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Part A - Research Results

A.1 Scientific Highlights 2006

Task 1 - Hydrosoluble ligands and their complexes

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

T1a) *Water soluble ruthenium complexes stabilised by the phosphadamantane PTA ligand (PTA = 1,3,5-triaza-7-phosphadamantane) (CNR, UAL).* This part of the collaborative research line centred on the coordination capacity of PTA has been continued mainly at **UAL**. The syntheses and X-ray diffraction crystal structures of some complexes of formula $[\text{CpRuX}(\text{WSP})_{2-x}(\text{PPh}_3)_x]\text{Y}$ (WSP = Water Soluble Phosphine) ($x = 0, 1$) were the subject of a joint article [A6]. Further collaborative work on this topic is foreseen as part of a PhD project (Mrs I. Mallqui, currently at **CNR**). PTA modifications are in progress at **CNR** as an independent project.

T1b) *Synthesis of water soluble vinylidenes and allenylidenes stabilised by hydrosoluble phosphines. (CNR, UAL)* $\text{Cp}^R\text{Ru}(\text{WSP})_2\text{Cl}$ complexes prepared conjointly in Florence and Almeria have been used at **UAL** to obtain new water soluble vinylidene and allenylidene complexes such as $[\text{Ru}\{\text{Cp-1,3-}(\text{CONC}(\text{CH}_3)_3)_2\}(\text{C}=\text{C}=\text{CPh}_2)(\text{L})(\text{L}')]\text{Y}$ ($\text{L} = \text{PPh}_3$; $\text{L}' = \text{PTA, PTAMe}^+$). A manuscript describing the synthesis and the evaluation of their properties in metathesis reactions is under preparation.

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 in the first year. These complexes were found active catalysts of the hydrogenation of olefins, aldehydes and ketones in aqueous solutions and/or in aqueous-organic biphasic systems. The results were published in a paper and disclosed in two conference posters (See also T6b) New water-soluble N-heterocyclic carbene complexes were synthesized in the second year starting with $[\text{Rh}_2(\text{OH})_2]$ and $[\text{Ir}_2(\text{OME})_2]$ precursors; their characterization and study of their catalytic properties are underway. Preliminary data have been disclosed at conferences [D38], [D40]. A (partially) COST-sponsored visit of M. Fekete from UD to UAL resulted in the synthesis of several new vinylidene- and allenylidene-Ru(II) complexes containing also an N-heterocyclic carbene ligand.

T1d) *Synthesis of a water soluble white phosphorus complexes. (CNR)* The synthesis of the stable mononuclear species $[\text{CpRu}(\text{PR}_3)_2(\text{P}_4)]\text{Cl}$ in which a white phosphorus molecule is coordinated to different ruthenium moieties (including a few water soluble), together with the hydrolysis studies were the subject of a paper which has been published [C8]. Further work in this area has been redirected towards dinuclear compounds and their hydrolysis products [C43].

T1e) *Synthesis of water soluble phosphines containing amino acid residues. (CNR, UAL)* 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 has been synthesised as part of a joint PhD project at UAL and CNR. Complexes of rhodium, iridium and ruthenium of these phosphines have been also synthesized. These preliminary results are part of a communication which has been recently submitted.

T1f) *Water soluble ruthenium complexes stabilised by water soluble phosphines and the Cp derivative containing an amino acid $\{\text{Cp-1,3-}(\text{CONC}(\text{CH}_3)_3)_2\}$ (UAL, CNR).* The synthesis of the ruthenium complexes $[\text{Ru}\{\text{Cp-1,3-}(\text{CONR})_2\}\text{Cl}(\text{L})(\text{L}')]\text{Y}$ ($\text{R} = \text{alkyl, aryl}$; $\text{L} = \text{PPh}_3, \text{PTA, mPTA, TPPMS}$; $\text{L}' = \text{PPh}_3, \text{PTA, mPTA, TPPMS}$; $\text{mPTA} = 1\text{-methyl-1,3,5-triaza-7-phosphadamantane, TPPMS} = \text{PPh}_2(\text{Ph-m-SO}_3^-)$) were continued at **CNR** by Mrs Mallqui, former ESR at **UAL**. The study of the catalytic properties of these complexes in transfer hydrogenation and hydrogenation of olefins, ketones and imines in water is foreseen in the Fourth Year.

T1g) *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 $\text{R}_2\text{P-CH}_2\text{-N-CH}_2\text{-PR}_2$, 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**) [joint paper published 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) [publication in press C34].

T1h) Synthesis of dendritic complexes (CNRS/LCC/a). Several organometallic complexes derived from some of the dendritic ligands elaborated in T1g) 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 [publication in press C34], as well as some examples of PdCl_2 complexes of unsymmetrical dendrimers. Work is still in progress to study the complexation ability of the various types of dendritic ligands described in task T1g, either in situ or by isolation of the complexes.

T1i) 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 $[\text{Re}(\text{CO})_3(\text{bipyridyl})\text{L1}]\text{PF}_6$, **S1PF₆**, 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 complex more hydrophilic (e.g. ClO_4^- , NO_3^- or CF_3SO_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 $[\text{Re}(\text{CO})_3(\text{bispyridyl})\text{L1}]\text{ClO}_4$ (**S1ClO₄**). While for the starting sensor, **S1PF₆**, the maximum amount of water tolerated in an acetonitrile solution is 20%, the exchange of the counter ion to 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 reaction with molybdate as a $\text{MoO}_2(\text{sensor})_2$ species and have determined its crystal structure. This serves as an excellent demonstration of the coordination mode. Studies by mass spectrometry demonstrate that the same Re_2Mo species is present in solution. They have also studied its photochemistry 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 LLCT) and electron transfer between them occurs at a rate that is dependent on pH.

T1j) 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 electrocatalytical techniques for iron ion identification were devised based on these siderophores and commercially available ones.

T1l) Synthesis of new water soluble ruthenium complexes with activity towards DNA. (UAL, CNR). The results describing binding properties of the new water soluble ruthenium(II) chiral complexes $[\text{RuCpX}(\text{L})(\text{L}')]^{\text{n}+}$ ($\text{X} = \text{Cl}$, I. $\text{L} = \text{PPh}_3$; $\text{L}' = \text{PTA}$, mPTA; $\text{L} = \text{L}' = \text{PTA}$, mPTA) towards DNA have resulted in a paper been published [A6]. A second paper extending these studies to a variety of hydrosoluble ruthenium complexes with TPPMS ligands has been submitted [A17].

T1m) Synthesis and equilibrium studies of water-soluble ruthenium(II) carbonyl-phosphine-hydrides (UD). The known hydrogenation and hydroformylation catalyst, $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$ (mtppps = monosulfonated triphenylphosphine) was prepared by a new procedure. It was shown that in aqueous solution this complex readily loses chloride and yields the cationic $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{mtppps})_3]^+$. This transformation is unusual since in organic solvents it is the phosphine ligands which are expected to dissociate. The chloride dissociation equilibrium is effected by the solvent (as shown by measurements in methanol/water mixtures) and by the chloride concentration. The equilibrium constant was determined. The aqua complex was also synthesized on an independent way. The results were published and also communicated as poster [D14], as a paper [C15] in 2005 and on a poster in 2006 [D41].

T1n) 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 $[\text{Pt}(\mu\text{-OH})(\text{nFdpps})_2](\text{BF}_4)_2$, where nFdpps is 1,2-bis(diphenylphosphino)ethane (dpps), 1,2-bis(bis-2,4-difluorophenylphosphino)ethane (2Fdpps), 1,2-bis(bis-2,3,4,5-tetrafluorophenylphosphino)ethane (4Fdpps) and 1,2-bis(dipentafluorophenylphosphino)ethane (dfpps),

respectively (prepared by Prof. R. Michelin's group) was also investigated. The complexes undergo reduction processes.

[Cu(Hpta)₄](NO₃)₅ {Hpta = *N*-protonated form of 1,3,5-triaza-7-phosphaadamantane (pta)} has been easily prepared by reacting Cu(NO₃)₂ and pta in aqueous acidic solution at room temperature. The unprotonated pta derivative [Cu(pta)₄](NO₃) 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.

T1o) Syntheses of complexes with water soluble tris(pyrazolyl)methanesulfonate and related scorpionate ligands (IST) Series of complexes with the water soluble tris(1-pyrazolyl)methanesulfonate species (SO₃Cpz₃⁻) or related scorpionate ligands e.g. hydrotris(1-pyrazolyl)methane (HCpz₃) have continued to be synthesized and characterized for various transition metals, namely V, Re or Fe. They include e.g. [VCl₃(SO₃Cpz₃)], [VCl₃(HCpz₃)], [ReOCl(SO₃Cpz₃)(PPh₃)Cl], [ReO₃(SO₃Cpz₃)], [ReO{SO₃C(pz)₃{OC(CH₃)₂pz}}][ReO₄], [ReCl₃(HCpz₃)], [ReCl₃{HC(3,5-Me₂pz)₃}] [ReCl₄{η²-HC(pz)₃}], [FeCl₂(HCpz₃)], Li[FeCl₂(SO₃Cpz₃)] and derivatives. The tris(pyrazolyl)methanesulfonate complexes are the first of rhenium, iron and vanadium to be reported. They have been tested as catalysts for alkane functionalization reactions (see Task 6).

T1p) Self-assembly synthesis of water soluble di-, tri- or polynuclear and polymeric copper complexes (IST). The synthesis of mono-, di-, tri- or polynuclear copper complexes with N,O-polydentate ligands was continued, usually by self-assembly from copper(II), an amino-alcohol and an aromatic carboxylic acid. Some 1D- and 2D-coordination polymers were thus obtained, with the acid acting as a spacer.

Of particular interest was the self-assembly synthesis in water, at room temperature, with dinuclear copper triethanolamine and aqua-sodium building blocks as well as benzene-1,2,4,5-tetracarboxylate linkers which leads to the formation of a heteronuclear Cu-Na assembly with a two dimensional metal-organic framework, providing the first example of an aqua-soluble copper containing coordination polymer that hosts infinite chains of decameric water clusters (H₂O)₁₀ formed by quasiplanar cyclic water octamers with two pendent water molecules. An unprecedented heterotrimetallic Fe/Cu/Co complex bearing two Cu(μ-O)₂Co(μ-O)₂Fe cores was easily prepared by one-pot reaction of Cu powder with Co(SCN)₂, FeCl₃ and diethanolamine. Some of these complexes act as catalysts for alkane oxidations and models for particulate methane monooxygenase (see Task 6).

T1q) Syntheses of water soluble organometallic polymers with formula [{{CpRu(H₂O)(PTA)₂}[AgCl₂]}_∞ (PTA = 1,3,5-triaza-7-phosphaadamantane) and [{{CpRu(DMSO)(PTA)₂}{AgX₂}}_∞ (UAL, CNR). A joint paper describing the crystal structure of [{{CpRu(DMSO)(PTA)₂}{AgX₂}}_∞ has been published [44]. The light-scattering studies on family of water soluble organometallic family of complexes of general formula [{{CpRu(H₂O)(PTA)₂}{AgX₂}}_∞ has been continued only at UAL.

T1r) Synthesis and Electrochemistry of hydrosoluble ruthenium complexes with high biological activity (IST) The topic of this task was not carried on during the Third Year of the project.

T1s) 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)Cl₂] (dppets = 1,2-bis[di-*m*-sodiumsulfato]-phenylphosphino)ethane; NN = chiral or racemic diamine) bearing C₂-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.

T1t) Syntheses of platinum(II) complexes with PTA and purines. (UAL) The syntheses of various Pt(II) complexes combining water and organic soluble phosphines have been carried out. The platinum complexes cis-[PtCl(8-MTT)(PPh₃)(PTA)] and cis-[Pt(8-MTT)₂(PPh₃)(PTA)] (MTTH₂ = 8-methylthiotheophylline, PTA = 1,3,5-triaza-7-phosphaadamantane), have been prepared from the precursor cis-[PtCl₂(PPh₃)(PTA)] which has been fully characterized by X ray diffraction determination. The presence of one lipophilic PPh₃ and one hydrophilic PTA provides an antiproliferative activity superior to the analogues bearing two PPh₃ or two PTA. The reactivity of cis-[PtCl₂(PPh₃)₂], cis-[PtCl₂(PTA)₂] and cis-[PtCl₂(PPh₃)(PTA)] with the bis-thiopurines bis(S-8-thiotheophylline)methane (MBTTH₂), 1,2-bis(S-8-thiotheophylline)ethane (EBTTH₂), and 1,3-bis(S-8-thiotheophylline)propane (PBTTH₂), has also been investigated. New binuclear complexes have been prepared, identified by spectroscopic techniques and their antiproliferative activity on T2 and SKOV3 cell lines has been evaluated.

T1u) Synthesis of new derivatives of PTA. (UAL). The new water soluble ligand dmPTA(CF₃SO₃) (dmPTA = N,N'-dimethyl-1,3,5-triaza-7-phosphaadamantane) was synthesized by reaction of PTA with MeCF₃SO₃ (PTA = 1,3,5-triaza-7-phosphatrimethylene[3.3.1.1^{3,7}]decane). This new ligand reacted with KOH to give the compound dmoPTA by eliminating methylene from the moiety CH₃NCH₂NCH₃ (dmoPTA = 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane). Complex [RuClCp(HdmoPTA)(PPh₃)](CF₃SO₃) was obtained by reaction of [RuClCp(PPh₃)₂] with dmPTA. The synthetic processes for dmoPTA and [RuClCp(HdmoPTA)(PPh₃)](CF₃SO₃) were determined by spectroscopic techniques. Most of the obtained results on this research line has recently been sent to publish in *Inorg. Chem.* [SYNTHESIS OF THE WATER SOLUBLE LIGANDS dmPTA, dmoPTA AND THE COMPLEX [RuClCp(HdmoPTA)(PPh₃)](CF₃SO₃) (dmPTA = N,N'-dimethyl-1,3,5-triaza-7-phosphaadamantane; dmoPTA = 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane; HdmoPTA = 3,7-H-3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane).

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*)MoO₂⁺, (Cp*)MoO₂(OH), (Cp*)MoO₃⁻ and (Cp*)MoO₃H₂⁺ from (Cp*)₂Mo₂O₅, kinetic studies on the formation process of [Cp*MoO₂(H₂O)_x]⁺ by protonation of [Cp*MoO₃]⁻ 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*)MoO₂(H₂O)]⁺ ion, which is in agreement with the ¹⁷O-NMR exchange experiments performed under such conditions (see below). The temperature dependence for the combined protonation/isomerization process of [(Cp*)MoO₂(OH)] to [(Cp*)MoO₂(H₂O)]⁺ gives a very negative activation entropy (-150 J/Kmol), whereas the pressure dependence gives a negative activation volume (-9 cm³/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 [Cp*MoO₂(H₂O)]⁺, which is followed by a rapid release of coordinated water. A theoretical study (by DFT at **UAB**) of the Cp*Mo^{VI} system in aqueous media has been completed. This work has elucidated the acid dissociation anomaly for the system [Cp*MoO₂(H₂O)]⁺ (the first acid dissociation is weaker than the second one) as resulting from a water dissociation equilibrium. Therefore, although complex [Cp*MoO₂(H₂O)]⁺ is intrinsically very acidic, its effective acidity is reduced by averaging with the much lower acidity of free water. A full paper reporting the results of these studies has been submitted to *Inorg. Chem.*.

Water exchange reactions on [(Cp*)MoO₃]⁻ were followed by ¹⁷O-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 H⁺ concentration which is ascribed to the formation of (Cp*)MoO₂(OH) that exchanges oxygen much faster than [(Cp*)MoO₃]⁻. At lower pH the exchange reaction becomes too fast to be studied by ¹⁷O labelling. Thus the [Cp*MoO₂(H₂O)]⁺ complex exchanges orders of magnitude faster than [(Cp*)MoO₂(OH)] which in turn exchanges orders of magnitude faster than [(Cp*)MoO₃]⁻. This is in good agreement with the tendency expected for the lability of Mo=O << Mo-OH << Mo-OH₂ under the *trans* effect of Cp*. A joint manuscript is in preparation.

T2b) Improved syntheses and mass spectrometric investigations of Cp*₂M₂O₅ (M = Mo, W) (CNRSLCC/b, HUJI). The optimization of the synthesis of these common starting materials has witnessed great progress during year 3. Conditions have now been found for the synthesis of Cp*₂Mo₂O₅ in a three-step, one flask reaction from Mo(CO)₆ with a > 90% yield, using H₂O₂ as an environmentally friendly oxidizing agent. A similar procedure works equally well for tungsten, up to the formation of the sodium salt, [Cp*WO₃]⁻Na. Suitable conditions for the last protonation step are being optimized. An X-ray structure has been obtained on the Na salt of the Mo system, showing an interesting and unusual hydrogen bonding network, [Na₄(H₂O)₁₆][Cp*MoO₃]₄·2H₂O. An electrospray mass spectrometric investigation of the tungsten system in a MeOH:H₂O medium has been carried out during a secondment of Chiara Dinoi at **HUJI**. A manuscript on this work will be written in 2007.

T2c) Aqueous reduction of Cp*₂W₂O₅ (CNRSLCC/b). The investigations outlined in last year's report on the zinc reduction of Cp*₂Mo₂O₅ have been published ([C2]). Analogous investigations have been carried out on the related W system during Year 3. Zinc reduction in MeOH:H₂O acidified by CF₃COOH or by CF₃SO₃H yields an air-sensitive green product, crystals of which (obtained for the triflate system) reveal the [Cp*₃W₃O₄(OH)₂]²⁺ cation (W^V). This is a less deep reduction than for the Mo system which affords the mixed-valence (Mo^{IV,IV,V}) cluster [Cp*₃Mo₃O₂(OH)₄]²⁺ (see last year report). This system is cleanly oxidized in air, to

yield air stable $[\text{Cp}^*_3\text{W}_3\text{O}_6]^+$ (a mixed-valence $\text{W}_3^{\text{V,V,VI}}$ cluster), which has been crystallographically characterized in three different forms. DFT calculations and NMR/EPR investigations allow complete characterization of the electronic structure for both clusters. An electrospray mass spectrometric investigation of the $[\text{Cp}^*_3\text{W}_3\text{O}_6]^+$ cluster in CH_2Cl_2 has been carried out during the secondment of Chiara Dinoi at **HUJ**. Electrochemical investigations at different pH are being carried out in Year 4 (Task 4). A publication on this topic is envisaged during 2007

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). As planned the studies of the interaction of water soluble hydrides $\text{CpM}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}, \text{W}$) with organic bases (pyridine, $(n\text{-octyl})_3\text{PO}$, $(n\text{-Bu})_3\text{PO}$) were continued toward the determination of thermodynamic parameters of the $\text{M-H}\dots\text{B}$ bond and of subsequent proton transfer. Experiment shows very low $\text{M-H}\dots\text{B}$ formation enthalpy ΔH of -1.8 to -3.5 kcal/mol. The hydrogen bond formation is the first step of low temperature proton transfer from the hydride to organic base, which was studied in solvents of different polarity and coordinating ability. Protic solvents such as CH_2Cl_2 compete with $\text{CpM}(\text{CO})_3\text{H}$ for binding a base and proton transfer does not occur. Increase of solvents polarity weakens hydrogen bonding thus preventing proton transfer. These findings can be further rationalized basing on theoretical single point SCRF calculations taking into account solvent effect within CPCM model. Calculations show that passing from gas phase to higher polarity solvents practically does not affect the energy of transition state ($\Delta\Delta\text{E} = 0.1$ kcal/mol), whereas the energies of $\text{M-H}\dots\text{B}$ complex decrease, and the energies of proton transfer product – $\text{M}\dots^+\text{HB}$ ion pair – increase. As the result the proton transfer is encumbered by H-bond weakening in the media of higher polarity. To overcome this problem the neat pyridine or excess $((\text{CH}_3)_2\text{N})_3\text{PO}$ in hexane were used. Proton transfer to $((\text{CH}_3)_2\text{N})_3\text{PO}$ was observed in hexane below 220K, $\Delta\text{H}_{\text{PT}}$ and $\Delta\text{S}_{\text{PT}}$ were obtained. Proton transfer is slow under these conditions, kinetics studies being in progress. The results have been reported on the international conference and joint INEOS/UAB paper has been published [A9].

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 is submitted to a special issue of *J. Mol. Structure* [A16]

T3c) Hydrogen bonding of water to main group hydrides (INEOS, UAB). Solvent effect on dihydrogen bonding was studied in more details by SCRF optimisation of model $\text{AlH}_4^-\text{CF}_3\text{OH}$ complex in different media using CPCM approach – from gas phase to water (gas-heptane-THF- CH_2Cl_2 -MeOH-MeCN- H_2O). For aprotic solvents both ΔG and ΔH of H-bond formation decrease in the order gas \gg heptane \gg THF $>$ CH_3CN , $\Delta\Delta\text{G}_{\text{gas-MeCN}}$ being ca -15 kcal/mol. Analysis of geometrical parameters and frequencies shows that it is not just lowering of energy in solution, it is destruction of H-bond because other fundamental properties of H-bond ($\Delta\nu_{\text{OH}}$, $r_{\text{H}\dots\text{H}}$) change in the same order. Protic media (MeOH and water) has more effect on H-bond, all properties of complex dramatically change: change of CH_3CN to same polarity MeOH decreases the $\Delta\text{E}_{\text{ZPE}}$ energy from -9 to -3 kcal/mol, $\Delta\nu_{\text{OH}}$ – from 1080 to 680 cm^{-1} , $r_{\text{H}\dots\text{H}}$ elongates from 1.311 to 1.327Å. CH_2Cl_2 has dielectric permittivity close to that of THF and is weaker proton donor than MeOH. Thus the interaction energies are about the same in THF and CH_2Cl_2 but $r_{\text{H}\dots\text{H}}$ and $\Delta\nu_{\text{OH}}$ changes in this solvent do not follow the trend obtained for aprotic solvents. A joint paper by INEOS and UAB has been published [A7].

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}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 (ΔH^\ddagger , ΔS^\ddagger and ΔV^\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 H_2O_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 or are presently in press.

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 Li^+ and 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, I_a , I_d and D mechanisms, and supports the mechanisms suggested on the basis of experimental data. A series of papers have been published or are presently in press.

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. Despite the presence of charges on the end groups, most of the dendritic complexes we have synthesized are only sparingly soluble in water. 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.

T3f) The effect of the solvent (water) on the catalytic H/D exchange in aqueous solutions. (UD) Previous experimental results suggested that the H/D exchange between H_2 and D_2O or D_2 and H_2O , catalyzed by $[\text{RhCl}(\text{TPPMS})_3]$, may proceed through the formation of a hydrido-dihydrogen-rhodium species obtained from e.g. $[\text{RhH}_2\text{Cl}(\text{TPPMS})_3]$ by protonation. DFT (B3LYP) calculations were performed on the protonation of the latter compound. Due to the effect of hydrogen bonding, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ clusters of various size had to be considered as protonating agents. The results indicate, that the H/D exchange process can take place with low energy barriers. The effect of bulk water on the energetics was examined by employing polarizable continuum models. The results were published as a journal article [C16] and also communicated as a poster. *Task completed.*

T3g) Detailed theoretical studies were started to discover the effects of the solvent water on the selectivity of hydrogenations of unsaturated aldehydes catalyzed by $[\{\text{RuCl}_2(\text{mtpms})_2\}_2]$ (UD). The peculiarity of the reaction is that in acidic solutions it yields selectively saturated aldehydes, while in basic solutions the exclusive product is the unsaturated alcohol. The DFT (B3LYP) calculations incorporating the effect of bulk water through the polarizable continuum model have revealed, that on both pathways the protonation of intermediate alkyl or alkoxy-complexes plays a determining role. The results were presented at four conferences [B6 – B8], [B15] and published in two journal articles [A5], [A8]. Attention was paid to the theoretical investigation of solvent effects on yet another reaction, the stereoselective hydrogenation of 1,2-disubstituted alkynes. These results were communicated at conferences [B16], [B17] and the manuscript of a journal article has been submitted.

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. P^{8+} , P^{4+} , P^{8-} and 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, H_2O_2 and organic peroxides (see T5d and T5e, respectively).

T4b) pH-potentiometric characterization of $[\text{RhCl}(\text{OAc})(\text{TPPMS})_2]$ (UD). Following first year results on $[\text{Rh}(\text{CO})(\text{OAc})(\text{TPPMS})_2]$ 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.*

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_2O 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-to-bpy charge transfer excited state (LLCT) is formed by the deprotected sensor in basic solution. It is also observed in the presence of molybdate or tungstate in acid solution. It is formed both by direct excitation and indirectly via the MLCT state. The rate of transfer between states is approx 10^{10} s^{-1} , 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 Re2Mo species at pH 4 and higher. However, evidence for a 1:1 complex has been found at pH 2.

T4d) Speciation of $\text{Cp}^*_3\text{W}_3^{12+}$ ($\text{Cp}^*\text{W}^{\text{VI}}$) and $\text{Cp}^*_3\text{W}_3^{13+}$ ($\text{Cp}^*_3\text{W}_3^{\text{V,V,VI}}$) (CNRS/LCC/b). As shown in Task 1, reduction of $\text{Cp}^*_2\text{W}_2\text{O}_5$ yields clusters $\text{Cp}^*_3\text{W}_3\text{O}_4(\text{OH})_2^{2+}$ and $\text{Cp}^*_3\text{W}_3\text{O}_6^+$ under low pH (<1) conditions. The two compounds are related to each other by a coupled one-electron-two-proton redox process. An electrochemical investigation of this process at various pH values (Pourbaix diagram) has been initiated in order to determine the proton dissociation constant of the two coupled redox species. This investigation is currently ongoing.

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. Two papers were published on this subject.

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 $\text{Cp}^*\text{Mo}^{\text{VI}}$ by sulfur compounds (CNRS/LCC/b, HUJI). Compound $\text{Cp}^*_2\text{Mo}_2\text{O}_5$ reacts with compounds containing S-H bonds in an aqueous medium, being reduced to lower oxidation state derivatives. The reaction with mercaptoacetic acid, HSCH_2COOH , yields the dinuclear Mo^{IV} derivative $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CO}_2)_2$; the sulphur containing substrate has acted in three different ways: as a reducing agent, as a ligand, and as a substrate for C-S activation (source of the bridging sulfido group). This work, described in last year's report, has been published [C3]. In year 3, a related reaction has been investigated using the very similar substrate mercaptopyruvic acid, $\text{HSCH}_2\text{CH}_2\text{COOH}$. Surprisingly, an oxo-bridged product, $\text{Cp}^*_2\text{Mo}_2(\mu\text{-O})(\mu\text{-SCH}_2\text{CH}_2\text{CO}_2)_2$, 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 can be proposed. A manuscript on this work is in preparation.

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⁺. 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⁺ 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 B₁₂), 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_2O_2 and organic peroxides by Fe(III) complexes (UEN). Rapid-scan techniques were employed to study the activation of H_2O_2 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⁺. A detailed study on the pH dependence of the activation of organic peroxides and peroxy acids by several Fe(III) porphyrine 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. Several papers are presently in press or being prepared for publication.

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. This development is currently being prepared for publication.

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_3Br , ethylene dibromide), pest control agents (DDT, alachlor), herbicides (simazine and atrazine) and other haloorganic compounds (haloalkanes). The catalytic activity of tetrathiomolybdate will be studied during the fourth year of the project in collaboration with Poli's group (CNRSLCC/b)

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 (CNRSLCC/a). We have used in the last years dendritic P,N ligand palladium complexes synthesized in situ in organic solvent for palladium-mediated asymmetric allylic substitutions. Excellent percentages of conversion (100%), yields in isolated product (up to 97%), and enantiomeric excesses (up to 95%) were obtained. This work has been published [C1]. No attempt has been done to continue this work this year.

T6b) Isomerization of allyl alcohols in biphasic medium catalyzed by a Ru-dendrimer (CNRSLCC/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 catalyse the isomerisation 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%). 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 $H_2O/iPrOH$ catalyzed by a Ru-dendrimer (CNRSLCC/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. A paper is in preparation (including also T6b).

T6d) *Water soluble ruthenium PTA complexes as catalysts for selective hydrogenation of α,β -unsaturated carbonyl compounds.* (PTA = 1,3,5-triaza-7-phosphaadamantane) (CNR, UAL). The work done in the first two years at CNR, regarding the water soluble $[\text{Cp}^R\text{RuX}_n(\text{PTA})_m](\text{PF}_6)_q$ complexes (T1) as homogeneous catalysts for the hydrogenation of benzylidene acetone under hydrogen pressure in biphasic conditions and in transfer hydrogenation of cinnamaldehyde using the $\text{HCO}_2\text{Na} / \text{H}_2\text{O}$ protocol was published [42]. The following preliminary work carried out in the second year during the secondment activity of Mrs Mallqui at CNR, regarding Ru catalysed transfer hydrogenations of ketones and imines gave contradictory results and will be subject of more detailed investigation during the fourth year.

T6e) *Water-soluble Ru-N-heterocyclic carbene complexes as catalysts of hydrogenation and redox isomerization processes.* (UD) The newly synthesized Ru(II)-NHC complexes (T1f) such as $[\text{RuCl}(\text{H}_2\text{O})(1\text{-butyl-3-methylimidazol-2-ylidene})(p\text{-cymene})]^+$ 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 $[\text{RuCl}(\text{H}_2\text{O})(1\text{-butyl-3-methylimidazol-2-ylidene})(p\text{-cymene})]^+$ 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_2 pressure. Under such conditions, unexpectedly high turnover frequencies ($>12000 \text{ h}^{-1}$) were observed – these studies continue in 2007.

T6f) *Catalytic hydrogenation of carbon dioxide, bicarbonates and carbonates.* (CNR, UAL, UD). Catalytic CO_2 and HCO_3^- reduction by H_2 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. Several water soluble ruthenium catalysts containing Cp and Cp* ligands and hydrosoluble phosphines (PTA, mPTA, TPPMS) have been tested. The catalytic hydrogenation of bicarbonate by $[\{\text{RuCl}_2(\text{TPPMS})_2\}_2]$ 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_3 and MgCO_3 under CO_2/H_2 pressure was studied at UD – the results form part of the PhD Thesis of Mr. I. Józszai and their publication is underway. Two STSMs within COST Action D29 were carried out independently by CNR personnel (not formally part of Aquachem) at EPFL, to investigate the catalytic reduction of CO_2 and bicarbonate in the presence of Rh(III) and Ir(III) cyclopentadienyl PTA complexes. A first manuscript describing the latter results is in preparation.

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 $[\{\text{RuCl}_2(\text{TPPMS})_2\}_2]$ is strongly dependent on the pH of the aqueous phase. In acidic solutions the major product was the *cis*-alkene, while in basic solutions the *trans*-alkene was obtained selectively. Such reactions were also run using the same catalyst precursor heterogenized on anion-exchange resins. For this purpose the microfluidics-based hydrogenation reactor (H-CubeTM) was used. The heterogenized complexes behaved similar to their soluble versions in acidic solutions and supplied *cis*-alkenes as main products (with selectivities up to 85%). The results were published in two papers [C20], [C21] and presented at international conferences [D15], [D42]. New heterogenized catalysts with cationic ligands have also been prepared and applied to the hydrogenation of acetylenes – these studies continue in 2007.

T6h) *pH-dependent regioselective hydrogenation of α,β -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 α,β -unsaturated aldehydes catalyzed by $[\{\text{RuCl}_2(\text{mtpms})_2\}_2]$. The peculiarity of the reaction is that in acidic solutions it yields selectively saturated aldehydes, while in basic solutions the exclusive product is the unsaturated alcohol. A thorough computational analysis of the reaction, both in acidic and basic media, has been carried out. The effect of the water solvent has been taken into account both as dielectric continuum media with a polarisable continuum model and with the explicit inclusion of a small cluster of water molecules. From these studies, the nature of intermediates and transition states in the catalytic cycle has been disclosed, and a plausible reaction mechanism has been proposed in which the solvent plays a major role. Three conference presentations and two UAB-UD joint publications [A5, A8] come up 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 $[\text{Ru}(\text{H})(\text{H})(\text{mtpms})_3]$ already in slightly acidic media which influences the regioselectivity of the process [D39].

T6i) Catalysis of the H/D exchange by [RhCl(TPPMS)₃]. (UD) The isotope exchange between D₂ and H₂O or H₂ and D₂O has been studied by DFT (B3LYP) calculations. The results show a strong influence of water and details of the second year results can be found in T3f. *Task completed* (see also T3f).

T6j) Catalytic epoxidation of olefins with (Cp')₂Mo₂O₅ complexes (CNRS/LCC/b-IST). The work done in collaboration between CNRS/LCC and b-IST (see previous annual reports) and published [A3] has been pursued in Toulouse during Year 3. In particular, a condition optimization (water content, pH) is being sought in order to render the catalytic system active when using the greener H₂O₂ as oxidant. For the moment, the high activities of the Cp*₂Mo₂O₅ system in a wet environment in the presence of tBuOOH have been confirmed and studies have been extended to H₂O-MeOH mixtures. Investigations using H₂O₂ are in progress and will be completed during Year 4.

T6k) Catalytic oxidations of substituted thiophenes using green oxidants. (CNR, CNRS/LCC/b) The work done by ER Dr Landaeta within the AQUACHEM activity in Florence regarding oxygen transfer to benzo- and dibenzothiophene mediated by [Ru(cuproine)₂(H₂O)₂](BF₄)₂, yielding the corresponding sulfones in good yield and 100% selectivity in acetonitrile solution has been published as a full article [C32]. The topic has been subject of further investigation within COST Action D29 during the STSM of Ms Chiara Dinoi (ESR at CNRS/LCC/b) at CNR, where [Cp*₂Mo₂O₅] and [Cp*₂W₂O₅] showed high activity towards oxidation of substituted dibenzothiophenes at 1:100 catalytic ratio, 75 °C in MeCN and high TONs. The work will be finished at CNRS/LCC/b and summarised in a forthcoming manuscript.

T6l) 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. The possibility of photocatalysis with RhPTA-complexes needs to be re-examined in collaboration with CNR.

T6m) Photoactivation of white phosphorus in water. (UAL). The P₄ activation in water has been accomplished by using new water soluble ruthenium complexes containing mTPPMS ligands. The selectivity of the transformation of white phosphorus was obtained by an accurate combination of both the used catalysis and visible light frequency. The results obtained are under patenting.

T6n) Electrocatalytic 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-ways joint publication, authoring the ER at HUJI [A10]. Further collaborative work in this area is foreseen in the presence of new compounds in this series.

T6o) Ru-N-heterocyclic carbene complexes as catalysts of alkyne oligomerization processes. (UD) The newly synthesized Ru(II)-NHC complexes (T1f) such as [RuCl(H₂O)(1-butyl-3-methylimidazol-2-ylidene)(p-cymene)]⁺ catalyzed the oligomerization of various alkynes (such as phenylacetylene) in purely organic solutions. The results were summarized in a journal article [C22]. *Task discontinued in 2006.*

T6p) Solar activation of the new water soluble ruthenium complexes obtained. (UAL) Water soluble published complexes containing PTA, mPTA and mTPPMS ligands were evaluated under visible solar lights. Neither of the checked complexes showed chemical reactivity different whether it was irradiated or not. The main conclusion obtained from the made research was that new mPTA ruthenium complexes are worth to be synthesized and checked in both thermal and photochemical conditions. As a result of this research premise the complex [RuCl₂(mPTA)₄] was synthesized which showed a clear different chemical reactivity in water solution whether it is irradiated by solar light or not. A communication is in preparation about the findings obtained.

T6q) Catalytic peroxidative oxidation of cyclohexane by copper complexes models of p-methane monooxygenase. (IST) The copper complexes (both homo- and heterometallic ones) with N,O-ligands synthesized by self-assembly as indicated in task 1 can act as models of particulate methane monooxygenase (pMMO), since they are highly active and selective catalysts for the peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone, by aqueous hydrogen peroxide in acidic medium (liquid biphasic catalysis) at room temperature and atmospheric pressure. The study of the effects on the catalytic activity of various factors was continued.

T6r) Catalytic peroxidative oxidation of alkanes by complexes with scorpionate ligands (IST) The Re, V and Fe complexes with the water soluble tris(pyrazolylmethanesulfonate) ligand (SO₃Cpz₃⁻) and related scorpionates (see Task 1) were tested successfully as catalysts or catalyst precursors for the peroxidative oxidation, by aqueous H₂O₂, of cyclohexane and cyclopentane to the corresponding alcohols and ketones, under mild conditions (room temperature), in biphasic aqueous/organic medium.

T6s) Catalytic single-pot oxidation of ethane by scorpionate complexes (IST) The 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), $[\text{ReCl}_3\{\text{HC}(\text{pz})_3\}]$, $[\text{ReOCl}_2\{\text{SO}_3\text{C}(\text{pz})_3\}(\text{PPh}_3)]$ and $[\text{ReO}_3\{\text{SO}_3\text{C}(\text{pz})_3\}]$, and their precursors $[\text{ReCl}_2\{\eta^2\text{-}N,O\text{-N}_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ and $[\text{ReOCl}_3(\text{PPh}_3)_2]$, act as selective catalysts (or catalyst precursors), in a single-pot process, for 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 (up to *ca.* 40 %) and under mild conditions (in some cases carboxylation can also occur to give propionic acid, but in a much lower yield). 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.

T6t) Catalytic Baeyer-Villiger oxidation of cyclic ketones by rhenium complexes (IST). This task was performed by an ESR, Paolo Sgarbossa. The Re(V) complexes $[\text{ReOCl}_3(\text{PPh}_3)_2]$, $[\text{ReOCl}_2(\text{picolate})(\text{PPh}_3)]$ and derivatives were tested successfully as catalysts or catalyst precursors for the aqueous peroxidative Baeyer-Villiger oxidation of 2-methylcyclohexanone to the corresponding lactones with conversions up to 58 %.

T6u) 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. The possible mechanisms, leading to the formation of the *Z* and *E* stereoisomers were computationally evaluated. 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. The formation of the different stereoisomers is determined by the order of the two hydrogenation steps. A joint UAB/UD article has been submitted [A13] and the results have been presented at two international conferences [B13,B16].

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) π -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 α,β -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 H₂ Elimination Reaction of Main Group Hydrides EH₄⁻ (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 [RuH₂(mtppps)_x] (x=3,4; mtppps=(meta-sulphonatophenyl)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 (η⁵-C₅H₅)M(CO)₃H (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] (CNRS/LCC/a-CNR) P. Servin, C. Rebut, 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 [Cp(Ru)(PTA)₂Cl] (PTA = 1,3,5-triaza-7-phosphaadamantane)" submitted (Communication)
- [A13] (UAB-UD) Kóvacs, G.; Ujaque, G.; Lledós, A.; Joó, F. "The role of water in the stereoselective hydrogenation of 1,2-diphenylacetylene catalyzed by the water soluble [{RuCl₂(mtppps)₂}₂]. A theoretical study" submitted (Article)
- [A14] (CNRS/LCC/b-UEN-UAB) J.-E. Jee, A. Comas-Vives, C. Dinói, G. Ujaque, R. Van Eldik, A. Lledós, R. Poli: "Nature of Cp*MoO₂⁺ in water and intramolecular proton transfer mechanism by stopped-flow kinetics and DFT calculations" submitted
- [A15] (CNRS/LCC/b-HUJI) C. Dinói, P. Prikhodchenko, F. Demirhan, J. Gun, O. Lev, J.-C. Daran, R. Poli: "Reduction of [Cp*₂Mo₂O₅] by mercaptopropionic acid in an aqueous medium. Isolation and characterization of a dinuclear oxo- and 3-sulfido-propionato(2-)-bridged molybdenum(IV) compound" in preparation
- [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 "Dihydrogen bonding and proton transfer to [RuH₂{P(CH₂CH₂PPh₂)₃}]: specific and non-specific influence of the environment" *J. Mol. Structure*, submitted
- [A17] (UAL-CNR) A. Romerosa, M. Saoud, T. Campos-Malpartida, C. Lidrissi, M. Serrano-Ruiz, M. Peruzzini, J.A. Garrido-Cárdenas, F. García-Maroto: "DNA Interaction Mediated by Water Soluble Cyclopentadienyl Ruthenium(II) Complexes containing Different Water Soluble Phosphines" *Eur. J. Inorg. Chem.* **2007**, *in press* (Article)

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” - 7th 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 α,β -unsaturated aldehydes with ruthenium(II) catalysts” *XXXIII Congresso Nazionale della Divisione di Chimica Inorganica della Società Chimica Italiana*; July 11-16th 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 α,β -unsaturated aldehydes with ruthenium(II) water-soluble complexes: a computational mechanistic study” *ISHHC-XII*; July 18-22nd 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)₂Ru(m-TPPMS)_x [x=3,4; m-TPPMS=(meta-sulphonatophenyl)diphenylphosphine]. A theoretical study of the reaction mechanism and selectivity” *Conference DFT2005*; September 11-15th 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(CH₃)₃)₂ ligand and PPh₃, PTA, mPTA and TPPMS” *XXIInd 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” *XXXVIIth ICCC, 37th 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] (CNRS/LCCb-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. “H₂ 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] (CNRS/LCC/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] (CNRS/LCC/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. Gribova, 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

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/LCC/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/LCC/b) F. Demirhan, B. Çagatay, D. Demir, M. Baya, J.-C. Daran, R. Poli: “Reduction of Cp*₂Mo₂O₅ 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 CF_3SO_3 ” *Eur. J. Inorg. Chem.*, **2006**, 757.
- [C3] (CNRS/CC/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 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/CC/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. Jóó: “Aqueous Organometallic Chemistry. Synthesis and Solution Equilibria of Trisodium Carbonylchlorotris[3-(diphenylphosphino-κP)benzenesulfonato]-hydridoruthenate(3-) ($[\text{RuH}(\text{Cl})(\text{CO})\{m\text{-}(\text{Ph}_2\text{P})\text{-C}_6\text{H}_4\text{-SO}_3\text{Na}\}_3]$) and Trisodium Aquacarbonyltris[3-(diphenylphosphino-κP)benzenesulfonato]-hydridoruthenate(2-) Tetrafluoroborate(1-) ($[\text{RuH}(\text{CO})(\text{H}_2\text{O})\{m\text{-}(\text{Ph}_2\text{P})\text{-C}_6\text{H}_4\text{-SO}_3\text{Na}\}_3][\text{BF}_4]$)”, *Helvetica Chimica Acta*, **2005**, 88, 566 (Article)

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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 H₂O₂" (poster) ISHHC XII, *12th 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) 1st 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 hémimétallocéniques de molybdène(VI) avec des composés souffrés" (poster) *GECOM-CONCOORD 2005*, Autrans, France, June 5-10, 2005
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- [D7] (CNR) M. Peruzzini "Catalytic activation of white phosphorus: reality or fairy tale?" *5th 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 P₄ to PH₃ 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" *5th International School of Organometallic Chemistry (ISOC)* Camerino, Italy, Sept 10-14, 2005 (Invited keynote lecture)
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- [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)
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- [D16] (UAB) A. Lledós “New Approaches in the Activation of Unreactive Bonds : Interplay between Experiment and Computation” XVIth FEChem Conference on Organometallic Chemistry; September 3-8th 2005, Budapest (Hungary) (invited plenary lecture)
- [D17] (UEN) A. Brausam and R. van Eldik: “New mechanistic insight into the long known reaction between Fe^{III}(edta) and hydrogen peroxide.” *Inorganic Reaction Mechanisms Meeting*, Athens (Greece), 2004 (Poster)
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- [D21] (UEN) R. van Eldik: “Mechanistic details of the interaction of NO with metal complexes in aqueous solution.” *5th 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.” *36th International Conference on Coordination Chemistry*, Merida (Mexico), 2004 (Invited lecture)
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- [D33] (UEN) A. Brausam and R. van Eldik: "Chasing intermediates: How do Fe(III)(TAML) complexes bleach dyes?" *9th 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." *9th International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidation*, Cologne (Germany), 2005 (Poster)
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- [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^{èmes} Journées Franco-Catalanes de Chimie Moléculaire*, Toulouse, France, February 1-2nd, 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" *42nd 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 $\{RuCl_2(mtppps)_2\}_2$ " *42nd 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^{Ind} ICOMC, 22nd 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" *231st 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, 35th 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, 35th Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D48] (UEN) Thermodynamic and kinetic studies on the binding of nitric oxide to the RSO₃⁻-substituted model complex for cytochrome P450, A. Franke, N. Hessenauer-Ilicheva, D. Meyer, G. Stochel, W.-D. Woggon and R. van Eldik, 35th Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D49] (UEN) From interchange to dissociative water exchange on aquated Al³⁺ ions, Hans Hanauer, R. Puchta, T. Clark and R. van Eldik, 35th Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D50] (UEN) Experimental and theoretical studies on ion pair interaction in ionic liquids containing the [emim]⁺-cation, P. Illner, R. Puchta and R. van Eldik, 35th 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, 35th 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, 35th 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, 35th Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D54] (UEN) High pressure ⁷Li NMR kinetic study of Li⁺ complexation by cryptands in gamma-butyrolactone, E.Pasgreta, R. Puchta, N. van Eikema Hommes, A. Zahl and R. van Eldik, 35th Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
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- [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, 35th 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, 35th Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
- [D58] (UEN) Mechanistic studies on the activation of H₂O₂ by a novel Fe^{III}-porphyrazine complex, A. Theodoridis, E. Kudrik and R. van Eldik, 35th Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).

- [D59] (UEN) Kinetics and mechanism of the reduction of (ImH)[*trans*-RuCl₄(dmsO)(Im)] by ascorbic acid in acidic aqueous solution, M. Brindell, D. Piotrowska, A. Szumlanska, R. van Eldik and G. Stochel, 35th 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, 35th Inorganic Reaction Mechanism Meeting, Krakow (Poland), 2006 (Poster).
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A.7 Single team Patents pending (since the beginning of the project)

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- [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).
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- [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.

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

- [F1] (UAL) GREEN CHEMISTRY A SOLUTION FOR THE WORLD: Andalusia meets Europe II. 18-21/12/2005. Almería (Spain)
- [F2] (UAL) Book EDITOR: 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] (UAL) PhD Theses

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.

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.

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.

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.*

The collaborative work between **UAL** and **CNR** in this area has followed on previous results. The protocol for the functionalization of the cyclopentadienyl ring with hydrosoluble fragments such as amides has been optimised. New hydrosoluble ligands based on aminoacidic moieties have been synthesised and used to prepare coordination compounds with ruthenium, rhodium and iridium. A communication paper was submitted. Preliminary studies on the catalytic behaviour in water phase hydrogenations with these complexes were started. Studies on DNA binding of hydrosoluble complexes has been studied at **UAL** and resulted in a publication. Finally as part of a joint PhD program, Ru(II) complexes of sulfonated diphosphines were obtained and will be tested as (chiral) precatalysts for water phase hydrogenations and transfer hydrogenation reactions.

HUJI group 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.

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**. The main objectives for the next year are the study of the complexation ability of all these ligands, and the development of new strategies for the synthesis of unsymmetrical dendritic ligands in which functions ensuring the water-solubility and the complexation are located in different areas.

The work at **IST** has been also directed towards the preparation of 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.

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.

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

The cationic $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{mtppps})_3]^+$ has been characterised by UD and independently prepared via chloride dissociation in water from $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$ (*mtppps* = monosulfonated triphenylphosphine). It was also observed that in aqueous solution $[\text{RuCl}_2(1\text{-butyl-3-methylimidazol-2-ylidene})(p\text{-cymene})]$ gives rise to the formation of $[\text{RuCl}(\text{H}_2\text{O})(1\text{-butyl-3-methylimidazol-2-ylidene})(p\text{-cymene})]^+$ and also to the dicationic $[\text{Ru}(\text{H}_2\text{O})_2(1\text{-butyl-3-methylimidazol-2-ylidene})(p\text{-cymene})]^{++}$ species. Spontaneous chloride dissociation from $[\text{RuCl}(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$, in the presence of small amounts of water in methanol solution afforded $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$ and $[\text{Ru}(\text{MeOH})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$, 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 $[(Cp^*Mo)_3(\mu-O)_2(\mu-OH)_4]^{2+}$ (removing an ambiguity in a paper previously published by another group), the related tungsten compounds $[(Cp^*W)_3(\mu-O)_4(\mu-OH)_2]^{2+}$ and $[(Cp^*W)_3(\mu-O)_6]^+$ have been prepared by a similar synthetic strategy (zinc reduction of $Cp^*_2W_2O_5$ in an acidified H_2O -MeOH mixed solvent) and fully characterized. The two clusters are related to each other by a reversible coupled one-electron-two-proton process.

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 $Cp^*_2Mo_2O_5$ and thioglycolic acid, leading to C-S bond cleavage, has been described in a previous report. During Year 3, the analogous reaction with mercaptopropionic acid, $HSCH_2CH_2COOH$, was shown by CNRSLCC/b to lead to a similar product, $Cp^*_2Mo_2(\mu-O)(\mu-SCH_2CH_2CO_2)_2$, except that no C-S bond cleavage occurs. This observation allows a better understanding of the molecular requirements for a successful C-S activation process.

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. Preliminary experiments have already demonstrated our ability to distinguish between homolytic and heterolytic cleavage of the peroxo 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.

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.*

A joint UAB/INEOS experimental/theoretical study has been carried out to study H-bonding interactions emphasizing the anfiprotic nature of H_2O , 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 $Cp^*MoO_3^-$ 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.

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^{VI} model system reveals that the [CpMoO₂(H₂O)]⁺ system is more stable than the sum of [CpMoO₂]⁺ and H₂O supporting the experimental study of the protonation kinetics. The calculation of the two [CpMoO₂(H₂O)]⁺ and [CpMoO₂(OH)₂]⁺ isomers shows a slightly greater stability for the latter in the gas phase, contrary to the experimental evidence. However, the explicit inclusion of one, then two water molecules attenuates and further reverses this stability order. The inclusion of three water molecules triggers proton dissociation, simulating the experimental behaviour at high pH. The transition state energy for the isomerization of [CpMoO₂(OH)₂]⁺ to [CpMoO₂(H₂O)]⁺ is also highly dependent on the number of water molecules explicitly included in the calculation. This study highlights the absolute need for the explicit inclusion of water molecules to properly simulate the behaviour of aqueous solutions.

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 *mtpms* 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.

Objective 7: *Catalytic studies in aqueous or biphasic media at different pH: CO₂ 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 α,β -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 α,β -unsaturated aldehydes with Ru(II) water-soluble complexes containing sulphonated phosphines. Hydrosoluble NHC has been also used to oligomerize alkynes.

Oxidation of substituted dbenzo- and dibenzothiophenes continued at CNR using Cp*₂Mo₂O₅/H₂O₂ and Cp*₂W₂O₅/H₂O₂ in collaboration with CNRSLCC/b. Preliminary results show that quantitative conversion of the substrates and very high TOFs can be reached by tuning of the reaction conditions, which were optimised as follows: substrate/cat = 100; MeCN; 75 °C; H₂O₂/substrate = 4. The reactions seem to proceed via fast oxidation of sulfide to sulfoxide which is then slowly converted to the sulfone, which can be recovered by simple separation at the end of the catalytic run. Further work is planned to calculate reaction kinetics and identify the intermediates, as well as to expand the scope of the protocol to other sulfides.

The catalytic oxidation of cycloalkanes to cycloalkanols and cycloketones has been accomplished by peroxidative oxidation, using aqueous H₂O₂, 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.

The catalytic activity of a series of water-soluble dendrimers having PTA-Ru complexes as end groups has been measured for the isomerization of an allylic alcohol into a ketone, and for the hydration of alkynes, by CNRSLCC/a, in collaboration with CNR. In both cases, a better activity has been observed with the dendrimers

compared to a model (monomeric) complex. This work will be expanded to test other types of catalyses implying dendrimers, in particular those recently synthesized.

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.

Research focused to find solar light active complexes has led to the synthesis of a new water soluble ruthenium complex that displays different chemical reactivity with and without solar light. That provides a very interesting compound to be investigated as in this complex is combined the water solubility, catalytic activity and solar activation.

➤ B.2 Work Plan

B.2.1 Schedule and Milestones 2006

Network Meetings and publications: The third year meeting, was held in Debrecen (Hungary) hosted by partner UD on January 12 – 13, 2007. The meeting was attended also by Junior scientists from Debrecen University. 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.

Recruitment and Training milestones: We have resolved the slow start in recruiting Young Researchers. The slowness of recruitment which was a common feature during the first year of the project has been overcome by most of the partners during the second year activity. At the moment of writing this report, all partners have completed the required hiring of ESRs and ERs who have in almost all cases already started their respective projects. As planned during the mid term review the distribution of the man-months was reconsidered, as partner UEN could not be on track in their recruitment plan. Training and secondment activities have been implemented with numerous short and long stages by almost all partners (see below).

B.2.2 Research Effort of the Participants

The use of the assigned number of person-months within CNRSLCC was changed. 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 will complete her Ph.D. thesis with a 6 month employment as ESR in the partner group at IST, to be fulfilled from February to July 2007. The one residual ER person-month that is unused by CNRSLCC/b was allotted to CNRSLCC/a. In the fourth year another change will be needed as partner UEN could not find a suitable ESR candidate. In agreement with the Scientific Officer in charge of the network, partners have agreed to extend the already recruited ER position in Erlangen (Dr Malgorzata Brindell) for four additional months and to make available to partner CNRSLCC/a the remaining ESR four months originally attributed to Erlangen. No contract amendment was necessary.

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 so far.

➤ B.3 Organisation and Management

B.3.1.

After the two additional meetings held during 2005, the First Annual Meeting at IST (Lisbon, Portugal), hosted by Prof. Armando Pombeiro that has been very useful to make the point of the scientific activity, to reinforce running collaboration, to know personally the young scientists recruited in the network and to promote further interactions between the partners, the second year meeting, originally planned to be held in Barcelona (UAB), was moved to Almería (UAL). This coincided with the first AQUACHEM workshop and the Working Group 0009/03 of COST Action D29 meeting.

The Third Year meeting was held in Debrecen (UD) from January 12 to 13, 2007, hosted by Prof. Joo and well organised by himself and coworkers with the support of the University of Debrecen. 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 2006 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. A major meeting chance for most of Aquachem members in 2006 was during the workshop “*Experiment & Theory in Transition Metal Chemistry: a meeting point*”, held in Bellaterra, Spain, from 27 to 29 September 2006, in coincidence with the Final Meeting of FP5 project “HYDROCHEM”. In view of the relevance of this workshop for most of the AQUACHEM teams, the meeting was sponsored by the network AQUACHEM conjointly with another RTN Network running in the 5th RFP (HYDROCHEM).

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 regularly updated all the Network activities on the Network website (<http://www.iccom.cnr.it/aquachem/>)

B.3.2. Network Meetings:

- Kick-off meeting, Florence, Italy, 12-13 February 2004.
- First Annual Meeting, Lisbon, Portugal, 4-5 February 2005 (host Prof. Pombeiro, IST, Lisbon).
- 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)
- Third Year Meeting, Debrecen, Hungary, 12-13 January 2007 (host Prof F. Joo, UD, Debrecen, Hungary)

The Minutes of the meetings are normally made available on the Intranet part of the Network website.

B.3.3. Networking

All network activities during the first three years of the AQUACHEM MC-RTN project are summarised in the table below. Details of visits and secondments are provided in another table (*vide infra*).

From/ To	CNR	LCC/a	LCC/b	UD	HUJ I	UAB	Yo K	UE N	IST	UAL	INEOS
CNR											
CNRSLCC/a											
CNRSLCC/b											
UD											
HUJI											
UAB											
YoK											
UEN											
IST											
UAL											
INEOS											

Colour Code:

Collaboration
Visit
Secondment

Secondments (from the beginning of the project)

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 ^a	CNRSLCC/b	CNR	23/11-22/12/2006	Catalytic oxidation of substituted thiophenes in MeCN/H ₂ O medium
P. Prikhodchenko	HUJI	CNRSLC C/b	7/04 - 21/05/2006	Molybdenum compounds synthesis and characterization
G. Kovács	UAB	UD	23/12/06 – 14/01/2007	Study of the reactivity of water-soluble complexes in the hydrogenation of dienes

^aThis 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 ^a	CNRS	UAB	20-21/01/04	Visit: Research seminar, draft of joint publication, discussion of research plans
A. Romerosa ^b	UAL	CNR	08-27/02/04	Visit: Scientific discussion and preparation of a first draft of a joint manuscript
R. Poli ^c	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 ^d	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 ^e	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 ^f	CNRSLCC/a	UAB	19-21/09/04	Visit: discussions, attendance of bilateral (Midi-

J.P. Majoral				Pyrénées – Catalogne) scientific event
R. Poli ¹	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 ^g	INEOS	CNRS	25/09-03/10/04	Visit (guest professor): discussions, planning for the continuation of the collaboration
M. Peruzzini ^h L. Gonsalvi ^h S. Duckett ^h A. Lledos ^h G.Ujaque ^h E. Shubina ^h N. Belkova ^h	CNR CNR YORK UAB UAB INEOS INEOS	CNRS	01-02/10/2004	Visit: Mid Term review and 2 nd annual meeting of RTN HYDROCHEM; planning of research activities within the framework of the AQUACHEM project
T. Campos ¹	UAL	UD	23/09-08/11/04	Scientific collaboration. Study of the HCO ₃ ⁻ , 1-octen-3-ol and 1-propen-3-ol hydrogenation and isomerization promoted by water soluble ruthenium complexes.
C. Ciardi ¹	UAL	CNR	01/10/- 31/12/2004	Scientific collaboration: Synthesis of functionalized phosphines. Shared thesis co-direction between UAL and CNR
A. Romerosa ^k	UAL	CNR	20-27/11/2004	Visit: Research seminar, scientific discussions, draft of joint publications with CNR scientists
C. Lidrissi ¹	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 ¹	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 ^m	INEOS	CNR	15/06-15/11/2005	Collaborative research: Synthesis of hydrides and macrocyclic complexes
S. Mañas ⁿ	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 ^d	INEOS	CNR	05/09-16/09/2005	Visit: discussions, planning for the continuation of the collaboration, preparation of a manuscript
M. Baya ^o	CNRSLCC/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 ⁿ	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 ^p
G. Kovacs	UD	UAB	1/03/06- 31/05/06	Visit: Three months research stay. Computational study of mechanisms of organometallic reactions in water ^a
L. Gonsalvi ^d	CNR	INEOS	10-15/10/06	Visit: scientific discussions, presentation, draft of joint publications with INEOS scientists
M. Peruzzini ^h L. Gonsalvi ^h I. Mallqui ^h R. Poli ^h R. Malacea ^h C. Dinoi ^h E. Manoury ^h F. Joo ^h P. Sgarbossa ^h S. Mazzega ^h S. Duckett ^h A. Lledos ^h G.Ujaque ^h G.Kovacs ^h E. Shubina ^h N. Belkova ^h	CNR CNR CNR CNRS CNRS CNRS UD IST IST YORK UAB UAB UAB 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. Filippov ^h L. Epstein ^h	INEOS INEOS			
O Lev and J. Gun	HUJI	INEOS	25/06-2/07/2006	Collaborative research, planning of future collaboration
N. Belkova ^o	INEOS	LCC	17/04 to 28/04/2006	Collaborative research: NMR investigation of H-bonding and proton transfer to Cp* <i>RuH</i> (dppe) and Cp* <i>W</i> (dppe) ₃ ; stopped-flow kinetics studies of Cp* <i>W</i> (dppe) ₃ 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 ^o	INEOS	LCC	22/05/ to 4/08/2006	Collaborative research: study of Cp* <i>Mo</i> (dppe) ₃ protonation by CF ₃ COOH; isomerization of Cp* <i>Fe</i> (dppe) ₂ ⁺ .
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 ^q Á. Kathó ^q	UD	UAL	06/06/06- 15/06/06	Visit: Discussions on topics of mutual interest
M. Fekete ^q	UD	UAL	03/10/06- 10/11/06	Collaborative research: synthesis of new water-soluble Ru-NHC complexes
E. Gutsul ^m	INEOS	CNR	08/11/2006- 15/12/2006	Collaborative research: synthesis of hydrosoluble copper complexes

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

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

- Final COST D17 meeting (WG D17/00003), Vienna (Austria) 28-29 March, 2006. participants were M. Peruzzini (CNR), A. Romerosa, E. Petersen (UAL)
- “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).

➤ 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 so far (person-months)</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	30	8	12	20
2. [CNRS] (a)	63 ^{a,d}	11 ^a	74 ^d	26	11	37
2. [CNRS] (b)				28	0	28
3. [UD]	0	36	36	0	21	21
4. [HUJI]	0	24	24	0	18	18
5. [UAB]	0	24	24	0	19	19
6. [YoK]	0	18	18	0	18	18
7. [UEN]	13 ^d	16 ^d	29 ^d	13	6	19
8. [IST]	36	9	45	19	0	19
9. [UAL]	33	10	43	32	0	32
10. [INEOS]	0	0	0	0	0	0
TOTAL	163 ^{b,d}	160 ^c	323	126	105	231

^a 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 will complete her Ph.D. thesis with a 6 month employment as ESR in the partner group at IST, to be fulfilled between February and July 2007. The one residual ER person-month that is unused by CNRSLCC/b was allotted to CNRSLCC/a. ^b Originally 165. ^c Originally 161. ^d After the quota change for UEN.

B.4.3. The recruitment situation after third year of the project is as follows:

Partner	ESR/ER	Name	M/F	Country	Starting date	Duration	Mentor
CNR	ER	Dr Vanessa Landaeta Perera	F	Venezuela	July 1, 2004	12	Dr L. Gonsalvi
UEN	ESR	Ms Raquel Urpi Bertran	F	Spain	July 1, 2004	12	Prof R. van Eldik
UAL	ESR	Mrs Inocenta Mery Mallqui Ayala	F	Peru	July 1, 2004	16	Prof A. Romerosa Nieves
IST	ESR	Ms Silvia Mazzega Sbovata	F	Italy	July 15, 2004	7	Prof. A. Pombeiro
YoK	ER	Dr Nicole Reddig	F	Germany	September 1, 2004	18	Prof R. Perutz
CNRS	ESR	Ms Chiara Dinoi	F	Italy	September 1, 2004	29	Prof R. Poli
CNRS	ESR	Mr Paul Servin	M	Sweden	November 1, 2004	34	Prof A.-M. Caminade
UAB	ER	Dr Andrea Rossin	M	Italy	November 8, 2004	12	Dr G. Ujaque
IST	ESR	Mr Yahuen Karabach	M	Belarus	January 15, 2005	6	Prof A. Pombeiro
HUJI	ER	Dr Petr Prikhodcenko	M	Russia	June 22, 2005	12	Prof O. Lev
UD	ER	Dr Wojciech Wojtków	M	Poland	July 1, 2005	12	Prof F. Joo
CNRS	ER	Dr M.del Mar Tristany	F	Spain	January 1, 2006	11	Prof A. M. Caminade
UAL	ESR	Ms Emma Petersen	F	The Netherlands	February 1, 2006	12	Prof A. Romerosa

IST	ESR	Mr Paolo Sgarbossa	M	Italy	March 1, 2006	5	Prof A. Pombeiro
CNR	ESR	Mrs Inocenta Mery Mallqui Ayala	F	Peru	May 2, 2006	18	Dr L. Gonsalvi
UAB	ER	Dr Gabor Kovacs	M	Hungary	June 1, 2006	12	Prof A. Lledos
HUJI	ER	Dr. Andrey Chernadyev	M	Russia	June 26, 2006	12	Prof O Lev
UD	ER	Dr. Guoying Zhao	F	People's Rep China	July 1, 2006	12	Prof F Joo
UEN	ER	Dr. Malgorzata Brindell	F	Poland	July 15, 2006	16	Prof R vanEldik
UD	ER	Dr. Ambroz Almassy	M	Slovakia	October 1, 2006	12	Prof F. Joo
IST	ESR	Ms Katrin Grunwald	F	Austria	December 1, 2006	6	Prof A. Pombeiro

Further recruitment in the fourth year (for the completion of all partners' schedule) is as follows:

IST	ER	Dr Laurent Benisvy	M	France	January 1, 2007	9	Prof A. Pombeiro
IST	ESR	Mr Riccardo Wanke	M	Italy	January 1, 2007	6	Prof A. Pombeiro
IST	ESR	Ms Chiara Dinoi	F	Italy	February 1, 2007	6	Prof A. Pombeiro
UAL	ER	Dr Rugiada Girotti	F	Italy	February 1, 2007	10	Prof A. Romerosa

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

B.4.4.1 Local research training (old and new)

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}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)

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/LCC/b):

- 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)

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 ^1H -, ^{31}P - and ^{13}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 ^1H -, ^{13}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 ^1H -, ^{13}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).

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 ^1H , ^{13}C and ^{31}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 ^1H , ^{13}C and ^{31}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 ^1H , ^{13}C and ^{31}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)

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)
- Microwaves in synthesis; theory and experiments (12 h – István Ország)

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 ¹H NMR. Hence, the ESR got training on the use of H₂ 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/LCC/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/LCC/b)

Ms Dinoi is doing 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}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}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).

Gabor Kovacs (UAB)

Dr. Kovacs has accomplished the secondment training in Debrecen (UD) between 23th December 2006 and 14th January 2007 carrying out preliminary investigations concerning “Study of the reactivity (catalytic activity and selectivity) of water-soluble complexes in the hydrogenation of dienes” and “Hydrogen transfer from formate to ketones in aqueous systems catalyzed by ruthenium and rhodium N-heterocyclic carbene complexes”

Petr Prikhodchenko (HUJI)

Secondment training in Toulouse:

Dr. Petr Prikhodchenko has accomplished the secondment training in Toulouse (CNR) (CNRS/LCC/b) between 7 April 2006 and 21 May 2006 carrying out preliminary investigations concerning synthesis and speciation of molybdenum sulfide and molybdenum-thiolate complexes. His training included advanced operation and characterization of stop flow dynamic studies and advances in inorganic-organic molybdenum synthesis techniques. Training was conducted by Ms. C. Dinoi under direct supervision and active participation of Professor Rinaldo Poli.

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/gsf2004.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 XIIth 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)

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 XIIth 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 "33rd Congresso di Chimica Inorganica della Società Chimica Italiana" Siena, Italy, July 11-16th 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.
- Attended the congress *XXIInd ICOMC, 22nd International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July 2006, where he presented a contribution.
- 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.
- Active participation in group meetings (once per 2 weeks)
- Spanish course (level 5, 90 hours) provided by the “Servei d’Idiomes” at the UAB

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
- Parcticipation in group meetings (1/week)
- Attended PhD courses in the Advanced chemistry program of the University of Almería. Also these courses contained an eximination 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 Sructural determination by X-ray (20h)
 - o Design and construciton ofcatalysts 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)

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 and helped with routine operations for Dr Prikhodchenko's secondment in Toulouse.

B.4.4.5 Presentations

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 phosphadmantane (PTA)-dendrimers*" AQUACHEM Meeting Lisbon, Portugal, 2005
- "*Organometallic catalysts in aqueous media. The use of dendritic PTA ligands*" AQUACHEM Midterm Review Meeting, Almeria, Spain, 2005
- "*The birth of a superdense dendrimer and some new dendrimer ligands for catalysis*" AQUACHEM Meeting Debrecen, Hungary, 2007

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_2O_2* AQUACHEM Meeting Lisbon, Portugal, 2005

Chiara Dinoi (CNRSLCC/b), *"Reactions of cyclopentadienylmolybdenum(VI) with sulfur compounds"* AQUACHEM Meeting Lisbon, Portugal, 2005; *"Reactions of hemimetallocenic 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 3rd Annual Meeting, Debrecen, Hungary, 2007

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(C₆F₅)(PTA)₂] 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.

International conferences:

Paul Servin (CNRS/LCC/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 (CNRS/LCC/b) has presented three posters:

"Réactions des complexes hémimétallocéniques de molybdène(VI) avec des composés souffrés", *GECOM-CONCOORD 2005*, Autrans, France, June 5-10, 2005

"Reactions of Hemimetalloenic Molybdenum(VI) Complexes with Sulfur Compounds", *5th International School of Organometallic Chemistry (ISOC)*, Camerino, Italy, Sept 10-14, 2005

"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.

Vanessa Landaeta (CNR) has presented two contributions

"Oxidación catalítica selectiva de aril tiofenos utilizando complejos de rutenio y H₂O₂", *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 H₂O₂", *ISHHC XII, 12th 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 α,β -unsaturated aldehydes with ruthenium(II) catalysts" XXXIII Congresso Nazionale della Divisione di Chimica Inorganica della Società Chimica Italiana; July 11-16th 2005, Siena (Italy) (oral presentation)

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

“Regioselective C=O hydrogenation of trans-cinnamaldehyde to cinnamyl alcohol with the water-soluble complexes (H)₂Ru(m-TPPMS)_x [x=3,4; m-TPPMS=(meta-sulphonatophenyl) diphenylphosphine]. A theoretical study of the reaction mechanism and selectivity” Conference DFT2005; September 11-15th 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 two contributions:

“Theoretical investigation of the stereoselective reduction of diphenylacetylene in aqueous acidic solutions catalyzed by water soluble Ru(II) phosphine complexes” *XXIIInd ICOMC, 22nd 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)

Ines Mallqui (CNR) has presented a contribution to the *XXIIInd ICOMC, 22nd International Conference on Organometallic Chemistry*, Zaragoza, Spain, 23-28 July 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.5 Difficulties

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. As for the second year difficulties were encountered by several partners due to the late payment of the second year payment. The change in the Financial Statement submission procedure introduced in SESAM has encountered some resistance especially from financial offices at some partner institutions but will eventually become common practice for the next reporting period.