zaragoza, Spain, 2006), P78, p. 266 (poster presentation) .
- [D70] (IST) **Y. Karabach**, A.M. Kirillov, M.F.C. Guedes da Silva, M.N. Kopylovich, A.J.L. Pombeiro, "Catalytic Activity of an Aqua-soluble Copper(II)-sodium Two-dimensional Coordination Polymer in the Peroxidative Oxidation of Cyclohexane", *ETTMC – Experiment and Theory in Transition Metal Chemistry*, (Barcelona, Spain, 2006), P11, p. 45 (poster presentation).
- [D71] (IST) **S. Sbovata**, M.F.C. Guedes da Silva, R.A. Michelin, A.J.L. Pombeiro, "Water-soluble Organonitrile Platinum(II) Complexes", *ETTMC – Experiment and Theory in Transition Metal Chemistry*, (Barcelona, Spain, 2006), P12, p. 46 (poster presentation).
- [D72] (IST) **P. Sgarbossa**, A.M. Kirillov, M.F.C. Guedes da Silva, P. Smolenski, A.J.L. Pombeiro, R.A. Michelin, "[PtCl(C<sub>6</sub>F<sub>5</sub>)(PTA)<sub>2</sub>] and Re-picolinate Complexes and their Application in the Catalytic Epoxidation of 1-Octene", *ETTMC – Experiment and Theory in Transition Metal Chemistry*, (Barcelona, Spain, 2006), P13, p. 47 (poster presentation).
- [D73] (IST) A.J.L. Pombeiro, "Metal and Ligand Effects on the Redox Potencial of Coordination Compounds", *4<sup>th</sup> Chianti Meeting on Electrochemistry*, (Siena, Italy, 2006), p. 11 (invited lecture).
- [D74] (IST) A.J.L. Pombeiro, "Vanadium Catalysed Alkane Functionalization Reactions under Mild Conditions", *5<sup>th</sup> Int. Symp. Chemical and Biological Chem. of V*, (S. Francisco, USA, 2006), 046 INOR853, p. 30 (invited lecture).

- [D76] (IST) T.F.S. Silva, L.M.D.R.S. Martins, A.J.L. Pombeiro, "Some Copper and Vanadium Tris(pyrazolyl)methane Complexes as Catalysts for the Peroxidative Oxidation of Cycloalkanes", *1<sup>st</sup> European Chemistry Congress*, (Budapest, Hungary, 2006), C-PO-139, p. 64 (poster presentation).
- [D77] (IST) L.M.D.R.S. Martins, E.C.B.A. Alegria, A.J.L. Pombeiro, "Scorpionate Iron Complexes as Catalysts for the Peroxidative Oxidation of Cyclohexane in Aqueous Medium", *1<sup>st</sup> International IUPAC Conference on Green-Sustainable Chemistry*, (Dresden, Germany, 2006), I.2-004, p. 239 (poster presentation).
- [D78] (INEOS) N.V.Belkova, V.A. Levina, A.I.Krylova, E.I. Gutsul, L.M. Epstein, E.S. Shubina, "Intermolecular hydrogen bonding of neutral transition metal hydrides with organic bases and other hydrides" *Experiment and Theory in Transition Metal Chemistry: a meeting point*, Bellaterra, Spain, Sept 28-29, 2006.
- [D79] (UD) A. Almássy, F. Joó: Preparation of water soluble Au(I)-NHC complexes and their catalytic activity in hydration of terminal alkynes (oral); XLIII. Colloquium on Complex Chemistry, May 23-25, Mátrafüred, Hungary
- [D80] (UD) M. Fekete, F. Joó F: transfer hydrogenation of aldehydes and ketones catalyzed by ruthenium(II)- and rhodium(I)-N-heterocyclic carbene complexes (oral, in Hungarian); XLIII. Colloquium on Complex Chemistry, May 23-25, Mátrafüred, Hungary
- [D81] (UD) H. H. Horváth, F. Joó: Catalytic properties of ionic Ru(II) and Rh(I) complexes in aqueous/organic biphasic systems and ion-exchange supports (oral, in Hungarian); XLIII. Colloquium on Complex Chemistry, May 23-25, Mátrafüred, Hungary
- [D82] (UD) A.Udvardy, Á. Kathó: Selective hydrogenation of sorbic acid catalyzed by Rh- and Ru-phosphine complexes (oral, in Hungarian); XLIII. Colloquium on Complex Chemistry, May 23-25, Mátrafüred, Hungary
- [D83] (UD) Cs. E. Nagy, G. Papp: Catalytic condensation reactions in aqueous and biphasic systems (oral, in Hungarian); XLIII. Colloquium on Complex Chemistry, May 23-25, Mátrafüred, Hungary
- [D84] (UD) M. Fekete, H. Horváth, A. Almássy, Á. Kathó, F. Joó: Synthesis and Catalytic Properties of Water-Soluble N-heterocyclic Carbene Complexes (poster); 3rd International Conference on Green and Sustainable Chemistry, 1-5 July 2007, Delft, The Netherlands
- [D85] (UD) H. H. Horváth, P. Juhász, F. Joó, Á. Kathó: Synthesis and Catalytic Properties of Rh(I) and Ru(II) Complexes of Alkylated Phosphotriazaadamantanes (poster); 3rd International Conference on Green and Sustainable Chemistry, 1-5 July 2007, Delft, The Netherlands
- [D86] (UD) A. Almássy, F. Joó: Synthesis and reactivity of water-soluble Au(I)-NHC complexes (poster); XXVIII. Conference of Organic Chemists: Advances in Organic Chemistry, September 16-20, Smolenice, Slovak Republic
- [D87] (UD) F. Joó: Metal-N-Heterocyclic Carbene Complexes as Catalysts of Hydrogenation, Transfer Hydrogenation and Redox Isomerization in Homogeneous and Biphasic Media (invited lecture); XXVIII. Conference of Organic Chemists: Advances in Organic Chemistry, September 16-20, Smolenice, Slovak Republic
- [D88] (UD) G. Papp, F. Joó: New classical and non-classical hydrides of Ru(II) in aqueous solution (poster); XXVIII. Conference of Organic Chemists: Advances in Organic Chemistry, September 16-20, Smolenice, Slovak Republic
- [D89] (UD) M. Fekete, H. Horváth, F. Joó: Synthesis and catalytic properties of new rhodium(I) and iridium(I) NHC complexes of the type  $[M(L)(bmim)(cod)]$  (M=Rh, Ir) (poster); XXVIII. Conference of Organic Chemists: Advances in Organic Chemistry, September 16-20, Smolenice, Slovak Republic
- [D90] (UD) Á. Kathó, P. Juhász, A. Udvardy: Synthesis and Catalytic Properties of Ru(II)-Arene Complexes of Alkylated Phosphotriazaadamantanes (poster); XXVIII. Conference of Organic Chemists: Advances in Organic Chemistry, September 16-20, Smolenice, Slovak Republic

- [D91] (UD) F. Joó: Recent results at the University of Debrecen, Hungary in the field of aqueous organometallic catalysis (oral); Aquachem 3rd Annual Meeting, 12-14 January, 2007, Debrecen, Hungary
- [D92] (UD) A. Almássy: Water soluble N-heterocyclic carbene complexes of transition metals (oral); Aquachem 3rd Annual Meeting, 12-14 January, 2007, Debrecen, Hungary
- [D93] (UD) A. Udvardy, Á. Kathó: Hydrogenation of sorbic acid catalyzed by Rh- and Ru-phosphine complexes (poster); Aquachem 3rd Annual Meeting, 12-14 January, 2007, Debrecen, Hungary
- [D94] (UD) G.-Y. Zhao, F. Joó: Capture and activation of carbon dioxide by task-specified ionic liquids (poster); Aquachem 3rd Annual Meeting, 12-14 January, 2007, Debrecen, Hungary
- [D95] (UD) F. Joó: New vistas for homogeneous catalysis (in Hungarian). Inaugural talk, Hungarian Academy of Sciences, October 9, 2007, Budapest, Hungary.
- [D96] (IST) T.C. Reis, E.C.B. Alegria, A.M. Kirillov, L.M.D.R.S. Martins, A.J.L. Pombeiro, "Electrochemical Behaviour of Benzoyl-Hydrazido and -Diazenido Rhenium Complexes with Chelating N,O-Ligands", X Iberic Meeting of Electrochemistry / XIV Meeting of the Portuguese Electrochemical Society, Coimbra, 2007, P19, p.59.
- [D97] (IST) T.F.S. Silva, L.M.D.R.S. Martins, A.J.L. Pombeiro, "Electrochemical Behaviour of New Scorpionate Oxovanadium Complexes", X Iberic Meeting of Electrochemistry / XIV Meeting of the Portuguese Electrochemical Society, Coimbra, 2007, P20, p.60.
- [D98] (IST) M.C. Granada, E.C.B. Alegria, A.M. Kirillov, M.D.R.S. Martins, A.J.L. Pombeiro, "Electrochemical Behaviour of Oxorhenium(V) Complexes with N,O-Ligands", X Iberic Meeting of Electrochemistry / XIV Meeting of the Portuguese Electrochemical Society, Coimbra, 2007, P34, p. 74.
- [D99] (IST) A.J.L. Pombeiro, "Oxidative Functionalization of Alkanes under Mild Conditions Catalysed by Transition Metal Complexes with N,O- or O- Ligands", 9<sup>th</sup> FIGIPAS Meeting in Inorganic Chemistry, Vienna, Austria, 2007, SL-11 (*invited lecture*).
- [D100] (IST) Y. Yu. Karabach, A.M. Kirillov, M. Haukka, M.F.C. Guedes da Silva, M.N. Kopylovich, A.J.L. Pombeiro, "New Copper(II) Containing Coordination Polymers with Diverse Architectures", 9<sup>th</sup> FIGIPAS Meeting in Inorganic Chemistry, Vienna, Austria, 2007, PO-76.
- [D101] (IST) K.R.Gruenwald, A.M. Kirillov, M. Haukka, A.J.L. Pombeiro, "Self-Assembly Synthesis and Characterization of New Mono- and Multinuclear Cu(II) Complexes with Aminopolyalcohol Ligands", 9<sup>th</sup> FIGIPAS Meeting in Inorganic Chemistry, Vienna, Austria, 2007, PO-78.
- [D102] (IST) A.J.L. Pombeiro, "Bioinspired Transition Metal Systems for the Mild Catalytic Oxidation of Light Alkanes", 13<sup>th</sup> International Conference on Biological Inorganic Chemistry (ICBIC), Vienna, Austria, 2007, SL 088, *J. Biol. Inorg. Chem.*, 2007, 12, Supplement 1, S160 (*invited lecture*).
- [D103] (IST) M.N. Kopylovich, Ya. Yu. Karabach, A.M. Kirillov, M. Haukka, M.F.C.G. da Silva, A.J.L. Pombeiro, "From Solution to Solid Phase: Synthesis of New Copper(II) Containing Coordination Polymers with Diverse Architectures". XVI International Conference on Chemical Thermodynamics in Russia (RCCT 2007) / X International Conference on the Problems of Solvation and Complex Formation in Solutions, Suzdal, Russia, 2007, 5/S – 560-561.
- [D104] (IST) C. Travassos, E.C.B. Alegria, L.M.D.R.S. Martins, A.J.L. Pombeiro, "Scorpionate Rhenium Complexes as Catalysts for the Baeyer-Villiger Oxidation with Aqueous H<sub>2</sub>O<sub>2</sub>", 3<sup>th</sup> International Conferences on Green and Sustainable Chemistry (GSC-3 Symposium), Delft, The Netherlands, 2007, P50, p. 50.
- [D105] (IST) R.R. Fernandes, M.V. Kirillova, J.A.L. da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, "Iron(IV) Catalyzed Oxidation of Cyclohexane by Hydrogen Peroxide under Mild Conditions", 3rd International Conference on Green and Sustainable Chemistry (GSC-3 Symposium), Delft, The Netherlands, 2007, P74, p. 74.
- [D106] (IST) A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, "Mild Peroxidative Oxidation of Alkanes Catalyzed by Multinuclear Cooper(II) Triethanolamine Complexes", 3<sup>rd</sup> International Conference on Green and Sustainable Chemistry (GSC-3 Symposium), Delft, The Netherlands, 2007, P108, p. 108.

- [D107] (IST) L.M.D.R.S. Martins, E.C.B.A. Alegria, A.S. Furtado, A.J.L. Pombeiro, "Unprecedented Use of Microwaves in the Synthesis of Scorpionate and Derived Pyrazole Rhenium Complexes", 41<sup>st</sup> IUPAC World Chemistry Congress (Chemistry Protecting Health, Natural Environment and Cultural Heritage), Turin, Italy, 2007, SO6P17, pp. 156-157.
- [D108] (UEN) Mechanistic information from volume profile analysis, R. van Eldik, Gordon Research Conference on Inorganic Reaction Mechanisms, Ventura (USA), 2007 (Poster)
- [D109] (UEN) From NO to peroxide activation by model iron(III) complexes, J.-E. Jee, A. Theodoridis, M. Wolak, A. Franke, N. Hessenauer and R. van Eldik, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Plenary lecture)
- [D110] (UEN) Oxidative degradation of Orange II by H<sub>2</sub>O<sub>2</sub> catalyzed by divalent transition metal ions, E. Ember and R. van Eldik, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Poster)
- [D111] (UEN) Low temperature rapid-scan detection of reactive intermediates in epoxidation reactions catalyzed by a new enzyme mimic of cytochrome P450, N. Hessenauer-Ilicheva, A. Franke, D. Meyer, W.-D. Woggon and R. van Eldik, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Poster)
- [D112] (UEN) Catalytic aspects of the reduction of (ImH)[*trans*-RuCl<sub>4</sub>(dmsO)(Im)] by ascorbic acid, M. Brindell, G. Stochel and R. van Eldik, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Poster)
- [D113] (UEN) Quantum mechanical calculations suggest that dissociative water exchange on aquated Al(III) can induce deprotonation, H. Hanauer, R. Puchta, T. Clark and R. van Eldik, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Oral presentation)
- [D114] (UEN) Solution structure and water-exchange kinetics of paramagnetic [Fe<sup>II</sup>(edta)(H<sub>2</sub>O)]<sup>2-</sup>, J. Maigut, R. Meier, A. Zahl and R. van Eldik, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Poster)
- [D115] (UEN) Influence of an extremely negatively charged porphyrin on the kinetics of NO binding to Fe(III) and subsequent reductive nitrosylation, J.-E. Jee, N. Jux, A. Zahl and R. van Eldik, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Poster)
- [D116] (UEN) Stopped-flow kinetic studies on inorganic reactions in ionic liquids, P. Illner and R. van Eldik, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Poster)
- [D117] (UEN) The first high pressure kinetic measurements with superoxide. Iron(III)-peroxo-iron(II)-superoxo equilibrium, K. Dürr, E. Hübner, N. Jux, R. van Eldik and I. Ivanovic-Burmazovic, 36<sup>th</sup> Inorganic Reaction Mechanism Meeting, York (UK), 2007 (Poster)
- [D118] (UEN) The splitting of the N-N-bond in the Chatt cycle: Kinetic, spectroscopic and theoretical investigations, A. Dreher, K. Mersmann, I. Ivanovic-Burmazovic, R. van Eldik and F. Tuczek, 233<sup>rd</sup> National Meeting of the American Chemical Society, Chicago (USA), 2007 (Oral presentation)
- [D119] (UEN) Kinetic and mechanistic patterns for irreversibly absorbed and freely diffusing cytochrome c at Au/SAM junctions, D.E. Koshtariya, T.D. Dolidze R. van Eldik and D.H. Waldeck, 19<sup>th</sup> International Symposium on Bioelectrochemistry and Bioenergetics, Toulouse (France), 2007 (Oral presentation)
- [D120] (UEN) Low temperature rapid-scan detection of reactive intermediates in epoxidation reactions catalyzed by a new enzyme mimic of cytochrome P450, N. Hessenauer-Ilicheva, A. Franke, D. Meyer, W.-D. Woggon and R. van Eldik, Heidelberg Forum of Molecular Catalysis, Heidelberg (Germany), 2007 (Poster)
- [D121] (UEN) Mechanistic information on the interaction of Vitamin B12 and model complexes with NO and nitrite, R. van Eldik, Gordon Research Conference on Vitamin B12 and Corphins, Biddeford (USA), 2007 (Invited oral presentation)
- [D122] (UAL) Photochemical properties of [RuCl<sub>2</sub>(mPTA)<sub>4</sub>]: a new water soluble ruthenium complex. Girotti, R; Mañas, S; Serrano, M; Aoulad, M; Romerosa, A. XXIII International Conference on Photochemistry. University of Cologne, Germany. July 29-August 3, 2007. P342, pp 586.
- [D123] (UAL) Synthesis and characterization of the new water soluble ligand dmpta and its ruthenium complexes (dmPTA = N,N'-dimethyl-1,3,5-triaza-7-phosphaadamantane). Adrián Mena-Cruz, Pablo Lorenzo-Luis, Antonio Romerosa, Mustapha Saoud, Manuel Serrano-Ruiz. XXXV Congresso Nazionale della Divisione di

Chimica Inorganica della Società Chimica Italiana. Actas del Congreso. I.S.U. Milano (Italia) Sala A. Levi, 3-7 September 2007. Oral Communication O01.

- [D124] (UAL) Photochemical isomerization of allylic alcohols under mild conditions mediated by water soluble ruthenium complexes. **R. Girotti**, S. Mañas, A. Romerosa. XVII EuCheMS Conference on Organometallic Chemistry: EiCJhemMs Events No. 346. September 1-6 2007, Sofia, Bulgaria. PP106. pag. 166
- [D125] (HUJI) Ovadia Lev, Vitaly Gutkin, Jenny Gun and Alexander Modestov, "On-line electrochemical flow cell – mass spectrometry" 58th ISE Annual Meeting "Exploring Frontiers of Electrochemistry" Sept 9-14, 2007 at Banff, Canada
- [D126] (CNRS/LCC/a) **M. Tristany**, R. Laurent, J.-P. Majoral, A.-M. Caminade : "Towards Janus-type and other types of bifunctional water-soluble dendritic catalysts" *CIAM Catalysis in Aqueous Media*, Toulouse (France), 30 November-1 December 2007 (Poster presentation)
- [D127] (CNRS-LCC/b) Chemistry and Catalysis with High Oxidation State Cp\*Mo and Cp\*W Complexes in Water, R. Poli, **C. Dinoi**, F. Demirhan, P. Sözen, G. Taban, *FIGIPAS07*, Vienna, Austria, July 4-7, 2007 (session lecture SL-15).
- [D128] (UAB) **Kovács. G.**; Ujaque, G.; Lledós, A.: Theoretical analysis of the gold(I) catalyzed hydroamination of 1,3-dienes, *Europacat 8*, Turku, Finland, 26-31 August 2007 (Poster)
- [D129] (UAB) **Kovács. G.**; Ujaque, G.; Lledós, A.: Theoretical analysis of the gold(I) catalyzed hydroamination of 1,3-dienes, *6th International Summer School of Organometallic Chemistry*, Camerino, Italy, 8-12 September 2007 (Poster)
- [D130] (CNR) Gonsalvi, L.; Peruzzini, M. "Aqueous phase catalysis, organometallic reactivity and much more: the renaissance of the water soluble monodentate phosphine PTA" *CIAM Workshop – Catalysis in Aqueous Media* Toulouse, France, 30 November-1 December 2007. (Plenary Lecture)
- [D131] (CNR) **Erlandsson, M.**; Landaeta, V. R.; Bosquain, S. S.; Dorcier, A.; Phillips, A. D.; Dyson, P.J.; Laurency, G.; Gonsalvi, L.; Peruzzini, M. "Comparative studies for the catalytic water phase carbon dioxide hydrogenation using iridium and ruthenium PTA complexes (PTA=1,3,5-triaza-7-phosphadamantane)" *CIAM Workshop – Catalysis in Aqueous Media* Toulouse, France, 30 November-1 December 2007.
- [D132] (CNR) **Landaeta, V. R.; Erlandsson, M.**; Vasquez-Perez, M. E.; Urbina-Blanco, C. A.; Phillips, A. D.; Gonsalvi, L.; Peruzzini, M. "Synthesis and characterisation of novel iridium complexes with water-soluble phosphine ligands" *CIAM Workshop – Catalysis in Aqueous Media*, Toulouse, France, 30 November-1 December 2007.
- [D133] (CNR) Bosquain, S. S.; Dorcier, A.; Dyson, P. J.; **Erlandsson, M.**; Gonsalvi, L.; Laurency, G.; Peruzzini, M. "Aqueous phase carbon dioxide and bicarbonate hydrogenation catalysed by cyclopentadienyl ruthenium complexes" *6th ISOC International School of Organometallic Chemistry*, Camerino, Italy, 8-12 September 2007.
- [D134] (YoK) **Perutz, R. N.** "Photo-induced Electron Transfer Catalysis and Selective Ion-Sensors" *17th International conference on photochemistry and photophysics of coordination compounds*, Keynote Lecture Dublin, 24-28 June 2007.

#### A.7 Single team Patents pending (since the beginning of the project)

- [E1] (IST) A.J.L. Pombeiro, A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M.F.C. Guedes da Silva, "New Di-, Tri-, Tetra- and Poly-nuclear Copper Complexes and Their Use as Catalysts for the Peroxidative Oxidation of Cyclohexane". Patent pending PT 103225 (date: 2005/01/19).
- [E2] (IST) A.J.L. Pombeiro, M.V. Kirillova, A.M. Kirillov and J.J.R. Fraústo da Silva, "Methyl(trioxo)rhenium and Other Rhenium Oxides as Catalysts for the Carboxylation and Hydroxylation of Alkanes". Patent pending PT 103345 (date: 2005/09/13).
- [E3] (IST) A.J.L. Pombeiro, J.J.R. Fraústo da Silva, J.A.L. Silva, M.V. Kirillova, P.M. Reis, A.M. Kirillov and A. Palavra, "Groups 5 and 6 Metal Oxides as Catalytic Systems for Oxidative Functionalization Reactions of Alkanes". Patent pending PT 103350 (date: 2005/09/16).



- [E4] (IST) A.J.L. Pombeiro, M.N. Kopylovich, A.M. Kirillov, V. Yu. Kukushkin and M. Haukka, "Method for the Preparation of New Unsymmetrical Imidoylamidine Nickel(II) Complexes bearing an Isoindolinone Moiety, Compounds thereof and Their Use as Colouring Materials", PT 103522 (priority date: 2006/07/12), patent pending.
- [E5] (IST) A.J.L. Pombeiro, A.M. Kirillov, M.N. Kopylovich, V.N. Kokozay, D.S. Nesterov, "Heterotrimetallic Fe/Cu/Co Complex, Preparation Method Thereof and Catalyst Comprising the Same for the Mild Oxidation of Cycloalkanes", PT 103526 (priority date: 2006/07/14), patent pending.
- [E6] (IST) A.J.L. Pombeiro, M.V. Kirillova, A.M. Kirillov, J.A.L. Silva, J.J.R. Fraústo da Silva, "Method of Conversion, under Mild Conditions and in Aqueous Medium, of Gaseous and Liquid Alkanes into Carboxylic Acids", PT 103640 (priority date: 2007/1/18), patent pending.
- [E7] (IST) A.J.L. Pombeiro, L.M.D.R.S. Martins, E.C.B.A. Alegria, "Use of Microwaves for the Synthesis of Tris(pyrazolyl)methanes", PT 103681 (priority date: 2007/03/09), patent pending.
- [E8] (IST) A.J.L. Pombeiro, L.M.D.R.S. Martins, E.C.B.A. Alegria, M.V. Kirillova, "New Complexes of Rhenium with Pyrazole or tris(1-pyrazolyl)methanes and Their Application as Catalysts for the Partial Oxidation, under Mild Conditions, of Ethane to Acetic and Acetaldehyde and of Cyclohexane to Cyclohexanol and Cyclohexanone", PT 103735 (priority date: 2007/05/11).

#### A.8 Workshops, Dissertations and Books (since the beginning of the project)

- [F1] (UAL-UAB)Workshop GREEN CHEMISTRY A SOLUTION FOR THE WORLD: Andalusia meets Europe II. 18-21/12/2005. Almería (Spain)  
(CNRS-LCC) CIAM Workshop – Catalysis in Aqueous Media, Toulouse, France, 30 November-1 December 2007
- [F2] Book EDITOR: (UAL) ANTONIO ROMEROSA (EDITOR)  
Green Chemistry a Solution for the World: Andalusia meets Europe II. Almería (Spain) 18-21 December 2005. ISBN: 84-96270-59-9 Legal deposit: AL-4-2006
- [F3] PhD Theses  
(UAL) Mustapha Saoud "Funcionalización de Acetilenos Terminales Mediante Complejos de Rutenio con Fosfinas Solubles en Agua".Universidad de Almería. Facultad de Ciencias Experimentales. 2006 (27/06). Sobresaliente CUM LAUDE. Por Unanimidad. TESIS EUROPEA.  
(UAL) Tatiana Campos Malpartida. "Síntesis de Nuevos Complejos de Ciclopentadienilo de Ru(II) solubles en Agua con Posibles Propiedades Catalíticas y Biológicas". Universidad de Almería. Facultad de Ciencias Experimentales. 2006 (11/07). Sobresaliente CUM LAUDE. Por Unanimidad. TESIS EUROPEA.  
(UAL) Chiara Ciardi. "A general synthetic pathway for new chiral phosphine ligands from naturally occurring amino acids: evaluation of some of their Rhodium, Iridium and Ruthenium complexes as mediators in standard catalytic processes"/"Procedimiento general para la síntesis de nuevas fosfinas quirales a partir de aminoácidos naturales: evaluación de algunos de sus complejos de Rodio, Iridio y Rutenio como mediadores en reacciones catalíticas modelo" Universidad de Almería. Facultad de Ciencias Experimentales. 2006 (21/07). Sobresaliente CUM LAUDE. Por Unanimidad. TESIS EUROPEA.  
(UAL) I. M. Mallqui Ayala: to be defended in July 2008.  
(CNRS/LCC/b) C. Dinoi: "Complexes oxydo de molybdène et de tungstène dans les hauts degrés d'oxydation en milieu aqueux : synthèse, réactivité et catalyse d'oxydation", Université Paul Sabatier, Toulouse, France, 20 December 2007. Très honorable (the highest mark)  
(CNRS/LCC/a) P. Servin: "Dendrimères phosphorés et catalyse en milieu aqueux" Université Paul Sabatier, Toulouse, France, 20 July 2007. Très honorable (the highest mark). European Thesis.

### **Part B – Comparison with the Joint Programme of Work (Annex I of the Contract)**

## ➤ B.1 Research Objectives

**Objective 1:** - *The design, synthesis and characterization of new hydrosoluble ligands (cyclopentadienyls, phosphines, porphyrins, azacrowns, bipyridyls, scorpionates, etc.) and macroligands (dendrimers), and the study of their co-ordination chemistry with metals of catalytic relevance.*

Many collaborative works based on the chemistry of PTA (1,3,5-triaza-7-phosphaadamantane) have been generated during the development of the Aquachem project (see below). The functionalization of the cyclopentadienyl ring with hydrosoluble fragments such as amides has been optimised and related transition metal complexes were synthesised. New hydrosoluble ligands based on aminoacidic moieties have been synthesised and used to prepare coordination compounds with ruthenium, rhodium and iridium. Sulfonated phosphines were used to coordinate Ru moieties and preliminary studies on the catalytic behaviour in water phase hydrogenations with these complexes gave interesting results (see below).

HUJI has synthesised a new class bis-hydroxyaminotriazines (BHTs) iron ligands and used this new, highly versatile group of tridentate iron(III) chelating agents for electroanalysis of trace iron levels in sea water and other aquatic systems. A paper has been published. HUJI has prepared new tridentate iron(III) chelating agents showing higher affinity to iron(III) than other tridentate iron(III) chelators and superior iron(III) over iron(II) selectivity compared to desferrioxamine-B (DFO), EDTA and other tridentate ligands.

Diverse hydrosoluble Cu(I), Re(VII), Fe(II), V(IV) and Pt(II) complexes with water-soluble phosphines (such as PTA and alkylated forms), scorpionates (namely a methanesulfonate derivative), aromatic polycarboxylic acids and amino-alcohols were obtained. The IST scorpionate has also been coordinated to low-valent Mo carbonyl complexes in collaboration with the CNRSLCC/b group. The first Cu-PTA complex, the first aqua-soluble Cu coordination polymer that hosts infinite chains of cyclic water clusters with two pendent water molecules and an unprecedented heterotrimetallic Fe/Cu/Co complex were obtained by the IST team.

Several original series of symmetrical phosphorus-based water-soluble or water-compatible dendritic ligands derived from PTA, P,N,P ligands, N,N ligands, scorpionate ligands have been synthesized by CNRSLCC/a. The complexation properties of some of these macroligands have been tested toward ruthenium derivatives, in collaboration with CNR, IST, and UAL. Many palladium complexes issued from dendrimers and monomers derived from pyridine, dipyrindine, scorpionate and PNP ligands (from tyramine or L-tyrosine) and Pd(OAc)<sub>2</sub> were also synthesized *in situ*. All of the corresponding complexes are soluble in mixtures water / organic solvent (in particular acetonitrile), with a large proportion of water (often 66%).

At UD several water-soluble 1,3-disubstituted imidazolium salts bearing pendant sulfoalkyl or sulfoaryl groups have been synthesized for the first time. These compounds yield N-heterocyclic carbene complexes with transition metal ions such as Ru(II), Rh(I) and Ir(I) which are useful catalysts for hydrogenation, transfer hydrogenation, hydration and redox isomerization processes. N-heterocyclic carbene complexes are often more robust than phosphine complexes used for the same catalytic purposes.

**Objective 2:** - *The design, synthesis and characterization of organometallic compounds with aqua, hydroxo, and oxo ligands.*

The cationic [RuH(H<sub>2</sub>O)(CO)(mtppps)<sub>3</sub>]<sup>+</sup> has been characterised by UD and independently prepared via chloride dissociation in water from [RuHCl(CO)(mtppps)<sub>3</sub>] (mtppps = monosulfonated triphenylphosphine). It was also observed that in aqueous solution [RuCl<sub>2</sub>(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)] gives rise to the formation of [RuCl(H<sub>2</sub>O)(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)]<sup>+</sup> and also to the dicationic [Ru(H<sub>2</sub>O)<sub>2</sub>(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)]<sup>2+</sup> species. Spontaneous chloride dissociation from [RuCl(NCMe)<sub>4</sub>(P<sup>+</sup>Pr<sub>3</sub>)](BF<sub>4</sub>)<sub>2</sub>, in the presence of small amounts of water in methanol solution afforded [Ru(H<sub>2</sub>O)(NCMe)<sub>4</sub>(P<sup>+</sup>Pr<sub>3</sub>)](BF<sub>4</sub>)<sub>2</sub> and [Ru(MeOH)(NCMe)<sub>4</sub>(P<sup>+</sup>Pr<sub>3</sub>)](BF<sub>4</sub>)<sub>2</sub>, respectively. The significance of these halide/aqua exchange equilibria is in that the aqua complexes have altered catalytic activities compared to their halide-containing counterparts.

Rhenium and molybdenum sensors for polyoxometallate anions have been synthesised and tested by the YoK team. The X-ray crystal structure of one Mo-based sensor of this type has been determined.

After the full characterization of cluster [(Cp\*Mo)<sub>3</sub>(μ-O)<sub>2</sub>(μ-OH)<sub>4</sub>]<sup>2+</sup> (removing an ambiguity in a paper previously published by another group), the related tungsten compounds [(Cp\*W)<sub>3</sub>(μ-O)<sub>4</sub>(μ-OH)<sub>2</sub>]<sup>2+</sup> and [(Cp\*W)<sub>3</sub>(μ-O)<sub>6</sub>]<sup>+</sup> have been prepared by a similar synthetic strategy (zinc reduction of Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub> in an acidified H<sub>2</sub>O-MeOH mixed solvent) and fully characterized. The two clusters are related to each other by a reversible coupled one-electron-two-proton process. Oxidation of [(tpms)Mo(CO)<sub>3</sub>], [(tpms)Mo(CO)<sub>3</sub>H] and [(tpms)Mo(CO)<sub>3</sub>I] complexes under a variety of conditions has opened access to the high oxidation state oxomolybdenum complexes [(tpms)<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>], [(tpms)<sub>2</sub>Mo<sub>2</sub>O<sub>4</sub>] and [(tpms)<sub>2</sub>Mo<sub>2</sub>O<sub>3</sub>Cl<sub>2</sub>]

**Objective 3:** - *Studies of substrate activation and stoichiometric reactivity. Activation of inorganic substrates such as water, dioxygen, dihydrogen, carbon and sulfur oxides, bicarbonate and carbonate, phosphorus, organic substrates (alkynes, alkenes, alcohols, thiols, nitriles,) etc. Activation of C-F, C-C and C-Heteroelement bonds.*

The interaction between  $\text{Cp}^*\text{Mo}_2\text{O}_5$  and mercaptocarboxylic acids,  $\text{HS}(\text{CH}_2)_n\text{COOH}$  with  $n = 1$  or  $2$ , has been completed by **CNRS/LCC/b** in years 1-3.

The activation of NO by transition metal complexes has been studied in detail by the UEN group, and the mechanistic understanding of such processes is well advanced. On the basis of this understanding it is now possible to continue further work on the activation of inorganic and organic peroxides for the oxidation of substrate molecules. The applied techniques include low temperature rapid-scan spectrometry and high pressure kinetic measurements. It was demonstrated that it is possible to distinguish between homolytic and heterolytic cleavage of the peroxy bond during the activation step. This is crucial information for the subsequent substrate oxidation step during which an oxygen atom is transferred to the substrate. This work has been extended to the oxidation of *cis*-stilbene by *m*-chloroperoxybenzoic acid catalyzed by a functional model Fe(III) complex for cytochrome P450. In addition, the most recent work on this topic has indicated that water soluble Fe(III) porphyrin complexes can be used very successfully to catalyse various substrate oxidation reactions by inorganic and organic peroxides and peroxy acids.

**Objective 4:** *Physico-chemical studies of complex-solvent interactions including spectroscopic, thermodynamic, kinetic and mechanistic investigations of the interaction between transition metal complexes and solvent molecules. Process to be studied entail: water coordination and exchange; proton transfer to and from a metal centre and ligands as a function of pH; hydrogen bonding interactions between water (as a proton donor) and transition metals or ligands (as a proton acceptor). Study of the effect of solvent composition on  $pK_a$ , rate constants, reaction enthalpies, etc.*

The main results were in the area of interaction of water with coordinated ligands such as hydrogen and oxygen. A joint UAB/INEOS experimental/theoretical study has been carried out to study H-bonding interactions emphasizing the amphiprotic nature of  $\text{H}_2\text{O}$ , which may serve at the same time as proton donor and proton acceptor, as well as an efficient medium where to carry out proton transfer reactions involving organometallic species. Bidentate "coordination" of water has been ascertained by IR and UV studies and confirmed by *ab initio* calculations methods in the interaction with organic boranes.

Detailed mechanistic studies of the protonation of oxo ligands in  $\text{Cp}^*\text{MoO}_3^-$  by stopped-flow kinetics at variable temperature and pressure have provided important activation information (negative activation entropy and negative activation volume), throwing light on the nature of the transition state and on the hydration state of the final product.

Mechanistic investigations at UEN have studied water exchange reactions on different Fe(III) porphyrin complexes and have shown that pH can control the nature of the complex centre in terms of its spin state and coordination number. In some cases, the water exchange reactions are accelerated by pH due to the stabilizing effect of coordinated hydroxide, whereas in other cases no water exchange reaction is observed at high pH due to the formation of a five-coordinate hydroxo complex. This clearly demonstrates how important pH will be in the activation of small molecules by such metal complexes since it controls the lability of the metal centre.

**Objective 5:** *The development or improvement of analytical instrumentation for in situ and online analysis of reaction intermediates, by-products and products of stoichiometric or catalytic reactions (ESI-MS, spectroelectrochemistry, photochemistry, NMR spectroscopy, etc).*

The Jerusalem team (HUJI) has improved the on-line electrochemical set up which can allow introduction of several reactant flows either before or after a radial electrochemical flow cell. The combined EC/ESI-MS instrument was improved and appropriate modelling to predict the conversion in the EC cell were devised.

The Jerusalem team demonstrated the usefulness of the new approaches for the speciation of Ruthenium compounds, iron ligation studies, inorganic polysulfide speciation, speciation of reduced molybdenum species studies of porphyrin speciation as well as chemical and electrochemical transformations of the above.

The Jerusalem team has introduced a new electrochemically driven preconcentration system for mercaptans aided by electrochemical stripping of the analytes in a radial flow miniature electrochemical cell and subsequent ESI-MS analysis of the analyte.

The York team (YoK) has installed a new system for in-situ photochemistry with NMR spectroscopy incorporating a YAG laser emitting at 532, 355 or 266 nm and a 600 MHz NMR spectrometer. This instrument will allow measurements at low temperature during irradiation of the sample.

**Objective 6:** *Theoretical studies, by ab initio and/or density functional methods, in parallel with the experimental studies. Targets of this activity will be the modelling of catalytic cycles and hydrogen bonded interactions. The analysis of solvent effects with different solvent/solute interaction models.*

A DFT study of the water coordination to a CpMo<sup>VI</sup> model system reveals details of the relative stability of [CpMoO<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup> vs. [CpMoO<sub>2</sub>]<sup>+</sup> + H<sub>2</sub>O and vs. [CpMoO(OH)<sub>2</sub>]<sup>+</sup>. The explicit inclusion of water molecules is crucial in order to obtain results in agreement with the experimental evidence. Extension of this work to the interaction between [CpMoO<sub>2</sub>]<sup>+</sup> and H<sub>2</sub>O<sub>2</sub> illustrates key features of the hydrogen peroxide activation for the catalyzed olefin epoxidation and for the oxidation of thiophene derivatives to sulfoxides and sulfones.

Theoretical (DFT) studies at UEN have assisted the mechanistic clarification of water and solvent exchange reactions on metal complexes. In addition, such calculations have also assisted the understanding of solvational effects of ionic liquids on the thermal and pressure activation parameters for typical ligand substitution and hydroformylation reactions of Pt(II) complexes.

The mechanism of the catalytic hydrogenation of different functionalities by means of water-soluble ruthenium complexes prepared by the UD team with sulfonated aromatic phosphine ligands were studied by DFT calculations. The ruthenium complex of *mtp*pm was used successfully for both the pH-dependent regioselective reduction of unsaturated aldehydes and the stereoselective reduction of alkynes holding aromatic groups. Theoretical methods were applied to account for the observed stereoselectivity. The calculations show that the hydrogenation proceeds by the participation of both the hydride ligand and solvent molecules. Since it was already known that appropriate inclusion of the solvent environment in the calculations is required for obtaining reasonable energetics, in addition to a continuum model 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.

NMR experiments were carried out by **CNRSLCC/a** to determine the influence of mixtures water / organic solvents on the thickness of signals of the internal structure of the dendritic ligands and complexes. This allowed to choose the best conditions to perform the catalytic experiments.

Several approaches for computation of the interaction energy in solution were probed by **INEOS/UAB**. The enthalpy values are found being well described by PCM correction, whereas special techniques are needed for calculation of Gibbs free energy in solution. An approach, which takes into account chemical nature of solute-solvent interaction, is proposed for the sufficiently accurate estimation of Gibbs free energy in solution.

**Objective 7:** *Catalytic studies in aqueous or biphasic media at different pH: CO<sub>2</sub> hydrogenation, oxidation of various substrates, hydrodehalogenation of fluorinated and chlorinated hydrocarbons, functionalization of alkanes, metathesis of alkenes, hydroxylation of white phosphorus, detoxication of poisonous nitriles, etc., including comparison of the catalytic activity and selectivity of the water-soluble metalladendrimers with that of the corresponding water-soluble monomers.*

The hydrogenation of  $\alpha,\beta$ -unsaturated oxo compounds, allylic alcohols and disubstituted alkynes have been largely investigated with different hydrosoluble complexes in both homogeneous and heterogeneous conditions. A combination of experimental and theoretical methods has been used to investigate the pH dependence of the regioselective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with Ru(II) water-soluble complexes containing sulphonated phosphines. Hydrosoluble NHC complexes have been also used for oligomerization and hydration of alkynes.

Oxidation of substituted dibenzo- and dibenzothiophenes has continued at **CNRSLCC/b** using Cp\*<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>/H<sub>2</sub>O<sub>2</sub> and Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub>/H<sub>2</sub>O<sub>2</sub> in collaboration with **CNR**. The reactions proceed quantitatively to the sulfones via the sulfoxide intermediates. The W system is ca. 100 times more active than the Mo system. Preliminary investigations show that the W compound is also an excellent catalyst of the epoxidation of cyclooctene by H<sub>2</sub>O<sub>2</sub> in MeCN; these investigations will be pursued at **CNRSLCC/b** beyond the termination of this contract.

The catalytic oxidation of cycloalkanes to cycloalkanols and cycloketones has been accomplished by peroxidative oxidation, using aqueous H<sub>2</sub>O<sub>2</sub>, under mild conditions, in biphasic aqueous/organic medium, at the IST team. Various Cu (mainly multinuclear), V, Re and Fe complexes as well as Cu/Fe/Co heterometallic compounds with different types of water-soluble ligands were found to be particularly effective and selective catalyst precursors for that reaction. Some of the Re complexes also catalyse the oxidation and carboxylation of ethane to acetic and propionic acids, whereas others act as catalysts for the aqueous peroxidative Baeyer-Villiger oxidation of a cyclic ketone to the corresponding lactones, also under mild conditions.

**CNRSLCC/a** has succeeded in synthesizing several series of dendritic ligands and complexes soluble in water or in mixtures water / organic solvent (monophasic or biphasic). The catalytic behaviour of dendritic PTA-Ru complexes for the hydration of alkynes or alcohol isomerization has been studied in collaboration with **CNR**, inducing a positive dendritic effect observed for the first time with an organometallic derivative in water.

Pyridine, dipyrindine and scorpionate dendritic Pd complexes were used for Sonogashira and Heck C-C bond forming catalysed reactions, in collaboration with **IST**. A joint collaboration of **CNRSLCC/a** with **UAL** and **CNR** allowed to demonstrate the successful use of two series of PNP dendritic ligands for catalysing three types of C-C bond forming catalysed reactions, that are Sonogashira, Suzuki and Heck reactions.

**Objective 8:** *Electrocatalytic studies in aqueous/biphasic media.*

The Jerusalem team (HUJI) has constructed an improved on-line electrochemical set up which allows introduction of several reactant flows either before or after a radial electrochemical flow cell that is connected on-line to an electrospray mass spectrometer. The system was used for the electrocatalytic studies involving iron and ruthenium complexes. The application of this on-line technique to a family of hydrosoluble ruthenium complexes prepared at CNR and UAL has resulted in a paper been published. The Jerusalem group used catechol-iron complexes for electrocatalytic sensing of iron using the electrocatalytic reduction of aqueous bromate and hydrogen peroxide.

**Objective 9:** *Photochemistry and photocatalysis in aqueous/biphasic media including solar-induced reactions.*

YoK team has continued studying the luminescence properties of the rhenium sensors and investigating their response to aqueous solutions of several oxometalates and metal cations. These studies have benefited from a series of time-resolved IR spectroscopy carried out at Rutherford-Appleton Laboratory by the ER researcher working at the project. The senior investigators have now added measurements on the time-resolved UV/vis spectra on the ultrafast timescale (performed with help of a COST collaboration) on the sensors and the free catecholamide-pyridine ligand. Results on a related complex investigated by a YoK graduate student have been published.

Photochemical studies promoted by solar light have been continued to be investigated by UAL.

➤ **B.2 Schedule, deliverables and milestones**

B.2.1 *Schedule and Milestones*

*Network Meetings and publications:* The fourth year meeting was held in Toulouse (France) hosted by partner CNRSLCC on November 30 – December 1, 2007. All Aquachem ESR and ER were required to give an oral presentation. A poster session was also manned by other scientists within and outside Aquachem partnership. In the occasion of the Aquachem final meeting, the Second Aquachem Workshop “CIAM- Catalysis in Aqueous Media” was organised by Prof R. Poli and A.-M. Caminade complementing nicely the Aquachem discussions and overviews.

*Recruitment and Training milestones:* All partners have completed the required hiring of ESRs and ERs. In some cases (CNR, CNRSLCC/a, UD, IST) further man-months were made available as the management costs were considerably less than expected at the beginning of the contract. After approval of the Scientific Officer, the appointments were made as detailed below. Training and secondment activities have been implemented with numerous short and long stages by almost all partners (see below).

B.2.2 *Recruitment Effort of the Participants*

The use of the assigned number of person-months within **CNRSLCC** was changed in 2006. **CNRSLCC/b** shifted 5 months from ER to ESR (no need of EC approval, on the basis of the contract Annex III, III.2 (o), because < 35% of the the indicative distribution between the categories (ESR/ER) in Annex I), in order to bring the contract of Ms. Chiara Dinoi from 24 to 29 months. Ms Dinoi has completed her Ph.D. thesis with a 6 month employment as ESR at IST, which was fulfilled from February to July 2007. The one residual ER person-month that was unused by CNRSLCC/b was allotted to CNRSLCC/a. In the fourth year another change was needed as partner UEN could not find a suitable ESR candidate. The already recruited ER position in Erlangen (Dr Malgorzata Brindell) was extended for four additional months and the remaining ESR four months originally attributed to Erlangen were made available to partner CNRSLCC/a. A temporary 3-months replacement was made necessary at UEN (Dr L. Orzel replaced Dr Brindell, both coming from the same Polish institution).

In 2007 the contract of ER Ambroz Almássy (UD) has been extended by two months. Chiara Dinoi (ESR, IST) had a total of 7.5 months (Feb.1st- Sept.15th), instead of the initially planned 6 months. Laurent Benisvy (ER, IST) had a total of 10.5 months (Jan.1st- Nov.15th), instead of the initially planned 9 months. CNR

converted management resources into a 5-month appointment for a ER (Dr Mikael Erlandsson, July-November 2007) after approval from the Scientific Officer at EC.

ESR and ER researchers were recruited taking into account the EC rules and transnational mobility. A dedicated page in the network website lists the recruited young researcher as well as the name of the tutor who is in charge of the training and transfer of knowledge. A few of the recruited scientists are Nationals from Third Countries (Dr. Vanessa Landaeta (Venezuela) 12 months at CNR; Ms Inocenta Ayala (Peru) 16 months at UAL and 8 at CNR (10 more expected in the fourth year), Mr Yauhen Karabach (Belarus) 6 months at IST, Dr Petr Prikhodcenko and Dr Andrey Chernadyev (Russia) 12 months each at HUJI, Dr Guoying Zhao (PR China) 12 months at UD, for a total of 80 person-months.

## ➤ B.3 Organisation and Management

### B.3.1.

The Fourth Year and Final meeting was held in Toulouse (France) hosted by partner CNRSLCC on November 30 – December 1, 2007 together with the Second Aquachem Workshop “CIAM- Catalysis in Aqueous Media” organised by Prof R. Poli and A.-M. Caminade, in accordance with the milestones planned in Annex I of the contract, which registered a good attendance also from invited speakers and scientist from French universities. All participants congratulate with the organisers for the kind hospitality and enjoyable social event.

As for previous years, some of the Network participants have met in 2007 at International Meetings and within individual visits sponsored either by this MC-RTN and by other bilateral or multilateral agreements. These visits have served to discuss on the development of bilateral projects and to plan possible cooperations.

In keeping with Annex I, the scientific achievements resulting from the Network activity were disseminated through publications in the open literature and communications at International Meetings (details in part A.2). The Network does not produce a Newsletter. The Network Manager has updated all the Network activities on the Network website (<http://www.iccom.cnr.it/aquachem/>).

### B.3.2. Network Meetings:

- a. Kick-off meeting, Florence, Italy, 12-13 February 2004.
- b. First Annual Meeting, Lisbon, Portugal, 4-5 February 2005 (host Prof. Pombeiro, IST, Lisbon).
- c. Second Year and Mid-Term review Meetings, Almeria, Spain, 18 – 20 December 2005 (host Profs. A. Romerosa, UAL, Almeria, Spain and Prof. A. Lledos, UAB, Barcelona, Spain)
- d. Third Year Meeting, Debrecen, Hungary, 12-13 January 2007 (host Prof F. Joo, UD, Debrecen, Hungary)
- e. Fourth Annual and Final Meeting, November 30-December 1, 2007 (host Prof R. Poli and A.-M. Caminade, CNRSLCC, Toulouse, France) together with “CIAM” second Aquachem Workshop.

The Minutes of the meetings are made available on the Intranet part of the Network website (password protected).

### B.3.3. Networking, Secondments, Visits.

**Secondments** (from the beginning of the project, final amount: 17.3 months)

Who	From	To	Dates	Purpose
P. Servin	CNRSLCC/a	CNR	01-28/05/2005	Catalytic tests with the dendritic complexes synthesized in CNRSLCC/a
V. Landaeta	CNR	INEOS	02-23/04/2005	Low temperature IR studies on hydrosoluble hydrides
Y. Karabach	IST	UD	14-26/06/2005	Catalytic homogeneous hydrogenation of alkynes
I. Mallqui	UAL	CNR	27/07-05/09/2005	Homogeneous hydrogenation of imines
A. Rossin	UAB	CNR	10/10-11/11/2005	Setting up of a laboratory for synthesis
C. Dinoi	CNRSLCC/b	UEN	01-30/11/2005	Mechanistic and speciation studies involving high oxidation state organometallic oxo complexes
N. Reddig	YoK	HUJI	07-24/2/2006	Electrochemistry and ESI-MS
W. Wojtkow	UD	UAL	18/4-18/5/2006	Study of catalytic applications of new water soluble ruthenium complexes
C. Dinoi	CNRSLCC/b	HUJI	1/7-1/8/2006	Electrochemical and CV studies on Cp*Mo and Cp*W species
P. Servin	CNRSLCC/a	IST	17/6-16/7/2006	Grafting of scorpionates on dendrimers
P. Servin	CNRSLCC/a	UAL	11/11-10/12/2006	Synthesis of P,N dendritic ligands
M. Tristany	CNRSLCC/a	UD	12/11-10/12/2006	Attempted hydrogenation of liposomes with

				dendritic catalysts
I. Mallqui	CNR	UAL	1/12/06-31/1/2007	Synthesis of modified Cp ligands
P. Sgarbossa	IST	UAL	29/7-11/8/2006	Synthesis of an amino acid's derivative of diphenylphosphine
C. Dinoi <sup>a</sup>	CNRSLCC/b	CNR	23/11-22/12/2006	Catalytic oxidation of substituted thiophenes in MeCN/H <sub>2</sub> O medium
G. Kovács	UAB	UD	23/12/06 – 14/01/2007	Study of the reactivity of water-soluble complexes in the hydrogenation of dienes
A. Almássy	UD	CNR	09/07/07 – 09/08/2007	Synthesis of water-soluble Ir(I)-tertiary phosphine complexes, and their application in biphasic hydrogenation and transfer hydrogenation of $\alpha,\beta$ -unsaturated carbonyl derivatives.
A. Chernyadev	HUJI	INEOS CNRSLCC/b	10/5-27/5/2007 28/05-10/06/2007	Synthesis of Cp*-substituted molybdenum sulfides
R. Girotti	UAL	YoK	25/9-2/11/2007	Photochemistry of ruthenium pta complexes

<sup>a</sup>This visit was further sponsored by COST D29 as a short term scientific mission

### Visits (excluding secondments; from the beginning of the project)

Who	From	To	Dates	Purpose
R. Poli <sup>a</sup>	CNRS	UAB	20-21/01/04	Visit: Research seminar, draft of joint publication, discussion of research plans
A. Romerosa <sup>b</sup>	UAL	CNR	08-27/02/04	Visit: Scientific discussion and preparation of a first draft of a joint manuscript
R. Poli <sup>c</sup>	CNRS	INEOS	29/05-08/06/04	Visit: discussions, planning for the continuation of the collaboration, Conference: "Modern trends in organoelement and polymer chemistry. International conference dedicated to 50th anniversary of A.N. Nesmeyanov Institute of Organoelement Compounds", Moscow, 30/05-4/06/2004.
M. Peruzzini <sup>d</sup>	CNR	INEOS	28/05-05/06/04	Visit: discussions, planning for the continuation of the collaboration, Conference: "Modern trends in organoelement and polymer chemistry. International conference dedicated to 50th anniversary of A.N. Nesmeyanov Institute of Organoelement Compounds", Moscow, 30/05-4/06/2004;
A. Romerosa <sup>e</sup>	UAL	INEOS	28/05-05/06/04	Visit: discussions, planning for the continuation of the collaboration, attendance of international conference
L. Gonsalvi	CNR	UAL	10-20/06/04	Visit: scientific discussions, draft of joint publications with UAL scientists
A.M. Caminade <sup>f</sup> J.P. Majoral	CNRSLCC/a	UAB	19-21/09/04	Visit: discussions, attendance of bilateral (Midi-Pyrénées – Catalogne) scientific event
R. Poli <sup>f</sup>	CNRSLCC/b	UAB	19-21/09/04	Visit: discussions, planning for the continuation of the collaboration, attendance of bilateral (Midi-Pyrénées – Catalogne) scientific event
E. Shubina <sup>g</sup>	INEOS	CNRS	25/09-03/10/04	Visit (guest professor): discussions, planning for the continuation of the collaboration
M. Peruzzini <sup>h</sup> L. Gonsalvi <sup>h</sup> S. Duckett <sup>h</sup> A. Lledos <sup>h</sup> G.Ujaque <sup>h</sup> E. Shubina <sup>h</sup> N. Belkova <sup>h</sup>	CNR CNR YORK UAB UAB INEOS INEOS	CNRS	01-02/10/2004	Visit: Mid Term review and 2 <sup>nd</sup> annual meeting of RTN HYDROCHEM; planning of research activities within the framework of the AQUACHEM project
T. Campos <sup>i</sup>	UAL	UD	23/09-08/11/04	Scientific collaboration. Study of the HCO <sub>3</sub> <sup>-</sup> , 1-octen-3-ol and 1-propen-3-ol hydrogenation and isomerization promoted by water soluble ruthenium complexes.
C. Ciardi <sup>j</sup>	UAL	CNR	01/10/- 31/12/2004	Scientific collaboration: Synthesis of functionalized phosphines. Shared thesis co-direction between UAL and CNR
A. Romerosa <sup>k</sup>	UAL	CNR	20-27/11/2004	Visit: Research seminar, scientific discussions, draft

				of joint publications with CNR scientists
C. Lidrissi <sup>l</sup>	UAL	CNR	30/01-28/02/2005	Collaborative research: study of water soluble iron complexes
R. Perutz	YoK	CNRS	28/2/05 – 21/03/05	Collaborative research and scientific discussion
C. Ciardi <sup>j</sup>	UAL	CNR	01/06-01/08/2005	Scientific collaboration: Synthesis of Rh and Ir complexes with new hydrosoluble phosphines. Shared thesis co-direction between UAL and CNR
E. Gutsul <sup>m</sup>	INEOS	CNR	15/06-15/11/2005	Collaborative research: Synthesis of hydrides and macrocyclic complexes
S. Mañas <sup>n</sup>	UAL	CNR	26/07-05/09/2005	Scientific collaboration: Synthesis of water soluble PTA complexes
A. J. L. Pombeiro	IST	INEOS	28-31/08/2005	Visit to discuss on-going research and plan future work.
N. Belkova <sup>d</sup>	INEOS	CNR	05/09-16/09/2005	Visit: discussions, planning for the continuation of the collaboration, preparation of a manuscript
M. Baya <sup>o</sup>	CNRS/LCC/b	INEOS	02/10 to 30/10/2005	Collaborative research: Study of hydrogen-bonding and proton transfer involving diamagnetic and paramagnetic hydride complexes
M. Saoud <sup>n</sup>	UAL	CNR	15/10-17/12/2005	Visit; discussions, preparation of PhD Thesis
M. Peruzzini	CNR	UAL	16-17/12/2005	Visit; discussions, planning of future collaboration
N. Belkova	INEOS	UAB	15-18/12/05	Discussion and draft of joint publications
G. Kovacs	UD	UAB	1/03/05-30/05/05	Visit: Three months research stay. Training in computational techniques and collaborative work <sup>p</sup>
G. Kovacs	UD	UAB	1/03/06-31/05/06	Visit: Three months research stay. Computational study of mechanisms of organometallic reactions in water <sup>a</sup>
L. Gonsalvi <sup>d</sup>	CNR	INEOS	10-15/10/06	Visit: scientific discussions, presentation, draft of joint publications with INEOS scientists
M. Peruzzini <sup>h</sup> L. Gonsalvi <sup>h</sup> I. Mallqui <sup>h</sup> R. Poli <sup>h</sup> R. Malacea <sup>h</sup> C. Dinoi <sup>h</sup> E. Manoury <sup>h</sup> F. Joo <sup>h</sup> P. Sgarbossa <sup>h</sup> S. Mazzega <sup>h</sup> S. Duckett <sup>h</sup> A. Lledos <sup>h</sup> G. Ujaque <sup>h</sup> G. Kovacs <sup>h</sup> E. Shubina <sup>h</sup> N. Belkova <sup>h</sup> O. Filippov <sup>h</sup> L. Epstein <sup>h</sup>	CNR CNR CNR CNRS CNRS CNRS UD IST IST YORK UAB UAB UAB INEOS INEOS INEOS INEOS INEOS	UAB	27/9/2006	Visit: Final meeting of RTN HYDROCHEM; planning of research activities within the framework of the AQUACHEM project
O Lev and J. Gun	HUJI	INEOS	25/06-2/07/2006	Collaborative research, planning of future collaboration
N. Belkova <sup>o</sup>	INEOS	LCC	17/04 to 28/04/2006	Collaborative research: NMR investigation of H-bonding and proton transfer to Cp*RuH(dppe) and Cp*W(dppe)H <sub>3</sub> ; stopped-flow kinetics studies of Cp*W(dppe)H <sub>3</sub> protonation.
R. Poli	CNRS/LCC/b	INEOS	29/06 to 14/07/2006	Visit: discussions, planning for the continuation of the collaboration; preparation of joint manuscripts; joint with attendance of VII Conference on Mechanisms of Catalytic Reactions in St. Petersburg
P. Dub <sup>o</sup>	INEOS	LCC	22/05/ to 4/08/2006	Collaborative research: study of Cp*Mo(dppe)H <sub>3</sub> protonation by CF <sub>3</sub> COOH; isomerization of Cp*Fe(dppe)H <sub>2</sub> <sup>+</sup> .
E. Shubina	INEOS	IST	31-07/06-08/2006	Visit: Discussions on topics of mutual interest and presentation of a seminar
V. Bregadze	INEOS	IST	31-07/06-08/2006	Visit: Discussions on topics of mutual interest and presentation of a seminar
F. Joó <sup>q</sup>	UD	UAL	06/06/06-	Visit: Discussions on topics of mutual interest



Á. Kathó <sup>q</sup>			15/06/06	
M. Fekete <sup>q</sup>	UD	UAL	03/10/06-10/11/06	Collaborative research: synthesis of new water-soluble Ru-NHC complexes
F. Joó <sup>q</sup> Á. Kathó <sup>q</sup>	UD	UAL	12/07/07-23/07/07	Visit: preparation of a manuscript on Ru(II)-catalyzed redox isomerizations Discussion of topics of mutual interest (further collaboration)
M. Fekete <sup>q</sup>	UD	UAL	16/10/07-16/11/07	Collaborative research: photochemically assisted transition metal catalysis in water
A. Romerosa <sup>q</sup>	UAL	UD	31/07/07 - 07/08/07	Visit: Discussion of joint experiments on solar photocatalysis
A. Mena Cruz	UAL	UD	06/10/07 - 18/11/07	Collaborative research: redox isomerization of allyl-alcohols with a new Ru(II)-phosphine type catalyst.
A. Lledos and G. Ujaque <sup>f</sup>	UAB	LCC	1-2/02/2007	Visit: discussions, planning for the continuation of the collaboration; preparation of joint manuscripts, joint with the participation to a French-Catalan workshop.
R. Poli	LCC	HUJI	6 to 13/04/2007	Visit: discussions, planning for the continuation of the collaboration; preparation of joint manuscripts.
P. Dub <sup>o</sup>	INEOS	LCC	18/06/ to 05/09/2007	Collaborative research: synthesis and NMR investigations of an osmium hydride complex.
V. Levina <sup>o</sup>	INEOS	LCC	25/06/ to 10/08/2007	Collaborative research: catalyzed hydroamination of non activated olefins.
R. Poli <sup>o</sup>	LCC	INEOS	23 to 30/09/2007	Visit: discussions, planning for the continuation of the collaboration; preparation of joint manuscripts; joint with attendance of XVIII Mendeleev Conference in Moscow.

<sup>a</sup> Visit sponsored by UAB. <sup>b</sup> Visit sponsored by COST-D29. <sup>c</sup> Visit sponsored by an INTAS network. <sup>d</sup> Visit sponsored by a CNR/RAS bilateral project. <sup>e</sup> Visit sponsored by an INTAS network. <sup>f</sup> Visit sponsored by the Catalan government. <sup>g</sup> Visit sponsored by the Université de Bourgogne (invited professor programme). <sup>h</sup> Visits sponsored by the EC (Project RTN HYDROCHEM). <sup>i</sup> Visit sponsored by COST (COST Chemistry Action D29). <sup>j</sup> Visit sponsored by the Spanish Ministry of Research (Ministerio de Educación y Ciencia. Estancias cortas Becarios F.P.U.). <sup>k</sup> Visit sponsored by the SOCRATES-ERASMUS Program between the Universities of Almería (Spain) and Florence (Italy). <sup>l</sup> Visit sponsored by COST (COST Chemistry Action D17). <sup>m</sup> Visit sponsored by INTAS (INTAS YS grant 2005). <sup>n</sup> Visit sponsored by UAL. <sup>o</sup> Visit sponsored by a CNRS-INEOS bilateral programme (PICS). <sup>p</sup> Visit sponsored by the EC (HPC-Europa Transnational Access). <sup>q</sup> Visit sponsored by the Hungarian-Spanish Bilateral Intergovernmental Collaboration (Accion Integrada) <sup>r</sup> Visit sponsored by a joint CNRS/Catalan program

**Informal meetings** between the Network participants have taken place during international conferences:

- “VII Conference on mechanisms of catalytic reactions”, St. Petersburg, Russia, 3-8 July, 2006: participants were R. Poli (LCC), N. Belkova (INEOS).
- “XXII International Conference on Organometallic Chemistry”, Zaragoza, Spain, 23-28 July, 2006: participants were R. Poli, J. J. Brunet, M. Gouygou, E. Manoury, A. Labande, M. Rodriguez, J. Houghton, (LCC), M. Peruzzini, R. Malacea (CNR), A. Lledós, G. Ujaque, J. Hayes, S. Moncho, M. Baya (UAB), E. Shubina, N. Belkova, O. Filippov (INEOS), A.J.L.Pombeiro, R.Wanke, A. Kirillov, M. Kirillova, P. Sgarbossa (IST).
- “Experiment and Theory in Transition Metal Chemistry: a meeting point”, Bellaterra, Spain, 28-29 September, 2006: participants were R. Poli, E. Manoury, C. Dinoi (LCC), M. Peruzzini, L. Gonsalvi, R. Malacea (CNR), S. Duckett, J. Lopez Serrano (YORK), A. Lledós, G. Ujaque, J. Hayes, E. Veilly (UAB), K. Almeida (SHELL), A. Albinati, P. Georgiev (UMI), L. Epstein, E. Shubina, N. Belkova, O. Filippov (INEOS), Y.Karabach, P. Sgarbossa, S. Svobota (IST).
- “3<sup>rd</sup> International Conference on Green and Sustainable Chemistry” Delft, the Netherlands, 1-5 July, 2007: participants were L. Gonsalvi (CNR), F. Joó (UD) and Á. Kathó (UD).
- 2<sup>èmes Journées Franco-Catalanes de Chimie Moléculaire</sup>, 1-2 February 2007, A.-M. Caminade (LCC), A. Lledos (UAB).
- 2<sup>ème colloque Maroc-Français en Chimie Moléculaire</sup> 12-15 November 2007 A.-M. Caminade (LCC), A. Lledos (UAB).
- Second Aquachem Workshop *CIAM-Catalysis in Aqueous Media*, Toulouse (France), 30 November-1 December 2007, all partners.
- “FIGIPAS07”, Vienna, Austria, 4-7 July, 2007: participants were R. Poli (LCC), E. Shubina (INEOS), M. Peruzzini (CNR).

- “XVIII Mendeleev Conference”, Moscow, Russia, 23-28 September, 2007: participants were R. Poli, P. Dub (LCC), E. Shubina, N. Belkova, L. Epstein, O. Filippov, E. Gutsul, V. Levina (INEOS).

## ➤ B.4 Training

B.4.1. As already reported for the first and second year, the vacant positions have been advertised primarily through e-mail by each scientist in charge to other scientists working in the same scientific area and on the CORDIS website. Posting on other web pages has been done by each Network participant on an individual basis. Once again personal contacts and advertisements as well as direct e-mailing of colleagues has had the highest impact in terms of generating applications from qualified candidates.

B.4.2. Recruitment has been as follows:

<i>Participant</i>	<i>Contract deliverable of Young Researchers to be financed by the contract (person- months)</i>			<i>Young Researchers financed by the contract (person-months) ALL UPDATE</i>		
	<i>ESR (a)</i>	<i>ER (b)</i>	<i>Total (a+b)</i>	<i>ESR (c)</i>	<i>ER (d)</i>	<i>Total (c+d)</i>
1. [CNR]	18	12+5 <sup>e</sup>	35	8	17	35
2. [CNRS] (a)	63 <sup>a,d</sup>	11 <sup>a</sup>	74 <sup>d</sup>	34	11	45
2. [CNRS] (b)				29	0	29
3. [UD]	0	36	36	0	36	36
4. [HUJI]	0	24	24	0	24	24
5. [UAB]	0	24	24	0	24	24
6. [YoK]	0	18	18	0	18	18
7. [UEN]	13 <sup>d</sup>	16 <sup>d</sup>	29 <sup>d</sup>	13	16	29
8. [IST]	36	9	45	36	9	45
9. [UAL]	33	10	43	33	10	43
10. [INEOS]	0	0	0	0	0	0
<b>TOTAL</b>	163 <sup>b,d</sup>	165 <sup>c</sup>	328	163	165	328

<sup>a</sup> The use of the assigned number of person-months within CNRSLCC was changed. CNRSLCC/b shifted 5 months from ER to ESR, in order to bring the contract of Ms. Chiara Dinoi from 24 to 29 months. Ms Dinoi has completed her Ph.D. thesis with a 6 month employment as ESR at IST, fulfilled between February and July 2007. The one residual ER person-month that is unused by CNRSLCC/b was allotted to CNRSLCC/a. <sup>b</sup> Originally 165. <sup>c</sup> Originally 161. <sup>d</sup> After the quota change for UEN. <sup>e</sup> After transfer of money from management

B.4.3. The recruitment situation at the end of the project was as follows:

Entry	Partner	ESR/ER	Name	M/F	Country	Starting date	Duration	Mentor
1	CNR	ER	Dr Vanessa Landaeta Perera	F	Venezuela	July 1, 2004	12	Dr L. Gonsalvi
2	UEN	ESR	Ms Raquel Urpi Bertran	F	Spain	July 1, 2004	12	Prof R. van Eldik
3	UAL	ESR	Mrs Inocenta Mery Mallqui Ayala	F	Peru	July 1, 2004	16	Prof A. Romerosa Nievas
4	IST	ESR	Ms Silvia Mazzega Sbovata	F	Italy	July 15, 2004	7	Prof. A. Pombeiro
5	YoK	ER	Dr Nicole Reddig	F	Germany	September 1, 2004	18	Prof R. Perutz
6	CNRS	ESR	Ms Chiara Dinoi	F	Italy	September 1, 2004	29	Prof R. Poli

7	CNRS	ESR	Mr Paul Servin	M	Sweden	November 1, 2004	34	Prof A.-M. Caminade
8	UAB	ER	Dr Andrea Rossin	M	Italy	November 8, 2004	12	Dr G. Ujaque
9	IST	ESR	Mr Yahuen Karabach	M	Belarus	January 15, 2005	6	Prof A. Pombeiro
10	HUJI	ER	Dr Petr Prikhodcenko	M	Russia	June 22, 2005	12	Prof O. Lev
11	UD	ER	Dr Wojciech Wojtków	M	Poland	July 1, 2005	12	Prof F. Joo
12	CNRS	ER	Dr M.del Mar Tristany	F	Spain	January 1, 2006	11	Prof A. M. Caminade
13	UAL	ESR	Ms Emma Petersen	F	The Netherlands	February 1, 2006	12	Prof A. Romerosa
14	IST	ESR	Mr Paolo Sgarbossa	M	Italy	March 1, 2006	5	Prof A. Pombeiro
15	CNR	ESR	Mrs Inocenta Mery Mallqui Ayala	F	Peru	May 2, 2006	18	Dr L. Gonsalvi
16	UAB	ER	Dr Gabor Kovacs	M	Hungary	June 1, 2006	12	Prof A. Lledos
17	HUJI	ER	Dr. Andrey Chernadyev	M	Russia	June 26, 2006	12	Prof O Lev
18	UD	ER	Dr. Guoying Zhao	F	People's Rep China	July 1, 2006	12	Prof F Joo
19	UEN	ER	Dr. Malgorzata Brindell	F	Poland	July 15, 2006	10+4 <sup>a</sup>	Prof R vanEldik
20	UEN	ER	Dr Lukas Orzel	M	Poland	April 1, 2007	3 <sup>a</sup>	Prof R vanEldik
21	UD	ER	Dr. Ambroz Almassy	M	Slovakia	October 1, 2006	12+2 <sup>b</sup>	Prof F. Joo
22	IST	ESR	Ms Katrin Grunwald	F	Austria	December 1, 2006	6	Prof A. Pombeiro
23	IST	ER	Dr Laurent Benisvy	M	France	January 1, 2007	9	Prof A. Pombeiro
24	IST	ESR	Mr Riccardo Wanke	M	Italy	January 1, 2007	6	Prof A. Pombeiro
25	IST	ESR	Ms Chiara Dinoi	F	Italy	February 1, 2007	6	Prof A. Pombeiro
26	UAL	ER	Dr Rugiada Girotti	F	Italy	February 1, 2007	10	Prof A. Romerosa
27	CNR	ER	Dr Mikael Erlandsson	M	Sweden	July 1, 2007	5 <sup>c</sup>	Dr L. Gonsalvi

<sup>a</sup> In 2007, Dr Brindell had to return to Poland for 3 months; the appointment was put on hold and Dr Orzel was recruited as temporary substitution. <sup>b</sup> The contract of Dr. Almássy has been extended by 2 months with prior consent of the Scientific Officer at EC. <sup>c</sup> The appointment of Dr Erlandsson derived from a category money transfer (from management) at CNR with prior consent of the Scientific Officer at EC.

B.4.4. The measures taken to train the ESR/ER have been as follows:

**B.4.4.1 Local research training (from the beginning of the project)**

Vanessa Landaeta (CNR): already trained in inert atmosphere synthesis and handling techniques;

- Synthesis of ruthenium water soluble complexes (16 h training by Dr L. Gonsalvi)
- Synthesis of water soluble polyaza ligands (6 h training by Dr. F. Vizza)

- Catalytic oxidation reactions (32 h training by Dr. L. Gonsalvi)
- Operation of IR, UV, GC, and GC/MS instrumentation (4 h training by Dr. L. Gonsalvi).
- Acquisition and processing of  $^{13}\text{C}$  NMR spectra with Varian VXR 300 NMR spectrometer (3 h training by Dr. M. Peruzzini)
- Literature survey on catalytic methods for oxidation of thiophenes, (self, 1 week)
- Acquisition of NMR spectra at Bruker AVANCE 400 spectrometer (8 h training, Dr P. Barbaro)
- Manipulation and synthesis of air-sensitive hydrides (8 h training, Mr. F. Zanobini)
- Collecting literatures and preparing an advanced draft of two manuscripts (2 weeks training, Dr. M. Peruzzini, Dr C. Bianchini)

Paul Servin (CNRS/SLCC/a):

- Synthesis of dendrimers: several weeks (training by Dr. R. Laurent and C. Rebout)
- Manipulations under inert atmosphere: 10 h (training by Dr. R. Laurent)
- Basic operations of multinuclear FT-NMR spectrometry (Bruker AC200 and AM250): 15 h (training by Dr. R. Laurent)
- Basic use of data bases (Beilstein, SCIFinder): 2 h (training by Dr. A.M. Caminade)
- Practical NMR software course: 3 h (delivered by F. Lacassin)
- Win NMR courses: 3 h (delivered by F. Lacassin)
- Basic operations of Gas Chromatography (GC): 2 h (training by E. Manoury)
- How to run and work up 2D NMR spectra from 300 MHz (Bruker): 2 h (delivered by F. Lacassin)
- Literature survey of catalysis in water: continuous (self)
- How to use an automatic chromatography machine, 1/2 day, (training by Dr R. Laurent)
- Basic catalytic experiments: several days (training by Dr R. Laurent)
- Revision of two scientific manuscripts (discussion and training by Dr AM. Caminade)
- Writing a PhD thesis: several months (under the supervision of Dr A.M. Caminade)

M. Mar Tristany (CNRS/SLCC/a):

- Synthesis of dendrimers: several weeks (training by Dr. R. Laurent and C. Rebout)
- Basic operations of multinuclear FT-NMR spectrometry (Bruker AC200 and AM250): 15 h (training by Dr. R. Laurent)
- Practical NMR software course: 3 h (delivered by F. Lacassin)

Chiara Dinoi (CNRS/SLCC/b then IST):

- Operations under controlled atmosphere: 20 h (training by Prof. R. Poli)
- Basic operations of multinuclear FT-NMR spectrometry (Bruker AC200 and AM250): 10 h (training by Dr. A. Labande)
- Operations of a Perkin-Elmer Spectrum GX FT-IR spectrophotometer: 2 h (training by Dr. Miguel Baya)
- Introduction to electronic literature search tools: 2 h (training by Prof. R. Poli and by P. Eyraud)
- Operations of a Vacuum Atmosphere HE-63P glove-box: 1 h (training by S. Vincendeau)
- Operation of Princeton Applied Research Scanning Potentiostat (model 362) for cyclic voltammetry: 5 h (training by Prof. R. Poli and Alix Saquet)
- Basic operations of EPR spectrometry (Elexsys E500 BRUKER): 10 h (training by Dr. A. Mari)
- Operations of Gas Chromatography (GC): 6 h (training by Dr. A. Labande)
- Literature survey on scorpionate compounds (1 week)
- Practice on the synthesis of scorpionate compounds, namely tris(pyrazolyl)methanesulfonate and its coordination (3 weeks).
- Practice of electrochemical techniques (cyclic voltammetry and controlled potential electrolysis) (4 weeks).
- Practice of using coordination compounds in catalytic systems for peroxidative oxidations of alkanes (1 weeks).
- Acquisition and processing of gas chromatograms.
- She delivered a couple of talks on her own research during the Group meetings.

Andrea Rossin (UAB):

- Use of large supercomputation resources (4 hr, training by Dr. Gregori Ujaque)
- Solvent effect calculations (4 hr, training by Dr. Gregori Ujaque)
- Literature survey on catalytic hydrogenation of unsaturated aldehydes, (self, 1 week)
- Use of Gaussian03 and ADF computer packages (20 hr, training by Dr. Gregori Ujaque)

Nicole Reddig (YoK) already trained in:

-Schlenk-Techniques; Operation of UV/Vis and cyclic voltammetry instrumentation; -Synthesis of transition metal complexes; Single Crystal structure determination (solution and refinement)

Received training in York as follows:

- Luminescence spectroscopy including work on Fluorimeter (8 h training by Dr. L. Abbott and H. Batey).
- Operation of IR instrumentation (4 h training by Prof. Perutz and Dr. N. Jasim)
- Acquisition and processing of  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{13}\text{C}$ -NMR spectra with Bruker 300 DX spectrometer (20 h training by H. Fish and Dr. N. Jasim)
- Acquisition and processing of single crystal X-ray determination on a Bruker AXS Smart 6000 diffractometer (20 h training by Dr. A. C. Whitwood and Dr. A.-K. Duhme-Klair)
- Glove box training (1 h by Dr. N. Jasim)
- Graduate course on MO Theory of transition metal complexes, given by O Eisenstein (April 2005)
- Training in Laser time-resolved Emission and Absorption spectroscopy (2 days by Dr. A. Macpherson)
- Training in Laser time-resolved IR spectroscopy at Rutherford-Appleton Laboratory (2 weeks by Dr. M. Towrie and Dr. K. Royane)
- Training in Single Photon Counting Techniques at Rutherford-Appleton Laboratory (2 weeks by Dr. S. Botchway)
- Training in infrared-spectroelectrochemistry at the University of Amsterdam (1 week by Dr. F. Hartl)

Raquel Urpi-Bertran (UEN):

Graduate students in Erlangen:

- Series of advanced lectures in Inorganic and Bioinorganic Reaction Mechanisms (12 lectures of 2 h each)
- Operation of stopped-flow and rapid scan equipment (1 week)
- Use of flash-photolysis equipment (2 weeks)
- Experiments on high pressure NMR system (2 weeks)
- Data collection and calculation of rate and activation parameters (3 weeks)
- Synthesis and characterization of metal complexes (3 weeks)

Malgorzata Brindell (UEN):

- Operation of stopped-flow and rapid scan equipment (2 weeks)
- Experiments on high pressure stopped-flow system (3 weeks)
- Data collection and calculation of rate and activation parameters (2 weeks)
- Synthesis and characterization of metal complexes (3 weeks)

Silvia M. Sbovata (IST)

- Inert atmosphere synthesis and handling techniques (1 week)
- Literature survey on water soluble phosphines and complexes (2 weeks)
- Synthesis of water soluble phosphines (4 weeks)
- Acquisition and processing of  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR spectra with Varian 300 spectrometer (1 week)
- Practice of electrochemical techniques (cyclic voltammetry and controlled potential electrolysis) (2 weeks)

Yauhen Yu. Karabach (IST)

- Literature survey on copper complexes and their uses (2 weeks).
- Practice of synthetic methods for coordination compounds and their purification (3 weeks).
- Practice of using coordination compounds in catalytic systems for peroxidative oxidations of alkanes (2 weeks).
- Acquisition and processing of multidimensional NMR spectra with a Varian 300 spectrometer (1 week).
- Acquisition and processing of gas chromatograms with a Fisons GC 8000 series gas chromatograph.

Paolo Sgarbossa (IST)

- Inert atmosphere synthesis and handling techniques (1 week)
- Literature survey on water soluble phosphines and complexes (2 weeks)
- Synthesis of water soluble phosphines (4 weeks)
- Acquisition and processing of  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR spectra with Varian 300 spectrometer (1 week)
- Experimental procedures for oxidation catalysis (10 weeks)
- Practice of electrochemical techniques (cyclic voltammetry and controlled potential electrolysis) (4 weeks)

Katrin Grunwald (IST)

- Literature survey on copper complexes and their uses (2 weeks).
- Practice of synthetic methods for coordination compounds and their purification (2 weeks).

- Practice of using coordination compounds in catalytic systems for peroxidative oxidations of alkanes (2 weeks).
- Acquisition and processing of multidimensional NMR spectra (1 week).
- Acquisition and processing of gas chromatograms with a Fisons GC 8000 series gas chromatograph.
- Practice of electrochemical techniques (cyclic voltammetry and controlled potential electrolysis) (4 weeks).
- She delivered a couple of talks on her own research during the Group meetings.

#### Gabor Kovacs (UAB)

- Computational treatment of the organometallic reactivity (30 hr, training by Prof. A. Lledós)
- Solvent effect calculations (4hr, training by Prof. A. Lledós)
- Use of large supercomputation recourses (6 hr, training by Dr. Gregori Ujaque)
- Hybrid QM/MM calculations (20 hr, training by Dr. Gregori Ujaque)

#### Inocenta Mery Mallqui Ayala (UAL then CNR):

- Inert atmosphere synthesis and handling techniques (40 h training by M. Serrano Ruiz)
- Synthesis of ruthenium water soluble complexes (25 h training by A. Romerosa)
- Operation of IR and UV instrumentation (2 h by T. Campos, M. Serrano Ruiz)
- Acquisition and processing of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra by a Bruker DRX300 spectrometers (30 h by M. Serrano Ruiz).
- Acquisition and processing of multidimensional NMR spectra by a Bruker DRX300 spectrometers (20 h by A. Romerosa and T. Campos).
- Literature survey on water soluble ligand syntheses, (self, 1 week)
- Synthesis of sulfonated phosphines and related Ru complexes (100h by Dr L. Gonsalvi, Dr M. Erlandsson)
- Acquisition and processing of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra by a Bruker AC200 spectrometer (10 h by M. Peruzzini)

#### Emma Petersen (UAL)

- Operation of IR instrumentation (2 h by M. Serrano Ruiz)
- Acquisition and processing of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra on a Bruker DRX300 spectrometer (2 h by M. Serrano Ruiz and C. Ciardi)
- Chromatography on silica (3h by M. Serrano Ruiz)
- Amino acid synthesis (6h by C. Ciardi)
- Crystal growth (4h M. Serrano Ruiz)
- Acquisition and processing of multidimensional NMR spectra by a Bruker DRX300 spectrometers (5 h by M. Serrano Ruiz).

#### Petr Prikhodchenko (HUJI)

- Electrospray ionization mass spectrometry (50 training hours by Dr. J. Gun)
- Combined on line hydrodynamic voltammetry and ESI-MS techniques (50 training hours by O. Lev Gun).
- Electrochemical techniques (30 training hours by Dr. Gun).

#### Andrey Chernadyev (HUJI)

- Electrospray ionization mass spectrometry (50 training hours by Dr. J. Gun)
- Combined on line hydrodynamic voltammetry and ESI-MS techniques (50 training hours by O. Lev, J. Gun).
- Electrochemical techniques (30 training hours by Dr. Gun).
- Operation of IR instrumentation (4 h training by Dr. Prichodchenko)
- Nanocenter equipment: including XPS by Vitaly Gutkin (40 training hours by V. Gutkin)
- SEM and TEM microscopies (30 training hours by Vitaly Gutkin)
- NMR training – (50 training hours by O.Lev and R. Hoffman)

#### Guoying Zhao (UD)

- Acquisition and processing of NMR spectra on the Bruker NMR equipment of the Department of Chemistry, UD (5 hours – Gábor Papp)
- Synthesis of water-soluble ligands and complexes (6 h – Gábor Papp)
- Operation of the HPLC (Waters) and GC (HP) equipments in the group of F. Joó (4 h -Henrietta H. Horváth)

#### Ambroz Almassy (UD)

- Acquisition and processing of NMR spectra on the Bruker NMR equipment of the Department of Chemistry, UD (5 hours – Gábor Papp)

- Synthesis of water-soluble ligands and complexes (6 h – Gábor Papp)
- Operation of the HPLC (Waters) and GC (HP) equipments in the group of F. Joó (4 h -Henrietta H. Horváth)
- Operation of the Spectrum 1 and Paragon 1000 FTIR equipments (4 h – Gábor Papp)
- Microwaves in synthesis; theory and experiments (12 h – István Országh)
- ACS Hungary Short Course on *Frontiers in Organic Synthesis*, October 10-12, Budapest, Hungary (modern methods of organic synthesis)

#### Riccardo Wanke (IST)

- Inert atmosphere synthesis and handling techniques (1 week)
- Literature survey on scorpionate compounds (2 weeks)
- Practice on the synthesis of scorpionate compounds, and their functionalization (3 weeks).
- Practice of using coordination compounds in catalytic systems for peroxidative oxidations of alkanes (2 weeks).
- Practice of microwave assisted synthesis.
- Acquisition and processing of multidimensional NMR spectra (1 week).
- Acquisition and processing of gas chromatograms..
- Practice of electrochemical techniques (cyclic voltammetry and controlled potential electrolysis) (4 weeks).
- He delivered a couple of talks on her own research during the Group meetings.

#### Laurent Benisvy (IST)

- Syntheses of N-containing compounds and studies of their coordination to metals.
- Acquisition and processing of multidimensional NMR spectra.
- Practice on EPR spectrometry.
- Acquisition and processing of gas chromatograms.
- Practice of electrochemical techniques (cyclic voltammetry and controlled potential electrolysis) (4 weeks).
- He delivered a couple of talks on her own research during the Group meetings.

#### Mikael Erlandsson (CNR)

- already trained in inert atmosphere organic synthesis and handling techniques
- Synthesis of ruthenium and iridium water soluble complexes (16 h training by Dr R. Malacea)
- Acquisition of NMR spectra at Bruker AVANCE 400 spectrometer (8 h training, Dr L: Gonsalvi)
- Use of high pressure equipment (autoclaves, sapphire tube, 16 h training by Dr R. Malacea and Dr L Gonsalvi)

#### B.4.4.2 Secondment research training

The AQUACHEM Network foresees that each ESR or ER researcher will spend at least 1/12 of their appointment period (e.g. 1 months for a 1-year appointment) in at least one laboratory in addition to their principal place of work. The secondment activity has started in the second year with some slowness, which reflects the related slowness in the start off of the project. A programme to continue and increase the secondment avoiding an imbalanced distribution of secondments between the partners has been part of the discussion agenda of the first and second year meetings.

At present the secondment activity has been as follows:

#### Vanessa Landaeta (CNR):

Dr Landaeta has spent a three weeks period (April 2005) in the INEOS EAS laboratory (hosting scientist Prof. Elena Shubina) to carry out low temperature IR studies of the proton transfer interactions between weak proton donors and a few hydrosoluble iridium hydrides which have been synthesised in Florence.

#### Inocenta Mery Mallqui Ayala (UAL then CNR):

PhD student Mallqui-Ayala has spent 6 weeks in CNR laboratories (July - September 2005) (hosting scientist Dr. M. Peruzzini) to carry out the study of the catalytic properties of the complexes synthesized at UAL during the first year of ESR fellowship. Mrs Mallqui-Ayala has been involved in studying the catalytic hydrogenation of ketones and imines under biphasic aqueous conditions. During 2006, she has joined ICCOM as ESR. Secondment activities were carried out by Mrs Mallqui going to UAL (1 month, December 2006)

- Basic operations of Gas Chromatography (GC): 4 h (training by L. Gonsalvi)
- High pressure reactions (autoclave): 6 h (training by L Gonsalvi)
- Attendance of advance organometallic chemistry classes (PhD program at UAL)

Yauhen Yu. Karabach (IST)

The ESR Y. Karabach (IST) spent 11 days (June 16th-26th) in Prof. Ferenc Joo's laboratory (UD), where he tested the use of a few copper complexes he had prepared in Lisbon as catalysts for the hydrogenation of 1-octen-3-ol to 1-octane-3-ol (see task 6d). The reactions were monitored by  $^1\text{H}$  NMR. Hence, the ESR got training on the use of  $\text{H}_2$  gas, on experiments of olefin hydrogenation and on reaction monitoring by NMR.

Paul Servin (CNRS/SLCC/a):

Mr Paul Servin, currently doing his PhD in Toulouse (laboratory of Dr Caminade), has spent a month in Florence in secondment activity to trained in homogeneous catalysis.

- Basic operations of Gas Chromatography (GC): 2 h (training by L. Gonsalvi)
- High pressure reactions ("autoclave"): 6 h (training by L. Gonsalvi)

He has spent a second month in Lisbon, and a third month in Almeria in secondment activities.

-Back to basic utilization of 300 MHz: 3 h

He has spent another month in Lisbon (IST) in secondment activity. During this period he has been trained on:

- the synthesis of scorpionate-type compounds (training by R. Wanke) and coupling to dendrimers,
- the setting up the self-assembly technique with dendrimers (training by Y. Karabach),
- performing reactions of copper and tri-ethanol amine platinum complexes with dendrimers (training by A. Kirillov and P. Sgarbossa).

He has spent another month in Almeria (UAL) in secondment activity. During this period he has been trained on: Synthesis of organometallic Ru complexes

M. Mar Tristany (CNRS/SLCC/a):

Dr Mar Tristany has spent one month in Debrecen in secondment activities.

- Catalysis under hydrogen (training by Dr Agnes Katho)
- Preparation of liposomes (training by Dr Eva Csajbok)
- Basic operations of Gas Chromatography (training by Dr Gabor Papp)

Andrea Rossin (UAB):

Dr Rossin has been in Florence (CNR) doing secondment activity between October and November 2005. During this period Dr Rossin has been trained in setting up a laboratory for the synthesis and manipulation of organometallics compounds. (12 h training by Dr Gonsalvi, Mr Zanobini).

Chiara Dinoi (CNRS/SLCC/b)

Ms Dinoi has completed her PhD in Toulouse under the supervision of Prof. Rinaldo Poli. As secondment activity, she has been in Erlangen (team of Prof Rudi Van Eldik) for one month during Year 2, in Jerusalem for one month and in Florence for one month during Year 3.

Secondment training in Erlangen: NMR spectroscopy of  $^{17}\text{O}$ , an unusual nucleus to be observed by conventional NMR methods. The work done by Ms Dinoi has been useful for getting information about the mechanism ruling the formation and the interconversion of polyoxomolybdenum complexes prepared in Toulouse.

- Training in  $^{17}\text{O}$  NMR spectroscopy (10 h, training by Dr. Achim Zahl).
- Training in UV-visible spectrophotometry (6h, training by Joo-Eun Jee). Operations of several UV-visible spectrophotometer: Shimadzu UV-2100, Hewlett-Packard 8542A, Varian Cary 1G.
- Operations of a SX 18.MV (Applied Photophysics) stopped-flow apparatus ( 12 h, training by Joo-Eun Jee).
- Training in the Origin Computer Program (6 h, training by Joo-Eun Jee).

Secondment training in Jerusalem:

- Operation of Electrospray ionization mass spectrometry 10 h (training by Dr. J. Gun and Dr. P. Prikhodchenko)
- Basic operation of Combined on line hydrodynamic voltammetry and ESI-MS techniques 20 h (training by Dr. J. Gun and Dr. P. Prikhodchenko)

Secondment training in Florence:

- Principles and application of catalytic oxidation protocols and safety issues related to peroxides: 15h (training by Dr L. Gonsalvi, COST D29)
- Operations of Gas Chromatography (GC): 6 h (training by Dr. L. Gonsalvi )
- Operations of Combined Gas Chromatography and mass spectrometry technique (4h training by Dr. L. Gonsalvi)
- Operation of UV/Vis instrumentation (2h training by Dr. P. Barbaro).

Secondment training in Toulouse:

- She spent 12 days (September 4<sup>th</sup>-15<sup>th</sup>) in Prof. Rinaldo Poli (CNRS/SLCC/b) laboratory, where she finalized some experimental work and continued the writing up of her Ph.D. thesis.



### Gabor Kovacs (UAB)

Dr Kovacs has spent three weeks in UD laboratory (December 2006 -January 2007) (hosting scientist...)

### Laurent Benisvy (IST)

- The ER L.Benisvy (IST) spent 21 days (October 1<sup>st</sup>-20<sup>th</sup>) in Prof. Rudi van Eldik (Erlangen) laboratory , where he undertook a kinetic study of the reactions of hydrogen peroxide with dinuclear Cu(II) and Ni(II) complexes, bearing salicylamidate-type ligands, by using stopped-flow spectrophotometry, acid-base titrations, electrochemical and EPR studies.

### B.4.4.3 Complementary training

#### Vanessa Landaeta (CNR):

- Attended the Conference *Green Solvents For Synthesis*, Bruchsal, Germany, 3/6-10-2004 (<http://events.dechema.de/gsfs2004.html>) The participation of Dr Landaeta to this conference was encouraged as the aim of the meeting was quite in line with the AQUACHEM training activity of the ER. The aim of the Bruchsal meeting was indeed to highlight innovative concepts for the substitution of volatile organic solvents in solution phase synthesis in academia and industry. Emphasis were given to the development and application of alternative reaction media and phase-separable reagents (aqueous phase, ionic liquids, supercritical media, fluorinated phases, thermoregulated systems, soluble polymers etc.) in all areas of chemical synthesis.
- Attending/attended several CNR and University seminars given by Senior and Junior scientists.
- Preparation and revision of two scientific manuscripts (discussion and training by Dr. M. Peruzzini)
- Attended the NMR basic course on the use of BRUKER NMR spectrometers held in Milan (Bruker, May 2005, 3 days intensive course). The course included both practical and theoretical training on new generation spectrometers.
- Attended the XII<sup>th</sup> International Symposium on the Relations between Homogeneous and Heterogeneous Catalysis held in Fiesole (Italy) in July 2005. In such occasion she presented a poster contribution.
- Dr Landaeta was fluent in Italian. Therefore, it was no necessary for her to attend any Italian course

#### Paul Servin (CNRSLCC/a):

- Regular attendance of research seminars given by visiting scientists (ca. 1/week)
- Active participation to group meetings (ca. 1/15 days)
- Regular presentation of his own work during group meetings (every three months, 20 to 23 people in the audience)
- Active participation to group meetings (1 per week)
- Chemistry courses:
  - Advanced organometallic chemistry and catalysis: 20 h (delivered by the Université Paul Sabatier)
  - Stereoselective synthesis and catalysis: 20 h (delivered by the Université Paul Sabatier)
- French language course, spoken: 50 h (delivered by the Pole Universitaire Européen de Toulouse)
- French language course, spoken: 150 h (delivered by the Alliance Française)
- One day training about "Organization of companies" (delivered by the Université Paul Sabatier)
- One day training about "Labour contracts and laws" (delivered by the Université Paul Sabatier)
- Participation to the organization of IDS5 (the fifth International Dendrimer Symposium) in Toulouse, France (August 28 - September 1, 2007), for which A.M. Caminade and J.P. Majoral were the Chairs. More than 300 attendees were coming from 32 countries.

#### M. Mar Tristany (CNRSLCC/a):

- Regular attendance of research seminars given by visiting scientists (ca. 1/week)
- Regular presentation of his own work during group meetings (every three months, 20 to 23 people in the audience)
- Active participation to group meetings (1 per week)
- French language course, spoken: 50 h (delivered by the Alliance Française)

#### Andrea Rossin (UAB):

- Attended the XII<sup>th</sup> International Symposium on the Relations between Homogeneous and Heterogeneous Catalysis held in Fiesole (Italy) in July 2005. In such occasion he orally presented his research activity.
- Attended the "33<sup>rd</sup> Congresso di Chimica Inorganica della Società Chimica Italiana" Siena, Italy, July 11-16<sup>th</sup> 2005. In such occasion he presented an oral contribution on the results obtained in the AQUACHEM Activity.
- Intensive Spanish course : 90 h (delivered by the UAB Idiomes Campus)

Raquel Bertran (UEN):

- Participation in weekly group seminars, departmental colloquia, SFB 583 “Redox-active metal complexes” colloquia and workshops

Chiara Dinoi (CNRSLCC/b):

- Regular attendance of research seminars given by visiting scientists (ca. 1/week)
- Active participation to group meetings
- French language course: 56 h
- Regular attendance of research seminars given by visiting scientists (ca. 1/week)
- Active participation to group meetings
- English language course: 50 h
- Attendance of the course: “Advanced NMR Spectroscopy”, 10 h (Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques, 27/09/05-12/10/05)

Inocenta Mery Mallqui Ayala (UAL then CNR):

- Attending/attended several seminars and PhD lectures into the “Advanced Chemistry” PhD program of the University of Almería.
- The mother language of the PhD student Mallqui-Ayala is the Spanish, thus it was no necessary for her to attend any Spanish course.
- Italian course to start in 2007.
- Active participation in group meetings at CNR (approximately every two weeks)

Nicole Reddig (YoK)

- Active participation in group meetings (once per 2 weeks)
- Attendance at symposia (e.g. Edinburgh Dalton Symposium, Leeds)
- Graduate Course in mo theory of transition metal complexes (Eisenstein, April 05)

Yahuen Karabach (IST)

- Active participation to group meetings
- Regular presentation of his own work during group meetings
- Attendance of the congress *Current and Future Trends in Polymeric Materials*, Prague, Czech Republic, where he presented a contribution.

Petr Prikhodchenko (HUJI)

- Attending/attended a comprehensive course in English (10 hours/week).
- Active participation in group meetings of Dr. Gun (2 hours/week).

Andrey Chernadyev (HUJI)

- Attended the NMR basic course. The course included both practical and theoretical training on NMR spectrometers: 30 hr.
- Regular attendance of research seminars given by visiting scientists (ca. 1/week)
- Active participation to group meetings

Wojciech Wojtkov (UD)

- Hungarian language course, 2 weeks, 8 h/day
- Active participation in the weekly seminars of the Institute of Physical Chemistry
- Active participation in the group meetings of Prof. Joó (approximately every three weeks)

Gabor Kovacs (UAB)

- Attended the congress *XXIInd ICOMC, 22nd International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July 2006, where he presented a contribution.
- Attended the workshop “*Experiment & Theory in Transition Metal Chemistry: a meeting point*”, Bellaterra, Spain, 27-29 September 2006, where he gave an oral presentation.
- Attended the *6th International Summer School of Organometallic Chemistry*, Camerino, Italy, 8-12 September 2007, where he presented a contribution.
- Attended the *Europacat 8 Conference*, Turku, Finland, 26-31 August 2007, where he presented a poster.  
Intensive Spanish course: 90 h (delivered by the UAB Idiomes Campus)

Intensive Catalan course: 90 h (delivered by the UAB Idiomes Campus)

Emma Petersen (UAL)

- Spanish language course (40 tuition hours at the Language school of the University of Almería)
- Attended/attending several research seminars given by visiting scientists
- Participation in group meetings (1/week)
- Attended PhD courses in the Advanced chemistry program of the University of Almería. Also these courses contained an examination in the form of an exam or oral presentation, which were all passed.
  - o Enzyme structure and catalytic mechanisms (30 hour selfstudy )
  - o Catalysis (30h, 2 weeks, 3 h/day)
  - o Organometallics and organic synthesis (30h, 5 weeks, 3 days a week 2 hours)
  - o Bio-organic chemistry and molecular modeling (60 hour)
  - o Structural determination by X-ray (20h)
  - o Design and construction of catalysts for enzymatic synthesis (30, 1 week, 2 h/day)
  - o Experimental training (120h by A. Romerosa and M. Serrano Ruiz)

Guoying Zhao (UD)

- 2 weeks introductory Hungarian language course (UD Summer Course, 8h/day)
- Active participation in the weekly seminars of the Institute of Physical Chemistry
- Active participation in the group meetings of Prof. Joó (approximately every three weeks)

Ambroz Almassy (UD)

- Active participation in the weekly seminars of the Institute of Physical Chemistry
- Active participation in the group meetings of Prof. Joó (approximately every three weeks)
- Debrecen Summer University – Intensive Hungarian Language Course, 2 weeks, April, 2007

B.4.4.4 Mentoring

Vanessa Landaeta (CNR): tutoring on literature search and GC analysis to a newly hired postdoctoral researcher at CNR-ICCOM.

Andrea Rossin (UAB) has supervised the stay at the UAB group of G. Kovacs (UD)

Chiara Dinoi (CNRSLCC/b) has supervised two graduate students (Gülnur Taban and Pelin Sözen, Celal Bayar University, Muradiye-Manisa, Turkey) during short stay visits in Toulouse within the framework of a bilateral programme.

Gabor Kovacs (UAB); Tutoring of the secondment of Emma Petersen (UAL) in the UAB group (from March 15, 2007 to May 15, 2007).

Mikael Erlandsson (CNR): tutoring on synthesis to a newly hired PhD student and to a visiting young researcher at CNR-ICCOM.

Paul Servin (CNRSLCC/a): has supervised a master student (R. Geagea) in Toulouse for several weeks.

B.4.4.5 Presentations at internal group and Network meetings

*Internal group meetings:* each YR has been requested to give periodical presentations.

Paul Servin (CNRSLCC/a) has given a presentation at 10 group meetings

- “Towards phosphadamantane (PTA)-dendrimers” AQUACHEM Meeting Lisbon, Portugal, 2005
- “Organometallic catalysts in aqueous media. The use of dendritic PTA ligands” AQUACHEM Midterm Review Meeting, Almería, Spain, 2005
- “The birth of a superdense dendrimer and some new dendrimer ligands for catalysis” AQUACHEM Meeting Debrecen, Hungary, 2007
- He has defended his PhD European thesis on July 20, 2007 in Toulouse, France “Dendrimères phosphorés et catalyse en milieu aqueux”

Mar Tristany (CNRSLCC/a) has given a presentation at 3 group meetings

- “Towards water-soluble dendrimer-based catalysts” AQUACHEM Meeting Debrecen, Hungary, 2007

N. Reddig (YoK): has given presentations in seven group meetings

- Improvements to the water-solubility of  $[Re(CO)_3bpyL]^+$ , AQUACHEM Meeting Lisbon, Portugal, 2005.

- *The Excited State of Molybdate Sensors and the Structure of the Molybdate-Rhenium Sensor Complex* AQUACHEM Midterm Review Meeting, Almeria, Spain, 2005

Vanessa Landaeta (CNR): *Ruthenium catalysed selective oxidation of aryl thiophenes with H<sub>2</sub>O<sub>2</sub>* AQUACHEM Meeting Lisbon, Portugal, 2005

Chiara Dinoi (CNRSLCC/b then IST), *Reactions of cyclopentadienylmolybdenum(VI) with sulfur compounds* AQUACHEM Meeting Lisbon, Portugal, 2005; *Reactions of hemimetalloenic molybdenum (VI) complexes with Sulfur Compounds* AQUACHEM Midterm Review Meeting, Almeria, Spain, 2005

Andrea Rossin, *The selective hydrogenation of unsaturated aldehydes by Ru(II) Complexes in water solutions*. AQUACHEM Meeting Lisbon, Portugal, 2005; *Selectivity of C=O hydrogenation in alpha,beta-unsaturated aldehydes with Ru(I) water-soluble complexes: A computational analysis* AQUACHEM Midterm Review Meeting, Almeria, Spain, 2005

Silvia Mazzega, *Water soluble phosphines and reactions with Pt(II) centers* AQUACHEM Meeting Lisbon, Portugal, 2005

Inocenta Mallqui Ayala (UAL then CNR)

*New water soluble ruthenium complexes containing the ligand 1,2-bis(N-ter-butylcarbamoyl)cyclopentadienyl* AQUACHEM Meeting Lisbon, Portugal, 2005; *Synthesis of new allenylidene ruthenium complexes supported by Cyclopentadienyl ligands with aminoacidic residues* AQUACHEM Midterm Review Meeting, Almeria, Spain, 2005

Yuhean Karabach (IST)

*New 1D and 2D water-soluble Cu(II) polymers derived from pyromellitic acid* AQUACHEM Midterm Review Meeting, Almeria, Spain, 2005

Wojciech Wojtkov (UD) *Reactions of alkynes in formic acid* AQUACHEM Midterm Review Meeting, Almeria, Spain, 2005

Petr Prikhodchenko (HUIJ) *EC/ESI-MS studies of transition metal complexes* Midterm Review Meeting, Almeria, Spain, 2005

Gabor Kovacs (UAB) *Theoretical investigation of the stereoselective reduction of diphenylacetylene in aqueous acidic solutions catalyzed by water soluble ruthenium(II) phosphine complexes* AQUACHEM 3<sup>rd</sup> Annual Meeting, Debrecen, Hungary, 2007

Mikael Erlandsson (CNR): oral presentation at AQUACHEM 4<sup>th</sup> Annual Meeting, Toulouse, France, 30 November-1 December 2007

*International conferences:*

Paul Servin (CNRSLCC/a) has presented two oral communications:

*Synthesis of PTA bearing phosphorus dendrimers*, *Journées Jeunes Chercheurs de la SFC*, Toulouse, France, April 7-8, 2005

*New dendritic water-soluble ruthenium (II) catalysts*, *XVeme Journée de Chimie du Grand Sud-Ouest*, Montpellier, France, November 25, 2005

Chiara Dinoi (CNRSLCC/b) has presented three posters and one oral communication:

- *Réactions des complexes hémimétalloéniques de molybdène(VI) avec des composés souffrés*, *GECOM-CONCOORD 2005*, Autrans, France, June 5-10, 2005 (poster).
- *Reactions of Hemimetalloenic Molybdenum(VI) Complexes with Sulfur Compounds*, *5th International School of Organometallic Chemistry (ISOC)*, Camerino, Italy, Sept 10-14, 2005 (poster).
- *Acid-base chemistry of Cp\*<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub> and <sup>17</sup>O NMR studies of water exchange in the Cp\*Mo(VI) oxo systems*, *Journées de la Chimie de Coordination*, Toulouse, France, 3-4 April 2006 (poster).
- C. Dinoi, M. Ciclosi, S. Vincendeau, R. Poli, L. Gonsalvi, M. Peruzzini: *Efficient oxidation of thiophene derivatives catalyzed by organomolybdenum and -tungsten oxido complexes*, *Catalysis in Aqueous Media Workshop*, Toulouse, France, November 30- December 1, 2007 (oral communication).

Vanessa Landaeta (CNR) has presented two contributions

*Oxidación catalítica selectiva de aril tiofenos utilizando complejos de rutenio y H<sub>2</sub>O<sub>2</sub>*, *VII Congreso Venezolano de Química*, Merida, Venezuela, 6/10-11-2005, *in Spanish*. Abstract CA35 (oral presentation).

“Ruthenium – Catalyzed Selective Oxidation of Aryl Thiophenes Using H<sub>2</sub>O<sub>2</sub>“ *ISHHC XII, 12<sup>th</sup> International Symposium on Relations between Homogeneous and Heterogeneous Catalysis* Fiesole, Italy, 18-22 July 2005 (poster presentation).

Nicole Reddig (YoK) attended Int Symp Photophys Photochem Coordination Compounds (ISPPCC) in Pacific Grove, California, July 2005. Presented poster entitled ‘Luminescence-based oxometallate sensing in aqueous media’; she has attended various departmental seminars and three 1-day symposia: “*Photons, electrons and inorganic chemistry*”, York; RSC Dalton Division Symposium, October 2005 in Edinburgh, with R R Schrock, R. H. Holm and others and a Symposium on Sensors, November 2005 in Leeds.

Andrea Rossin (UAB) has presented three contributions:

“Computational studies of selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with ruthenium(II) catalysts” XXXIII Congresso Nazionale della Divisione di Chimica Inorganica della Società Chimica Italiana; July 11-16<sup>th</sup> 2005, Siena (Italy) (oral presentation)

“Regioselective C=C/C=O hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with ruthenium(II) water-soluble complexes: a computational mechanistic study” ISHHC-XII; July 18-22<sup>nd</sup> 2005, Firenze (Italy) (oral communication)

“Regioselective C=O hydrogenation of trans-cinnamaldehyde to cinnamyl alcohol with the water-soluble complexes (H)<sub>2</sub>Ru(m-TPPMS)<sub>x</sub> [x=3,4; m-TPPMS=(meta-sulphonatophenyl) diphenylphosphine]. A theoretical study of the reaction mechanism and selectivity” Conference DFT2005; September 11-15<sup>th</sup> 2005, Genève (Switzerland) (poster presentation)

Yauhen Karabach (IST) has presented a contribution at the congress *Current and Future Trends in Polymeric Materials*, Prague, Czech Republic.

Gabor Kovacs (UAB) has presented four contributions:

“Theoretical investigation of the stereoselective reduction of diphenylacetylene in aqueous acidic solutions catalyzed by water soluble Ru(II) phosphine complexes” *XXII<sup>nd</sup> ICOMC, 22<sup>nd</sup> International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July 2006 (poster presentation)

“Theoretical investigation of the stereoselective reduction of diphenylacetylene in acidic aqueous solutions catalyzed by water-soluble phosphine complexes of ruthenium(II)” *Experiment & Theory in Transition Metal Chemistry: a meeting point* Barcelona, Spain, 27-29 September, 2006 (oral presentation)

“Theoretical analysis of the gold(I) catalyzed hydroamination of 1,3-dienes” *Europacat 8*, Turku, Finland, 26-31 August 2007 (poster presentation)

“Modelització de la reactivitat organometàlica en aigua: hidrogenació de molècules insaturades”, *XIII<sup>ena</sup> Reunió de la Xarxa de Química Teòrica de Catalunya*, Tarragona, Spain, 4-5 July 2007 (oral presentation)

A. Almássy (UD) has presented three contributions:

-“Water soluble N-heterocyclic carbene complexes of transition metals (oral)”; *Aquachem 3rd Annual Meeting*, 12-14 January, 2007, Debrecen, Hungary

-“Synthesis and Catalytic Properties of Water-Soluble N-heterocyclic Carbene Complexes (poster)”; *3rd International Conference on Green and Sustainable Chemistry*, 1-5 July 2007, Delft, The Netherlands

-“Synthesis and reactivity of water-soluble Au(I)-NHC complexes (poster)”; *XXVIII. Conference of Organic Chemists: Advances in Organic Chemistry*, September 16-20, Smolenice, Slovak Republic

Guo-Ying Zhao (UD) made a poster presentation: Capture and activation of carbon dioxide by task-specified ionic liquids (poster); *Aquachem 3rd Annual Meeting*, 12-14 January, 2007, Debrecen, Hungary

Mikael Erlandsson (CNR): Comparative studies for the catalytic water phase carbon dioxide hydrogenation using iridium and ruthenium PTA complexes (PTA=1,3,5-triaza-7-phospha-adamantane) *CIAM Workshop – Catalysis in Aqueous Media*, Toulouse, France, 30 November-1 December 2007, poster presentation;

“Aqueous phase carbon dioxide and bicarbonate hydrogenation catalysed by cyclopentadienyl ruthenium complexes” *6<sup>th</sup> ISOC International School of Organometallic Chemistry* Camerino, Italy, 8-12 September 2007 poster presentation

Inocenta Mallqui Ayala (CNR) “Catalytic hydrogenations in water phase using ruthenium(II) complexes bearing sulfonated phosphines and diamines” *CIAM Workshop – Catalysis in Aqueous Media* Toulouse, France, 30 November-1 December 2007 (poster presentation)

“Synthesis and reactivity of water soluble allenylidene ruthenium complexes bearing Cp(CONC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> ligand and PPh<sub>3</sub>, PTA, mPTA and TPPMS” 6<sup>th</sup> ISOC International School of Organometallic Chemistry Camerino, Italy, 8-12 September 2007, poster presentation.

Y. Karabach, “Catalytic Activity of an Aqua-soluble Copper(II)-sodium Two-dimensional Coordination Polymer in the Peroxidative Oxidation of Cyclohexane”, *ETTMC – Experiment and Theory in Transition Metal Chemistry*, Barcelona, Spain, 2006

S. Sbovata, “Water-soluble Organonitrile Platinum(II) Complexes”, *ETTMC – Experiment and Theory in Transition Metal Chemistry*, Barcelona, Spain, 2006.

P. Sgarbossa, “[PtCl(C<sub>6</sub>F<sub>5</sub>)(PTA)<sub>2</sub>] and Re-picolinate Complexes and their Application in the Catalytic Epoxidation of 1-Octene”, *ETTMC – Experiment and Theory in Transition Metal Chemistry*, Barcelona, Spain, 2006.

B.4.5. *Equal opportunity policy*: all advertisements clearly stated the Network’s equal opportunity policy and encouraged applications from women. At the end of the third year of the project, the ratio male/female was 3/4, therefore in line with the target.

B.4.6. *Multidisciplinarity*. The AQUACHEM network contains a very high level of multidisciplinarity joining together synthetic chemists, catalysis experts, supramolecular chemists, experts in photochemistry and electrochemistry, spectroscopy, and theoreticians. The secondment plan is conceived to expose each young researcher to these interdisciplinary aspects of research, as well as to train them on different experimental techniques.

B.4.7. *Connections to Industry*.

No industrial partner participates directly to the network. Contacts have been however established on bilateral basis by some of the partners to run activities somehow connected to Aquachem.

B.4.8. *Career development of Aquachem YS*.

- Silvia Sbovata (Italian), currently a post-doc. fellow in Italy (Padova).
- Paolo Sgarbossa (Italian), currently a post-doc. fellow in Italy (Padova).
- Katrin Grunwald (Austrian), currently a D.Phil. student in Austria.
- Yauhan Karabach (Bielorussian), currently a D.Phil. student at the IST group.
- Riccardo Wanke (Italian), currently a D.Phil. student at the IST group.
- Chiara Dinoi (Italian), currently finalizing her D.Phil. in Toulouse (at CNRSLCC/b) and looking for a research position.
- Andrea Rossin (Italian) is currently postdoctoral fellow at CNR ICCOM funded by an Italian Foundation.
- Laurent Benisvy (French), currently looking for an academic position in Europe.
- Vanessa Landaeta (Venezuelan) is assistant professor at Universidad Simon Bolivar, Caracas (Venezuela)
- Inocenta Mallqui (Peru) is finishing to write up the PhD thesis and waiting for defense.
- Mikael Erlandsson (Swedish) is currently postdoctoral fellow at CNR funded by a Swedish Foundation.
- Malgorzata Brindell (Polish) has returned to the Jagellonian University in Krakow (Poland) to continue an academic career.
- Lukasz Orzel (Polish) has returned to the Jagellonian University in Krakow (Poland) to continue an academic career.
- Andrey Chernyadyev (Russian) got a position as Senior researcher of new physico-chemical problems laboratory, Frumkin Institute of physical chemistry and electrochemistry RAS (Russia).
- Paul Servin (Swedish) will start to work on December 1st 2007 in a Start-up company in Berlin.
- Gábor Kóvacs (Hungarian) from 1st June 2007 post-doctoral fellow of the “Network of Theoretical Chemistry of Catalonia” at the UAB group.

## ➤ B.5 Difficulties

The main difficulties were related to the late recruitment process. This was however solved by a better planning already during the 3<sup>rd</sup> year as already reported. Man-month redistribution was needed to fill all the positions within the end of the project. This was done without the need for a contract amendment. From the second year on, difficulties were encountered by several partners due to the late annual payment.

## ➤ B.6 Suggestions and remarks

At the end of the final 4<sup>th</sup> year meeting, during the round table discussion some time was dedicated to collect the partners' observations, remarks and general feeling about pros and cons of the Aquachem consortium. Whereas all agreed on the high level of scientific achievements, training and good level of management, some remarks were made to the coordinator with request to deliver some suggestions to the EC.

First of all, a positive remark was made about the emphasis put by the network partners on the secondment activities. At the end of the 4 years of activity, all partners' institutions have been visited and have sent their YS for short or longer secondment periods, and this has strengthened existing collaborations and opened new joint projects which are likely to continue after the termination of the contract. All the YS present to the final meeting agreed on the added value, both scientific and personal, of such an experience and praised the EC for such opportunity.

Some uneasiness was reported by some group leader on other aspects, namely:

1. some groups were left with few person-months after negotiation. This hampered the possibility to train YS for longer periods, and to be active participants for the whole duration of the network
2. the policy of short term-high pay adopted during FP6 was criticised, as in some cases it generated an unbalance of salaries within groups, even to the point that the leading scientist was earning less than a newly recruited YS.
3. Another issue raised by some of the partner was the complicated system for financial report chosen by EC in the 6th FP, and the long delay needed to get refunding of the expenses, which often implied borrowing resources from other projects when possible or striving to stay within local team balances in the most unfavorable cases.

Suggestions for point 1 and 2 were to favour longer time-same pay appointments, thus allowing for a more balanced recruitment policy within each group giving the possibility to the YS to take full advantage of their stay, and terminate when possible the work started. For point 3, both the Coordinator and the Network Manager pointed out the feeling of general improvement of the procedures observed along the four years of activity.