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Part A - Research Results

A.1 Scientific Highlights

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 phosphaadamantane PTA ligand (PTA = 1,3,5-triaza-7-phosphaadamantane)* (**CNR, UAL**). The research line centred on the coordination capacity of PTA has been continued by the two partner institutions. A large number of complexes of formula $[CpRuX(WSP)_{2-x}(PPh_3)_x]Y$ (WSP = Water Soluble Phosphine) ($x = 0, 1$) have been synthesized and characterized by elemental analysis, spectroscopic methods and, for selected complexes, by X-ray diffraction analysis. Complexes where $x = 1$ are chiral at ruthenium as determined by X-ray crystallography (WSP = PTA or $PTAMe^+$). (see also **T1l**). A paper describing this chemistry is under publication in *Inorg. Chem.*.

T1b) *Synthesis of water soluble vinylidenes and allenylidenes stabilised by hydrosoluble phosphines.* (**CNR, UAL**) A variety of $Cp^RRu(WSP)_2Cl$ complexes have been prepared conjointly in Florence and Almeria and used by UAL to prepare new water soluble vinylidene and allenylidene complexes. This chemistry has been extended by UAL partner and the syntheses of the allenylidene complexes $[Ru\{Cp\text{-}1,3\text{-}(CONC(CH_3)_3)_2\}(=C=C=CPh_2)(L)(L')]$ (L = PPh_3; L' = PTA, $PTAMe^+$) and the evaluation of their properties in metathesis reactions such as ROM (ring opening metathesis), ROMP (ring opening metathesis polymerization) and RCM (ring closing metathesis) under mild conditions, have been carried out.

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 biphases. The results were published in a paper and disclosed in two conference posters (See also T6b) New water-soluble N-heterocyclic carbene complexes were synthetized in the second year starting with $[Rh_2(OH)_2]$ and $[Ir_2(OMe)_2]$ precursors; their characterization and study of their catalytic properties are underway.

T1d) *Synthesis of a water soluble white phosphorus complexes.* (**CNR**) After the first water soluble phosphorus derivatives were prepared in Florence. The chemistry of these unusual species has been started to be studied in detail. The complex $[CpRu(PR_3)_2(\eta^1\text{-}P_4)]Y$ which represent rare example of metal-coordinated η^1-P4 species, smoothly reacts with water yielding in very good yield the stable mononuclear species $[CpRu(PR_3)_2(PH_3)]Cl$ in which a phosphine ligand is coordinated to ruthenium. The dinuclear $\mu,\eta^{1:1}\text{-}P_4$ complex $[\{CpRu(PR_3)_2\}(\mu,\eta^{1:1}\text{-}P_4)]Y$ has been also characterised and its hydrolysis studied. Mechanistic details are under investigation. A paper has been published and a few presentations to international meetings have been given.

T1e) *Synthesis of water soluble phosphines containing amino acid residues.* (**CNR, UAL**) Progresses in this area have been made and the synthetic protocol already demonstrated for serine has been extended to a variety of protected aminoacidic residues including tyrosine, valine, leucine. Several metal complexes of rhodium and ruthenium have been also synthesized. Two communications describing this chemistry have been presented and a paper is currently under preparation.

T1f) *Water soluble ruthenium complexes stabilised by water soluble phosphines and the Cp derivative contaning a aminoacid $\{Cp\text{-}1,3\text{-}(CONC(CH_3)_3)_2\}$* (**UAL, CNR**). Syntheses of water soluble metal complexes with Cp derivatives including aminoacid groups. Synthesis of the ruthenium complexes $[Ru\{Cp\text{-}1,3\text{-}(CONC(CH_3)_3)_2\}Cl(L)(L')]$ (L = PPh_3, PTA, mPTA, TPPMS; L' = PPh_3, PTA,mPTA, TPPMS; mPTA = 1-methyl-1,3,5-triaza-7-phosphaadamantane, TPMS = $PPh_2(Ph\text{-}m\text{-}SO_3)^-$) and the study of their catalytic properties for hydrogen transfer and hydrogenation of olefins in water.

T1g) *Synthesis of free dendritic ligands* (**CNRSLCC/a**). The synthesis of two series of dendritic ligands has been carried out up to the third generation. They possess up to 24 or 48 phosphine end groups, depending on the initial number of functions of the core (3 or 6). The first series possesses chiral iminophosphines (up to 24) derived from (2S)-2-amino-1-(diphenylphosphinyl)-3-methylbutane. In this case, each end group is in fact a bidentate ligand constituted of one phosphine and one imine. This series is only soluble in organic solvents; it was elaborated for future comparative purposes with dendritic ligands soluble in water. The second series possesses PTA ligands (up to 48), grafted to the dendrimer through the alkylation of one N of PTA. Thus this series bears both positive charges and PTA, which induce a solubility in water, even for the third generation. Work is in progress to increase the density of ligand end groups by increasing the density of branches.

T1h) *Synthesis of dendritic complexes* (**CNRSLCC/a**). Organometallic complexes derived from the dendritic ligands elaborated in T1a) have been synthesized, either in situ, or isolated. In the first case, the bidentate chiral iminophosphines (up to generation 3) have been used to complex in situ $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$.[C1] In the second case, $[(\text{p-cymene})RuCl_2]$ was attached to the PTA^+ end groups; the corresponding dendritic complexes have been isolated up to generation 3 (48 $[(PTA)(\text{p-cymene})RuCl_2]^+$ end groups). These complexes are relatively soluble in water, especially when Cl^- is used as counter ion.[D2] In an alternative way, the PTA was first reacted with the metal, then the corresponding complex was reacted with the dendrimer possessing CH_2Cl end groups, to afford the same dendritic complex.

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 $[Re(CO)_3(\text{bipyridyl})L1]PF_6$, **$S1PF_6$**, 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 $[Re(CO)_3(\text{bispyridyl})L1]ClO_4$ (**$S1ClO_4$**). While for the starting sensor, **$S1PF_6$**, 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 $MoO_2(\text{sensor})_2$ species and have determined its crystal structure. This serves as an excellent demonstration of the coordination mode. They have also studied its photochemistry by time-resolved IR spectroscopy on a visit to the Rutherford-Appleton Laboratory in which we collected excellent data (compare **T5f**).

T1j) *Synthesis of bis-hydroxyaminotriazines (BHTs) ligand* (**HUJI**) *s*: 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. [I. Ekeltchik, J. Gun, O. Lev, R. Shelkov and A. Melman, Chem. Commun. (42): 5319-5321 2005 DOI:10.1039/B508138F ; I. Ekeltchik, J. Gun, O. Lev, R. Shelkov and A. Melman, in press Dalton 2006].

T1l) *Synthesis of new water soluble ruthenium complexes with activity towards DNA.* (**UAL, CNR**). The new water soluble ruthenium(II) chiral complexes $[RuCpX(L)(L')]^{n+}$ (X = Cl, I. L= PPh_3; L' = PTA, mPTA; L = L' = PTA, mPTA) described above(PTA = 1,3,5-triaza-7-phosphaadamantane; mPTA = *N*-methyl-1,3,5-triaza-7-phosphaadamantane) have been used in biological assays. The binding properties towards DNA of the new hydrosoluble complexes have been studied using the mobility shift assay. The ruthenium chloride complexes interact with DNA depending on the hydrosoluble phosphine bonded to the metal, while the corresponding compounds with iodide does not bind to DNA. A paper describing this chemistry is in publication.

T1m) *Synthesis and equilibrium studies of water-soluble ruthenium(II) carbonyl-phosphine-hydrides* (**UD**). The known hydrogenation and hydroformylation catalyst, $[RuHCl(CO)(m\text{tppms})_3]$ (*m*tppms = monosulfonated triphenylphosphine) was prepared by a new procedure. It was shown that in aqueous solution this complex readily looses chloride and yields the cationic $[RuH(H_2O)(CO)(m\text{tppms})_3]^+$. 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 synthetized on an independent way. The results were published and also communicated as a poster.

T1n) *Syntheses of platinum(II) complexes with water soluble phosphines.* **(IST)** This task was performed by an ESR, Miss S. Svobota. The syntheses of various Pt(II) complexes with water soluble phosphines have been carried out by reactions of $K_2[PtCl_4]$ or $[PtCl(Me)(COD)]$ with $P(C_6H_5)_2(m\text{-}C_6H_4SO_3Na)$ (tppms) or $P(CH_2OH)_3$, yielding products such as $[PtCl_2(\text{tppms})_2]$, $[PtCl(Me)(\text{tppms})_2]$ and $[Pt(Me)(\text{tppms})_3]Cl$. Their further reactions with organonitriles, such as NCC_6H_4OMe-*4* and NCMe, in the presence of a silver salt, were also initiated towards the syntheses of water soluble cationic organonitrile complexes whose reactivity will be investigated, namely towards various nucleophiles. The electrochemical behaviour of some amidine complexes of the type *cis*- and *trans*-$[PtCl_2\{N(H)=C(NR'R'')R\}_2]$ (R, R', R" = alkyl or aryl), prepared (Prof. R. Michelin's group) from nucleophilic addition of amines (NHR'R" = alkyl or aryl) to coordinated nitriles, was also started to be investigated. The complexes undergo oxidation processes, usually with coupled chemical reactions.

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 ($SO_3Cpz_3^-$) or related scorpionate ligands e.g. hydrotris(1-pyrazolyl)methane ($HCpz_3$) have been synthesized for various transition metals, namely V, Re or Fe. They include *e.g.* $[VCl_3(SO_3Cpz_3)]$, $[ReOCl(SO_3Cpz_3)(PPh_3)]Cl$, $[ReO_3(SO_3Cpz_3)]$, $[ReCl_3(HCpz_3)]$ and derivatives. They have been tested as catalysts for alkane functionalization reactions (see Task 6b)

T1p) *Self-assembly synthesis of water soluble di-, tri- or polynuclear copper complexes* **(IST)** Part of this task has been developed with the collaboration of an ESR, Mr. Y. Karabach. A number of copper complexes with N,O-polydentate ligands and with various nuclearities (mono-, di-, tri- or polynuclear ones) were obtained by self-assembly from copper(II) ions, an amino-alcohol (e.g. triethanolamine H_3tea) and an aromatic carboxylic acid (e.g. terephthalic or pyromellitic acid). Some 1D- and 2D-coordination polymers were thus obtained, with the acid acting as a spacer. Examples include the dimeric $[Cu_2(H_2tea)_2(C_6H_5COO)_2].2H_2O$, the trimeric $[Cu_3(H_2tea)_2(4\text{-}OC_6H_4COO)_2(H_2O)].4H_2O$, the tetrameric $[O{<}Cu_4(tea)_4(BOH)_4]BF_4]_2$ and the polymeric $[Cu_2(H_2tea)_2\{\mu\text{-}C_6H_4(COO)_2\text{-}1,4\}]_n.2nH_2O$ species whose molecular structures were established by X-ray diffraction analysis. These complexes were tested as catalysts for alkane oxidations and models for particulate methane monooxygenase (see Task 6a).

T1q) *Syntheses of water soluble organometallic polymers with formula* $[[\{CpRu(H_2O)(PTA)_2\}[AgCl_2\}]_\infty$ *(PTA= 1,3,5-triaza-7-phosphaadamantane) and* $[\{CpRu(DMSO)(PTA)_2\}\{AgX_2\}]_\infty$ (**UAL, CNR**). The crystal structure of $[\{CpRu(DMSO)(PTA)_2\}\{AgX_2\}]_\infty$ was obtained by X-ray diffraction showing that the complex is an organometallic polymer in solid state. Solution of the DMSO complex in water give the complex $[\{CpRu(H_2O)(PTA)_2\}\{AgX_2\}]_\infty$ by substitution of the DMSO by water. This new complex is a polymer in solution as shown by light scattering. The resulting hydrodynamic diameter indicates a monodisperse sample of about 500 nm which suggest that the coordination polymer does not dissociate in water. A joint paper has been published. A family of water soluble organometallic family of complexes of general formula $[[\{CpRu(H_2O)(PTA)_2\}\{AgX_2\}]_\infty$ was obtained and studied by light-scattering at UAL. The study of the hydrodynamic diameter of the complexes showed a clearly dependence from the X nature, the pH and temperature of the solution.

T1r) *Synthesis and Electrochemistry of hydrosoluble ruthenium complexes with high biological activity* (**IST**). A series of hydrosoluble mixed chloro-azole-ruthenium complexes of the type $[Ru^{III/II}\,Cl_{6-n}\,(azole)_n]^z$ (n = 3,4 or 6; azole = 1-butylimidazole, imidazole, benzimidazole, 1-methyl-1,2,4-triazole, 4-methylpyrazole, 1,2,4-triazole, pyrazole and indazole) prepared in Prof. Keppler's group, as a development of anticancer drugs of the general formula $[RuCl_4(azole)_2]^-$, was investigated in detail by electrochemical methods in aqueous and organic media, using cyclic voltammetry, square wave voltammetry and controlled potential electrolysis. The complexes undergo a single-electron $Ru^{III/II}$ reduction or $Ru^{II/III}$ oxidation, the former followed, at a sufficiently long time scale by metal dechlorination on solvolysis. The redox potential values agree with those predicted by Lever's parametrization method, and the yet unknown E_L ligand parameters for various azole ligands were estimated for the first time. The E_L values for all the azole ligands correlate linearly with their basicity (p*K*a value of the corresponding azolium acid). In addition, a logarithmic dependence between the homogeneous rate constants for the reductively induced stepwise replacement of chloro ligands by solvent molecules and the Ru^{III}/Ru^{II} redox potentials was observed. Lower redox potential values (higher net electron donor character of the ligands) result in enhanced kinetic rate constants of solvolysis upon reduction. The electrochemical behaviour of *trans*-$[RuCl_2(1,2,4\text{-triazole})_4]Cl$ was shown to depend on the pH. The significance of some features of the electrochemical behaviour in terms of biological activity was recognized.

Task 2 - *High oxidation state organometallic aqua ions*
(CNRS-LCC/a, CNRS-LCC/b, UAB, UEN, INEOS, IST; Task Coordinator CNRS-LCC/b)

T2a) *Studies of the* Cp^*Mo^{VI} *aquated complexes* (**UEN, CNRSLCC/b, UAB, HUJI**). Following on the first year studies on the formation of aquated complexes of the type $(Cp^*)MoO_2^+$, $(Cp^*)MoO_2(OH)$, $(Cp^*)MoO_3^-$ and $(Cp^*)MoO_3H_2^+$ from $(Cp^*)_2Mo_2O_5$, kinetic studies on the formation process of $[Cp^*MoO_2(H_2O)_x]^+$ by protonation of $[Cp^*MoO_3]^-$ have been carried out at variable temperature and variable pressure at **UEN**, on a sample provided by **CNRSLCC/b**. A theoretical study of the mechanism has been undertaken by the **UAB**

group. The temperature dependence gives a very negative activation entropy (-150 J/Kmol), whereas the pressure dependence gives a negative activation volume (-9 cm^3/mol). These results are completely unexpected on the basis of the initial mechanistic hypothesis, which involves a reversible protonation process followed by water elimination. It seems, therefore, that water does not leave the coordination sphere and that the slow step consists of an internal rearrangement from $[Cp^*MoO(OH)_2]^+$ to $[Cp^*MoO_2(H_2O)]^+$. Parallel DFT calculations carried out at CNRS-LCC/b indicate that the water dissociation leading from the model $[CpMoO_2(H_2O)]^+$ system to $[CpMoO_2]^+ + H_2O$ in unfavourable. Parallel studies on the related W system are planned during a secondment of Ms. Chiara Dinoi **(CNRSLCC/b)** at **UEN**. A combined electrochemical/mass spectrometry study of $Cp^*{}_2W_2O_5$ (Task 4) is also planned in collaboration with **HUJI**.

T2b) *Improved synthesis $Cp^*{}_2M_2O_5$ (M = Mo, W)* (**CNRSLCC/b**). A short-cut allowing to reduce the number of steps for the synthesis of the title compounds (from $Cp^*M(CO)_3^-/Cp^*M(CO)_3CH_3/Cp^*MCl_4/Cp^*MO_3^-/Cp^*{}_2M_2O_5$ to $Cp^*M(CO)_3^-/Cp^*MO_3^-/Cp^*{}_2M_2O_5$ has been investigated. After initial failed attempts to use H_2O_2 as the oxidant, it seems that bleach insures a good and selective conversion of $Cp^*M(CO)_3^-$ to $Cp^*MO_3^-$, at least for M = Mo. The conditions and yields are currently being optimized.

T2c) *Aqueous reduction of $Cp^*{}_2Mo_2O_5$* (**CNRSLCC/b**). The reduction of $Cp^*{}_2Mo_2O_5$ by zinc in H_2O/MeOH, acidified by CF_3COOH or by CF_3SO_3H, yields the triangular cluster $[(Cp^*Mo)_3(O)_2(OH)_4]^{2+}(Y^-)_2$. The structure of this compound unambiguously establishes the number of protons in the bridge system. The molecule shows Curie paramagnetism for one unpaired electron and the EPR spectrum indicates that this electron is delocalized over only two out of three Mo atoms. All the experimental findings are rationalized by DFT calculations.[0] Speciation studies of this compound as a function of pH and redox potential (Task 4) are planned for Year 3 of the project in collaboration with UEN, while the electroactivation of substrates will be investigated together with IST.

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**). The interaction of water soluble hydrides $CpM(CO)_3H$ (M = Mo, W) with organic bases (pyridine, $(n\text{-octyl})_3PO$, $(n\text{-Bu})_3PO$) was studied by variable temperature IR spectroscopy and confirmed theoretically by DFT/B3LYP calculations. The data obtained show clearly the formation of intermolecular hydrogen bonds between the neutral transition metal hydrides $CpM(CO)_3H$ and bases in solution; the result which does not have any precedent in the literature. This M-H…B hydrogen bond precedes the hydride deprotonation. Further studies of the nature of this interaction as well as of thermodynamics of the M-H…B bond formation and subsequent proton transfer are in progress. The results have been reported on the international conference and joint INEOS/UAB paper has been submitted.

T3b) *Solvent influence on hydrogen bonding to transition metal hydrides.* (**INEOS, CNR**). The ruthenium dihydride complex $[(triphos)Ru(PTA)(H)_2]$, prepared by CNR in year 1 of this project, has been transferred to INEOS. The PTA ligand of this compound is water-soluble. The N-atoms of the PTA cage are proton acceptor centers and the PTA ligand forms hydrogen bond in the presence of weak acids. However, this hydrogen bonded complex is not an intermediate of the proton transfer reaction in low polar media, which proceeds via dihydrogen bond formation yielding cationic non-classical complex $[(triphos)Ru(PTA)H(\eta^2\text{-}H_2)]^+$. The peculiarity of PTA ligand is not in its electronic influence on Ru-H bond properties (pKa 5.7 and cone angle 103° are comparable with those of *e.g.* PMe_2Ph and $P(OMe)_3$; the corresponding hydride complexes have been studied for the comparison) but rather in its own ability to serve as hydrogen bond acceptor. Being not very basic but sterically very easy accessible nitrogen atoms compete for alcohol molecule with a hydride ligand thereby reducing an effective proton donor concentration in the system. The dihydrogen bonding and proton transfer from substituted phenols to the ruthenium dihydride complex $[P(CH_2CH_2PPh_2)_3]RuH_2$ was studied in dichloromethane, THF and in THF/H_2O, THF/CH_3OH and THF/CH_3CN mixtures, showing the influence of solvent polarity and/or proton donor/proton acceptor properties on the position of the proton transfer equilibrium. Formation of ion pairs stabilized by the hydrogen bond between the non-classical cation $[RuH(\eta^2H_2)]^+$ and homoconjugated anion $[ArOHOAr]^-$ was determined in low-polar media. The increase of the media polarity upon the addition of even small amount of water favors proton transfer but leads to the dissociation of hydrogen bonded ion pairs $[RuH(\eta^2H_2)]^+$… $[ArOHOAr]^-$. The structural, energetic and electronic features of the dihydrogen bonded adducts and of proton transfer were investigated by means of DFT/B3LYP calculations of the model dihydride $[P(CH_2CH_2PH_2)_3]RuH_2$ and different proton donors. The specific and non-specific influence of the media properties on the dihydrogen bonding and proton transfer was studied by PCM calculations or by introducing the second proton donor or solvent molecule in the model system. The additional participation of external molecules, either from the solvent or the alcohol, strengthens remarkably the dihydrogen bonded adducts and eases the proton transfer process. A joint CNR/INEOS paper is under preparation.

T3c) *Hydrogen bonding of water to main group hydrides* (**INEOS, UAB**). The INEOS team has started a project aimed at developing new approaches based on IR and UV spectroscopic methods to study H-bonding interactions with H_2O serving at the same time as proton donor and proton acceptor as well as a medium where to carry out proton transfer reactions of organometallics. Different main group hydrides such as $BH_4(Bu_4N)$, $GaH_4(Bu_4N)$, $B_{10}H_{10}(Bu_4N)_2$, $B_{12}H_{12}(Bu_4N)_2$, having many basic centers and high formation constants at room temperature, have been tested as first models for this investigation. The interaction of H_2O with $BH_4(Bu_4N)$, $B_{10}H_{10}(Bu_4N)_2$, $B_{12}H_{12}(Bu_4N)_2$ results in dihydrogen bond formation where water seems to be in bidentate coordination. In order to further confirm this assignment the theoretical DFT/B3LYP study of the interaction of the boron hydrides with water was initiated, introducing the increasing number of H_2O molecules in the model. The interaction between main group hydrides and diprotic NH proton donors is under active investigation as well. The interaction of boron and gallium hydrides with H_2O, CH_3OH and fluorinated alcohol was experimentally studied by IR in CH_2Cl_2 and THF and by theoretical methods (DFT/B3LYP) in gas phase, THF and H_2O by a close collaboration with UAB scientists. The results obtained have allowed a comparison of the mechanism of the proton transfer reaction for transition metal and main group hydrides. The dihydrogen bonded complexes have been shown to be intermediate of both hydrolysis and alcoholysis reactions. The very low stability of the main group (η^2-H_2) complexes changer their role in proton transfer reactions from intermediates in transition metal complexes to transition states in main group hydrides. A joint paper by INEOS and UAB has been submitted.

T3d) *Water exchange reactions on seven-coordinate Fe 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 ($\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta V^{\#}$) 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 involved 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. [M. Wolak and R. van Eldik, J. Am. Chem. Soc., 127, 13312-15 (2005); J.-E. Jee, S. Eigler, F. Hampel, N. Jux, M. Wolak, A. Zahl, G. Stochel and R. van Eldik, Inorg. Chem., 44, 7717-31 (2005)]

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 Fe(III) complexes and solvent exchange on Be(II) complexes in different solvents. In all cases the transition state clearly depicts the intimate nature of the exchange mechanism in terms of A, I_a, I, I_d and D mechanisms. [R. Puchta, N.J.R. van Eikema Hommes and R. van Eldik, Helv. Chim. Acta, 88, 911-922 (2005)]

T3e) *Study of the solubility of dendritic complexes* (**CNRSLCC/a**). The interior of the dendrimers we synthesize is hydrophobic, thus the end groups must be chosen to ensure the solubility in water. The easiest way to fulfil this requirement is to have charges on the end groups. We have shown for the first time that the solubility in water not only depends on the presence of charges, but also on the nature of the counter-ion; the solubility in water of the positively charged dendrimers increases in the order of the counter-ion: $I^- < PF_6^- << Cl^-$. We have shown that the addition of a small quantity of an organic solvent increases the solubility in 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 $[RhCl(TPPMS)_3]$, may proceed through the formation of a hydrido-dihydrogen-rhodium species obtained from e.g. $[RhH_2Cl(TPPMS)_3]$ by protonation. DFT (B3LYP) calculations were performed on the protonation of the latter compound. Due to the effect of hydrogen bonding, $H_3O^+(H_2O)_n$ 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 presented at a conference and a paper is in preparation. The results were published as a journal article and also communicated as a poster.

T3g) Detailed theoretical studies were started to discover the effects of the solvent water on the selectivity of hydrogenations of unsaturated aldehydes catalyzed by [{$RuCl_2$(*m*tppms)$_2$}$_2$] (**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 summarized in two manuscripts (one of them already accepted) and presented at two conferences.

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. 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. This information is of fundamental importance in studies dealing with the activation of NO and H_2O_2 (see T5d and T5e, respectively). [M. Wolak and R. van Eldik, J. Am. Chem. Soc., 127, 13312-15 (2005); J.-E. Jee, S. Eigler, F. Hampel, N. Jux, M. Wolak, A. Zahl, G. Stochel and R. van Eldik, Inorg. Chem., 44, 7717-31 (2005)]

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

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 sometimes formed by direct excitation and sometimes indirectly via the MLCT state. It decays with complex kinetics: some forms are highly reactive decaying in a few ps while others last ca 20 ns.

Task 5 - *Substrate activation and mechanistic studies*

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

T5a) *Chemical reduction studies of Cp*Mo^{VI} by sulfur compounds* (**CNRSLCC/b**). The reaction of $Cp^*_2Mo_2O_5$ with compound $HSCH_2COOH$, in the absence of reducing agents, leads to the dinuclear Mo^{IV} complex [Cp*Mo(μ-SCH_2COO)]$_2$(μ-S), where the substrate has provided at the same time: (*i*) protons for the elimination of the oxo ligands as water; (*ii*) electrons for the metal reduction; (*iii*) the bridging sulfido ligand through a process of S-C bond activation. Future work will address the potential of this system for the electrocatalytic reduction of sulfurated and halogenated hydrocarbons (Task 6).

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 NO subsequently undergoes a reductive nitrosylation reaction that is catalyzed by nitrite. [A. Theodoridis and R. van Eldik, J. Mol. Cat. A, 224, 197-205 (2004); M. Wolak and R. van Eldik, J. Am. Chem. Soc., 127, 13312-15 (2005); J.-E. Jee, S. Eigler, F. Hampel, N. Jux, M. Wolak, A. Zahl, G. Stochel and R. van Eldik, Inorg. Chem., 44, 7717-31 (2005)]

T5c) *Activation of H_2O_2 by Fe(III) complexes* (**UEN**). Rapid-scan techniques were employed to study the activation of H_2O_2 by a series of Fe(III) complexes including porphyrin and non-porphyrin chelate systems. In all studied systems coordination of H_2O_2 to the Fe(III) centre is rapid and controlled by the water-exchange process. Coordinated peroxide is stabilized via deprotonation to form an intermediate hydroperoxo species, which is 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^+. The catalytic activity of the activation process was studied in the presence of typical substrate molecules that can undergo hydroxylation or epoxidation. Kinetic studies on the catalytic cycle were also performed as a function of pH, substrate, H_2O_2 and catalyst concentration, temperature and pressure. The work was partly published and a series of papers are presently under preparation. [A. Brausam and R. van Eldik, Inorg. Chem., 43, 5351-5359 (2004)]

T5d) *Speciation of polysulfide ligands: A new method* (**HUJI**). A new approach based on rapid, chemical derivatization in a single phase, was used to determine the disproportionation constants and the underlying thermodynamics of inorganic polysulfides, a class of important ligation agent and promoters of natural reactions. in aqueous solutions. This method resolves the dispute over the existence of hexasulfide in aqueous solutions and establishes the presence of even higher polysulfide chains in water. The Gibbs free energies of formation, enthalpy of formation and entropy under standard conditions were also resolved. The approach is based on single phase, fast methylation of polysulfides with methyl trifluoromethanesulfonate (methyl triflate), and subsequent determination of the dimethylpolysulfides by HPLC. Kinetic studies and isotope dilution studies were used in order to confirm quantitative equivalence between the observed distribution of dimethylpolysulfides and the polysulfide distribution in the water. A paper is in preparation.

T5e) *Mechanistic studies in ionic liquids* (**EUN**). 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. The results demonstrate that ionic liquids are indeed very suitable solvents to clarify mechanistic details of such reactions. [P. Illner, A. Zahl, R. Puchta, N.J.R. van Eikema Hommes, P. Wasserscheid and R. van Eldik, J. Organomet. Chem., 690, 3567-3576 (2005); C.F. Weber, R. Puchta, N.J.R. van Eikema-Hommes, P. Wasserscheid and R. van Eldik, Angew. Chem. Int. Ed., 44, 6033-6038 (2005)]

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**). The palladium complexes synthesized in situ in T1b) have been used for palladium-mediated asymmetric allylic substitutions (carried out in CH_2Cl_2). They were shown to be one of the best P,N-ligands usable for this purpose, in terms of percentage of conversion (100%), yield in isolated product (up to 97%), and enantiomeric excess (up to 95%). Furthermore, due to its large size, the third generation dendritic catalysts has been recovered and reused successfully two times; this is impossible with the corresponding monomeric catalyst. This work has been published.

T6b) *Isomerization of allyl alcohols in biphasic medium catalyzed by a Ru-dendrimer* (**CNRSLCC/a**). The 1-octen-3-ol has been isomerized to 3-octanone in a biphasic heptane/water medium, under vigorous stirring, in the presence of the first generation of the dendritic complex derived from PTA-Ru-p-cymene obtained in T1b). Six successive catalytic runs were made with the same system, by recovering the heptane phase containing the product (ketone) and reloading it with the alcohol, the water phase being reused. The first four runs gave a high conversion; a dropping of efficiency was observed only for runs 5 and 6. This catalytic experiment needs to be developed and investigated further.

T6c) *Water soluble ruthenium PTA complexes as catalysts for selective hydrogenation of α,β-unsaturated oxo compounds. (PTA = 1,3,5-triaza-7-phosphaadamantane)* (**CNR, UAL**). In the first year, the water soluble

$[Cp^RRuX_n(PTA)_m](PF_6)_q$ complexes (task1) were tested as homogeneous catalysts for the hydrogenation of benzylidene acetone under hydrogen pressure in biphasic conditions and in transfer hydrogenation of cinnamaldehyde using the HCO_2Na / H_2O protocol. These and related compounds have then been used by CNR and UAL as catalyst to promote hydrogen transfer reactions of both ketones and imines. The work has been accomplished during the secondment activity of Mrs Mallqui at CNR.

T6d) *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 $[RuCl(H_2O)$(1-butyl-3-methylimidazol-2-ylidene)(*p*-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 equilibra. The results were summarized in a paper submitted and were presented at three conferences.

T6e) *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 both first and second years thanks to 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. An intriguing feature of the catalytic hydrogenation of bicarbonate by $[\{RuCl_2(TPPMS)_2\}_2]$ is the complete lack of the reduction of hydrated CO_2. This question was investigated theoretically by the UD team, using DFT (B3LYP) calculations. It was revealed, that the reaction is taking place through an $[Ru{\cdot}CO_2]$ intermediate complex, however, this is not formed directly from the catalyst and hydrated CO_2 but via the protonation dehydration of a $[Ru{\cdot}HCO_3]$ species. The results are summarized in a paper accepted for publication.

T6f) *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 biphases by $[\{RuCl_2(TPPMS)_2\}_2]$ 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 hgydrogenation reactor (H-Cube^{TM}) 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 and presented at international conferences.

T6g) *pH-dependent regioselective hydrogenation of α,β-unsaturated aldehydes with Ru(II) water-soluble complexes.* **(UAB, UD)** A computational study of the selective hydrogenation of α,β-unsaturated aldehydes by $[RuCl_2(TPPMS)_2]_2$ has been performed in collaboration by the UAB and UD teams. Several years ago the UD group showed that water-soluble ruthenium(II) m-TPPMS complexes (m-TPPMS = triphenylphosphine meta-monosulphonato) perform selective C=C/C=O hydrogenation of α,β-unsaturated aldehydes in biphasic water/chlorobenzene medium. It was proved that the selectivity is pH-controlled. However, nothing was known about the nature of the intermediates in the catalytic cycle; the only experimental information available was the stoichiometry of the starting active species in the acidic and basic solutions. A thorough computational analysis of the reaction, both in acidic and basic media, has been carried out. 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. Three conference presentations and two UAB-UD joint publications come up from this work.

T6h) *Catalysis of the H/D exchange by $[RhCl(TPPMS)_3]$.* (**UD**) The isotope exchange between D_2 and H_2O or H_2 and D_2O has been studied by DFT (B3LYP) calculations. The results show a strong influence of water and details or the second year results can be found in **T3b**.

T6i) *Catalytic epoxidation of olefins with $(Cp')_2Mo_2O_5$ complexes* (**CNRSLCC/b-IST**). Complex $(C_5Bz_5)_2Mo_2O_5$ (Bz = CH_2Ph) has been synthesized by treatment of $(C_5Bz_5)Mo(CO)_3Me$ with excess ${}^tBuOOH$. Together with other $(Cp')_2Mo_2O_5$ complexes (Cp' = C_5Me_5, $C_5H^iPr_4$, $C_5H_2{}^tBu_3$) it has been shown to efficiently catalyze the epoxidation of cyclooctene in dry chloroform. The system is also catalytically active in an aqueous medium when using ${}^tBuOOH$ as oxidant, but no catalytic activity was observed when using H_2O_2.

T6j) *Catalytic oxidations using green oxidants.* (**CNR**) The complex $[Ru(cuproine)_2(H_2O)_2](BF_4)_2$ was found to be active in H_2O_2 activation and catalytic oxygen transfer to benzo- and dibenzothiophene, yielding the corresponding sulfones in good yield and 100% selectivity in acetonitrile solution at catalyst to substrate ratios as low as 1:1000, which is rivalling with the results reported in the recent literature. In the second year more catalytic tests trying biphasic water/organic solvent conditions and testing H_2O_2 concentration effects were carried out. The work done by Dr Landaeta within the AQUACHEM activity in Florence has been presented in two conference by the young scientist (ER) in charge of the project and a paper is under preparation.

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 will be re-exained in the light of synthetic developments in Florence.

T6m) *Photoactivation of white phosphorus in water.* (**UAL**) UAL team has an ongoing interest to develop new photocatalytic reactions and the search for new water soluble ruthenium photocatalysts is an important target of the AQUACHEM project. As a preliminary result of this research activity, we have discovered the photochemical activation of the new water soluble Ru complexes containing mPTA such as water soluble phosphine. Substitution reactions have been studied which leads to different products depending on the reaction is solar light irradiate P_4 molecule in water under solar irradiation. The photocatalysed reaction results in the formation of H_3PO_4 under very mild reaction conditions using solar light.

T6n) *Electrocatalytic activity of Ruthenium complexes.* (**HUJI, CNR,UAL**). HUJI determined the electrocatalytic activity and mechanism of electrocatalysis of $Ru(acac)_3$ and $RuCl_3$ for the oxidation of several tetraline derivatives by EC-ESI/MS. Electrooxidation of Ruthenium cyclopentadienyl PTA complexes was studies by ESI-MS, cyclic voltammetry and on-line electrochemistry/ESI-MS techniques in collaboration with Profs. O. Lev, M. Peruzzini and A. Romerosa (see T1b).

T6o) *Ru-N-heterocyclic carbene complexes as catalysts of alkyne oligomerization processes.* (**UD**) The newly synthesized Ru(II)-NHC complexes (**T1f**) such as $[RuCl(H_2O)(1\text{-butyl-3-methylimidazol-2-ylidene})(p\text{-cymene})]^+$ catalyzed the oligomerization of various alkynes (such as phenylacetylene) in purely organic solutions. The results were summarized in a submitted mansucript

T6p) *Solar activation of the new water soluble ruthenium complexes obtained (***UAL***).* The new water soluble ruthenium(II) chiral complexes $[RuCpX(L)(L')]^{n+}$ (X = Cl, I. L= PPh_3; L' = PTA, mPTA; L = L' = PTA, mPTA) (PTA = 1,3,5-triaza-7-phosphaadamantane; mPTA = *N*-methyl-1,3,5-triaza-7-phosphaadamantane) have been irradiated by solar light leading to new species showing different catalytic properties with resoect to the employed precursors. The species generated by sun light interaction with the water soluble ruthenium complexes were evaluated in different catalytic reactions such as hydrogen transfer on olefins.

T6q) *Catalytic peroxidative oxidation of cyclohexane by copper complexes models of p-methane monooxygenase.* (**IST**) The copper complexes with N,O-ligands synthesized by self-assembly as indicated in task 1c were shown to act as models of particulate methane monooxygenase (pMMO), an enzyme present in methanotrophs with a tri- or multinuclear Cu cluster that catalyzes alkane hydroxylation. In fact they are highly active and selective catalysts or catalysts precursors for the peroxidative oxidation of cyclohexane (in acetonitrile), to a cyclohexanol and cyclohexanone mixture, by aqueous hydrogen peroxide in acidic medium (liquid biphasic catalysis) at room temperature and atmospheric pressure. The effects on the catalytic activity of various factors, *e.g.* the relative amounts of cyclohexane, oxidant, catalyst, solvent and nitric acid, reaction time, catalyst recycling and impact of both carbon- and oxygen-centered radical traps (supporting mainly radical mechanisms) were investigated and allowed to achieve yields and TONs up to *ca.* 39% and 380, respectively, corresponding to the most active copper systems so far reported for the oxidation of cyclohexane under mild conditions. The catalysts can be reused upon recycling and, at least one of the complexes maintains almost the same level of activity even after five reaction cycles.

T6r) *Catalytic peroxidative oxidation of alkanes by complexes with scorpionate, N,O- and O- ligands* **(IST)** The complexes with the water soluble tris(pyrazolylmethanesulfonate ligand ($SO_3Cpz_3^-$) and related scorpionates (see Task 1b) were tested successfully as catalysts or catalysts precursors for the peroxidative oxidation, by aqueous H_2O_2, of cyclohexane to cyclohexanol and cyclohexanone, under mild conditions (room temperature), in biphasic aqueous/organic medium.

Various Re complexes with N,O-ligands related to models of Amavadine (a natural bare V complex whose biological function has not yet been ascertained) have been prepared and tested as catalysts for the peroxidative oxidation of cycloalkanes. Hence, the new η^2-(benzoylhydrazido)rhenium(v) complex $[Re\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}\{N{=}NC(O)Ph\}(PPh_3)]$ and the η^1-(benzoyldiazenido)rhenium(III) compounds $[ReCl\{N(CH_2\text{-}COO)(CH_2CH_2OH)(CH_2CH_2OH)\}\{N{=}NC(O)Ph\}(PPh_3)]$ and $[ReCl(O,N\text{-}L)\{N{=}NC(O)Ph\}(PPh_3)_2$ [O,N-L = $N(=O)CH_2COO$, $HN{=}C(Me)COO$, $C_5H_4N(COO)$, with chelating N,O-ligands (amino alkoxides, amino-, oxyamino-, imino- and pyridinocarboxylates) were prepared by treatment of $[ReCl_2\{N{=}NC(O)Ph\}(PPh_3)_2]$ with triethanolamine, *N,N*-bis(2-hydroxyethyl)glycine, *N*-hydroxyiminodiacetic acid, *N*-hydroxy-2,2'-iminodipropionic acid and picolinic acid respectively. The N,O-ligands in a couple of them resulted from fragmentation of the *N*-hydroxyiminodicarboxylic acids. The Re complexes are not significantly soluble in water but they act, in aqueous/organic biphasic medium, as catalysts for peroxidative oxidation, by radical mechanisms, of cyclohexane and cyclopentane to the corresponding alcohols and ketones, under mild conditions (room temperature, use of aqueous H_2O_2 and without added acid). This is an unprecedented use of inorganic Re coordination compounds as catalysts in alkane functionalization. Moreover, in pursuit of our search for systems with advantages over the current multi-stage industrial processes for low carboxylic acids, alcohols and ketones, we have found that some metal oxides can behave as convenient and highly active catalysts for the direct (single-pot) and selective (i) peroxidative hydroxylation and oxygenation (by aqueous H_2O_2 at room temperature and atmospheric pressure) of liquid alkanes (cyclopentane, cyclohexane), to the corresponding alcohols and ketones, and (ii) carboxylation (by CO, at 80°C) of gaseous and liquid alkanes to carboxylic acids.

T6s) *Catalytic hydrogenation of 1-octen-3-ol by copper complexes* **(IST)**
In a collaborative work between the IST and the UD groups, initiated during the secondment visit of an ESR (E. Karabach) from the former to the latter team, a few polynuclear copper complexes prepared by the Lisbon group (see Task 1b) were shown to act as catalysts for the hydrogenation of 1-octen-3-ol to 1-octane-3-ol, in aqueous solution, at low pressure and at 50°C. Concomitant isomerization of the substrate to the ketone was observed with only one of the complexes. The work is now being pursued in the Lisbon laboratory.

A.2 **Joint Publications in Refereed journals**

[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] (**CNR-UAL**) 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 [$\{RuCl_2(m\text{tppms})_2\}_2$] in acidic media.", *Organometallics* **2006***, 25*, 862-872 (**Article**)

[A6] **(UAL-CNR)** A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J.A. Garrido-Cárdenas, F. García-Maroto: "Synthesis, Characterization and DNA Activity of New Water Soluble Cyclopentadienyl Ruthenium(II) Complexes Incorporating Phosphines." *Inorg. Chem.* **2006**, *45*, 1289 - 1298 **(Article)**

[A7] (**INEOS-UAB)** O.A. Filippov, A.M. Filin, V.N. Tsupreva, N.V. Belkova, A. Lledós, G. Ujaque, L.M. Epstein, E.S. Shubina, "Proton Transfer and H_2 Elimination Reaction of Main Group Hydrides EH_4^- (E = B, Al, Ga) with Alcohols", *Inorg. Chem.* accepted (**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 [$RuH_2(\text{mtppms})_x$] (x=3,4; *m*tppms=(meta-sulphonatophenyl)diphenylphosphine). A theoretical study of the reaction mechanism and selectivity." submitted (**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 (η^5-C_5H_5)$M(CO)_3H$ (M = Mo, W) and Bases" submitted (**Article**)

A.3 **Joint Publications in Conference Proceedings**

[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-unsatured 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-unsatured 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-cynnamaldehyde to cynnamyl 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

➢ A.3 Joint Patents

(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.4 Publications acknowledging RTN AQUACHEM in Refereed journals without joint coauthorships

[C1] **(CNRSLCC/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] **(CNRSLCC/b)** F. Demirhan, B. Çagatay, D. Demir, M. Baya, J.-C. Daran, R. Poli: “Reduction of $Cp^*_2Mo_2O_5$ in an aqueous medium. Structure and properties of a triangular mixed oxo-hydroxo-bridged product, $[Cp^*_3Mo_3(\mu\text{-}O)_2(\mu\text{-}OH)_4](X)_2$, with X = CF_3CO_2 or CF_3SO_3” *Eur. J. Inorg. Chem.*, in press.

[C3] **(CNRSLCC/b)** F. Demirhan, G. Taban, M. Baya, **C. Dinoi**, J.-C. Daran, R. Poli : “Reduction of $[Cp^*_2Mo_2O_5]$ by thioglycolic acid in an aqueous medium. Synthesis and structure of $[\{Cp^*Mo(\mu\text{-}SCH_2COO)\}_2(\mu\text{-}S)]$”, *J. Organometal. Chem.*, in press.

[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 $[Ru^{III/II}Cl_{6-n}(azole)_n]^z$ (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 $RuCl_4(PTAH)_2{\cdot}4H_2O$ (PTA = 1,3,5-triaza-7-phosphaadamantane)” *Compt. Rend. Chimie.* **2005**, *8*, 1491 – 1496. (**Article**)

[C10] **(CNRSLCC/b)** E. Collange, L. Metteau, P. Richard, R. Poli “Synthesis and structure of a new organometallic polyoxomolybdate, $Cp^*_2Mo_6O_{17}$”, *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 $[trans\text{-}RuCl_4L(DMSO)]^-$ and $[trans\text{-}RuCl_4L_2]^-$ 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**, ASAP **(Article)**

[C15] **(UD)** G. Papp, H. Horváth, Á. Kathó, F. Joó: “Aqueous Organometallic Chemistry. Synthesis and Solution Equilibria of Trisodium Carbonylchlorotris[3-(diphenylphosphino-κP)benzenesulfonato]-hydridoruthenate(3-) ([RuH(Cl)(CO){m-(Ph$_2$P)-C$_6$H$_4$-SO$_3$Na}$_3$]) and Trisodium Aquacarbonyltris[3-(diphenylphosphino-κP)benzenesulfonato]-hydridoruthenate(2-) Tetrafluoroborate(1-) (RuH(CO)(H$_2$O)-{*m*-(Ph$_2$P)-C$_6$H$_4$-SO$_3$Na}$_3$] [BF$_4$]”, *Helvetica Chimica Acta*, **2005**, 88, 566 (**Article**)

[C16] **(UD)** G. Kovács, G. Schubert, F. Joó, I. Pápai: “Theoretical Mechanistic Study of Rhodium(I) Phosphine-Catalyzed H/D Exchange Processes in Aqueous Solutions”, *Organometallics*, **2005**, 24, 3059 (**Article**)

[C17] **(UD)** J. Kovács, F. Joó, and C. D. Frohning: “Anion effects in the formation of the active catalyst in the Ruhrchemie-Rhône Poulenc aqueous biphasic hydroformylation process. Are there any?” *Canadian J. Chem.*, **2005,** 83, 1033 (**Article**)

[C18] **(UD)** M. Fekete, F. Joó: Redox isomerization of allylic alcohols in aqueous-organic biphasic systems catalyzed by water-soluble Ru(II)-N-heterocyclic carbene complexes.” *Catal. Commun., submitted* (**Article**)

[C19] **(UD)** G. Kovács, G. Schubert, F. Joó, I. Pápai: “Theoretical investigation of catalytic HCO$_3^-$ hydrogenation in aqueous solutions.” *Catalysis Today*, *accepted for publication* (**Article**)

[C20] **(UD)** H. H. Horváth, F. Joó: “Stereoselective homogeneous catalytic hydrogenation of disubstituted alkynes in aqueous-organic biphasic media.” *React. Kinet. Catal. Lett.* **2005**, *85*, 355 (**Article**)

[C21] **(UD)** H. H. Horváth, G. Papp, C. Csajági, F. Joó: “Selective catalytic hydrogenations in a microfluidics-based high throughput flow reactor on ion-exchange supported transition metal complexes. A modular approach to the heterogenization of soluble complex catalysts.” *Catal. Commun., submitted* (**Article**)

[C22] **(UD)** P. Csabai, F. Joó, A. M. Trzeciak, J. J. Ziółkowski: “Catalytic activity of a half-sandwich Ru(II)-N-hetrocyclic carbene complex in the oligomerization of alkynes.” *J. Organomet. Chem., submitted for publication* (**Article**)

[C23] **(UEN)** A. Theodoridis and R. van Eldik: “The role of positively charged meso-substituents on the kinetics of the reductive nitrosylation of iron(III)-porphyrins. The catalytic role of nitrite.” *J. Mol. Cat. A*, **2004**, 224, 197-205 (**Article**)

[C24] **(UEN)** P. Illner, A. Zahl, R. Puchta, N.J.R. van Eikema Hommes, P. Wasserscheid and R. van Eldik: “Mechanistic studies on the formation of Pt(II) hydroformylation catalysts in imidazolium-based ionic liquids.” *J. Organomet. Chem.*, **2005,** 690, 3567-3576 (**Article**)

[C25] **(UEN)** R. Puchta, N.J.R. van Eikema Hommes and R. van Eldik: “Evidence for interchange ligand-exchange processes on solvated beryllium cations.” *Helv. Chim. Acta*, **2005**, 88, 911-922 (**Article**)

[C26] **(UEN)** C.F. Weber, R. Puchta, N.J.R. van Eikema-Hommes, P. Wasserscheid and R. van Eldik: “Transition-state effects of ionic liquids in substitution reactions of Pt(II) complexes.” *Angew. Chem. Int. Ed.*, **2005**, 44, 6033-6038 (**Article**)

[C27] **(HUJI)** I. Gun J, Ekeltchik I, Lev O, Shelkov R, Melman A “Bis-(hydroxyamino) triazines: highly stable hydroxylamine-based ligands for iron(III) cations”, *Chem Commun* **2005**, 5319-5321 (**Communication**)

[C28] (**HUJI**) I. Ekeltchik, J. Gun, O. Lev, R. Shelkov and A. Melman, “Bis-hydroxyaminotriazines: Versatile and high-affinity hydroxylamine ligands for iron(III) chelation” *Dalton* **2006** in press (**Article**)

[C29] (**HUJI**) : A. Goifman, J. Gun, F. Gelman, I. Ekeltchik, E. Worch, and O. Lev "Catalytic oxidation of thiol compounds by novel fuel cell - inspired Co-porphyrin and Co-imidazole catalysts", *Israel J. Chem.* **2006**, in press (**Article**)

[C30] (**CNR**) **: Landaeta V.**, Peruzzini M., Herrera V., Bianchini C., Sánchez–Delgado R. A., Goeta, A. E., Zanobini F.
"Synthesis, Characterization and Reactivity of Tribenzylphosphine Rhodium and Iridium Complexes"
J. Organomet. Chem. **2006**, *691*, 1039 - 1050.

[C31] (**CNR**)**: Landaeta V.,** Muñoz B. K., Peruzzini M., Herrera V., Bianchini C., Sánchez–Delgado R. A.
"Imine Hydrogenation by Tribenzylphosphine Rhodium and Iridium Complexes"
Organometallics, **2006**, *25*, 403 – 409.

Communications presented at conferences

➢ A.5 Publications in Conference Proceedings without joint coauthorship

[D1] (**CNR**) **Landaeta, V**.; Gonsalvi, L.; Peruzzini, M. "Ruthenium – Catalyzed Selective Oxidation of Aryl Thiophenes Using H_2O_2" (poster) ISHHC XII, *12th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis* Fiesole, Italy, 18-22 July 2005.

[D2] **(CNRSLCC/a)** R. Laurent, M. Zablocka, **P. Servin**, C. Padié, A.M. Caminade, J.P. Majoral: "Phosphorus dendrimers: complexation and catalysis" (poster) 1er colloque Maroco-Français de Chimie Moléculaire, Rabat, Morocco, 26/28-01-2005

[D3] **(CNRSLCC/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] **(CNRSLCC/a)** A.M. Caminade, R. Laurent, **P. Servin**, J.P. Majoral: "Organometallic phosphorus dendrimers and their use as catalysts" (oral) XVI FECHEM Conference on Organometallic Chemistry, Budapest, Hungary, 3/8-09-2005

[D5] **(CNRSLCC/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

[D6] **(CNRSLCC/b)** **C. Dinoi**, R. Poli, J.-C. Daran, M. Baya, F. Demirhan, G. Taban: "Reactions of Hemimetallocenic Molybdenum(VI) Complexes with Sulfur Compounds" (poster) *5th International School of Organometallic Chemistry (ISOC)*, Camerino, Italy, Sept 10-14, 2005

[D7] **(CNR)** M. Peruzzini "Catalytic activation of white phosphorus: reality or fairy tale?" *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 P_4 to PH_3 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)

[D10] **(CNR) Landaeta, V.**; Gonsalvi, L.; Peruzzini, M "Oxidación catalítica selectiva de aril tiofenos utilizando complejos de rutenio y H_2O_2" *VII Congreso Venezolano de Quimica* Merida, Venezuela, 6/10-11-2005, Abstract CA35. (oral communication)

[D11] **(CNR)** Peruzzini M. "Organometallic chemistry of white phosphorus" *XXX Reunión Bienal de la Real Sociedad Española de Química* Lugo, Spain, 19/23-09-2005. Conferencias y Comunicaciones Resumenes. Abstract GII-I7, p 169. (Invited session lecture)

[D12] **(IST) E. Yu. Karabach**, A.M. Kirillov, M.N. Kopylovich, M.F.C. Guedes da Silva, M. Haukka, A.J.L. Pombeiro, "New Self-Assembled Copper 1D- and 2D-Coordination Polymers as Catalysts for Biphasic Peroxidative Oxidation of Cyclohexane under Mild Conditions", *Current and Future Trends in Polymeric Materials,* Prague, Czech Republic, 2005, PC 23.

[D13] **(IST)** A.M. Kirillov, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, "Rhenium Benzoylhydrazido and -Diazenido Complexes with N,O-Ligands and Their Application in the Catalytic Peroxidative Oxidation of Cycloalkanes", *20th Intern. Conf. on Coordination and Bioinorganic Chemistry*, Smolenice, Bratislava, Slovakia 2005, 56.

[D14] **(UD)** H. Horváth, G. Papp, Á. Kathó, F. Joó: "Metamorphosis of the $[RuHCl(CO)(m\text{tppms})_3]$ catalyst during the hydrosilylation of alkynes in aqueous-organic biphysic systems." *Int. Conf. on Knowledge-based Materials and Technologies for Sustainable Chemistry* (Tallinn, Estonia, 2005), Book of Abstracts, p. 56 (poster presentation)

[D15] **(UD)** F. Joó, H. H. Horváth, G. Papp: „Hydrogenations on supported Ru(II)- and Rh(I)-complex catalyst using the H-Cube^{TM} reactor." *1st Int. Microfluidic-Based Hydrogenation Course*, Thales Nanotechnology Inc. (Budapest, Hungary, September 8, 2005) (invited oral presentation)

[D16] **(UAB)** A. Lledós "New Approaches in the Activation of Unreactive Bonds : Interplay between Experiment and Computation" XVIth FECHEM Conference on Organometallic Chemistry; September 3-8th 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)

[D18] **(UEN)** R. Meier, J. Maigut and R. van Eldik: "Ternary $Fe^{III/II}$(edta)-fluoride complexes – Efforts to optimize NO uptake by Fe^{II}(edta)." *Inorganic Reaction Mechanisms Meeting*, Athens (Greece), 2004 (Oral contribution)

[D19] **(UEN)** A. Theodoridis and R. van Eldik: "The role of positively charged meso-substituents on the kinetics of the reductive nitrosylation of an iron(III)-porphyrine." *Inorganic Reaction Mechanisms Meeting*, Athens (Greece), 2004 (Poster)

[D20] **(UEN)** R. van Eldik; "Mechanistic details on the binding of NO to different metal centers." *Inorganic Reaction Mechanisms Meeting*, Athens (Greece), 2004 (Plenary lecture)

[D21] **(UEN)** R. van Eldik: "Mechanistic details of the interaction of NO with metal complexes in aqueous solution." *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)

[D24] **(UEN)** R. van Eldik: "Electronic tuning of the lability of inert Co(III) and Pt(II) complexes." *228th National Meeting of the American Chemical Society*, Philadelphia (USA), 2004 (Invited lecture)

[D25] **(UEN)** R. van Eldik: "Elucidation of inorganic reaction mechanisms from high pressure kinetics." *42nd EHPRG Meeting on Advances in High Pressure Research*, Lausanne (Switzerland), 2004 (Plenary lecture)

[D26] **(UEN)** R. van Eldik: "Pressure tuning of fast electron and charge transfer processes in inorganic and bioinorganic chemistry." *Fast Reactions in Solution Discussion Group Meeting*, Burgos (Spain), 2004 (Plenary lecture)

[D27] **(UEN)** R. van Eldik: "Mechanistic interpretation of activation volumes. Correlation with other activation parameters." *Inorganic Reaction Mechanisms Meeting*, Liverpool (UK), 2005 (Plenary lecture)

[D28] **(UEN)** P. Illner and R. van Eldik: "Mechanistic study on the formation of active species in a hydroformylation reaction in two imidazolium-based ionic liquids." *Inorganic Reaction Mechanisms Meeting*, Liverpool (UK), 2005 (Poster)

[D29] **(UEN)** C. Weber, R. Puchta and R. van Eldik: "The ionic liquid [BMIM]BTA as a fascinating solvent for substitution reactions on a Pt(II) complex." *Inorganic Reaction Mechanisms Meeting*, Liverpool (UK), 2005 (Poster)

[D30] **(UEN)** R. van Eldik: "To be or not to be NO? A mechanistic approach in coordination chemistry" *INORG 2005*, Pietermaritzburg (South Africa), 2005 (Plenary lecture)

[D31] **(UEN)** R. van Eldik: "Elucidation of inorganic and bioinorganic reaction mechanisms from volume profile analysis." *Joint 20th AIRAPT - 43rd EHPRG Meeting*, Karlsruhe (Germany), 2005 (Plenary lecture)

[D32] **(UEN)** C.F. Weber, P. Illner, R. Puchta and R. van Eldik: "Mechanistic studies on the reactivity of Pt(II) complexes in imidazolium-based ionic liquids." *First International Congress on Ionic Liquids*, Salzburg (Austria), 2005 (Poster)

[D33] **(UEN)** A. Brausam and R. van Eldik: "Chasing intermediates: How do Fe(III)(TAML) complexes bleach dyes?" *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)

[D35] **(UEN)** R. van Eldik: "Mechanistic studies on the reaction of NO with cytochrome P450 and model iron(III) complexes." *3rd International SFB Conference on Metal Mediated Reactions Modeled after Nature*, Jena (Germany), 2005 (Invited lecture)

Single team Patents pending

[E1] A.J.L. Pombeiro, A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M.F.C. Guedes da Silva, "New Di-, Tri-, Tetra- and Poly-nuclear Copper Complexes and Their Use as Catalysts for the Peroxidative Oxidation of Cyclohexane". Patent pending PT 103225 (date: 2005/01/19).

[E2] A.J.L. Pombeiro, M.V. Kirillova, A.M. Kirillov and J.J.R. Fraústo da Silva, "Methyl(trioxo)rhenium and Other Rhenium Oxides as Catalysts for the Carboxylation and Hydroxylation of Alkanes". Patent pending PT 103345 (date: 2005/09/13).

[E3] A.J.L. Pombeiro, J.J.R. Fraústo da Silva, J.A.L. Silva, M.V. Kirillova, P.M. Reis, A.M. Kirillov and A. Palavra, "Groups 5 and 6 Metal Oxides as Catalytic Systems for Oxidative Functionalization Reactions of Alkanes". Patent pending PT 103350 (date: 2005/09/16).

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 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 continued and has resulted in the synthesis of many cyclopentadienyls based complexes containing neutral or cationic water soluble phosphines. Functionalization of the cyclopentadienyls ring with hydrosoluble fragments derived from protected aminoacids has been also accomplished. New hydrosoluble ligands based on aminoacidic moieties have been also synthesised and successfully used to prepare coordination compounds with ruthenium, rhodium and iridium. DNA binding of selected hydrosoluble complexes of this class has been studied at UAL.

A bilateral project aimed at synthesising water soluble phosphines bearing one or more moiety derived by amino acids has been started by UAL and CNR. A co-shared PhD thesis funded by the Spanish Ministry of Sciences is currently running. Some new phosphines of this new class of ligands and their com0plexes with rhodium, iridium and ruthenium have been prepared and characterized by spectroscopic methods. Some catalytic tests have been also accomplished

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.

The 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.

An original series of phosphorus-based water-soluble dendritic phosphines derived from alkylated PTA has been synthesized (generation 1: 12 PTA; generation 2: 24 PTA; generation 3: 48 PTA). The complexation properties of these macroligands have been tested toward several ruthenium and rhodium derivatives, in collaboration between LCCa and CNR. The corresponding complexes have been successfully isolated in the case of $[(p\text{-cymene})RuCl_2]_2$. The main objective for the next year is the synthesis of new series of water-soluble dendritic phosphines and the study of their complexation ability.

The work at IST has been also directed towards the preparation of some hydrosoluble Pt(II) complexes such as $[PtCl_2(tppms)_2]$, $[PtCl(Me)(tppms)_2]$ and $[Pt(Me)(tppms)_3]Cl$.

The first complexes with vanadium, iron and rhenium of the water soluble tris(1-pyrazolyl)methanesulfonate tripodal ligand have been prepared by IST team. The same team has also prepared polynuclear copper complexes stabilised by N,O-polydentate ligands. High nuclearity complexes featuring polymeric structures have been prepared by IST (copper) by self assembling of metal precursors with aminoalcohols and by UAL/CNR (ruthenium/silver) by attempted halide removal with silver salts in $[CpRu(PTA)Cl_2]$.

At IST, hydrosoluble mixed chloro-azole-ruthenium complexes of the type $[Ru^{III/II}\ Cl_{6-n}\ (azole)_n]^z$, prepared in Prof. Keppler's group, as a development of anticancer drugs, were investigated in detail by electrochemical methods in aqueous and organic media, by the IST group. Redox potential - structure relationships were applied to the estimate of the previously unknown Lever E_L ligand parameter for various azole ligands. The kinetic rate constants of solvolysis upon reduction were shown to correlate with the redox potential and with the antitumor activity. The dependence of the electrochemical behaviour on the pH was also recognized.

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

The cationic $[RuH(H_2O)(CO)(m\text{tppms})_3]^+$ has been characterised by UD and independently prepared via chloride disooctiation in water from $[RuHCl(CO)(m\text{tppms})_3]$ ($m$tppms = monosulfonated triphenylphosphine).

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

Progress has been made in the simplification of the synthetic procedures of high oxidation state oxo compounds ($Cp^*{}_2M_2O_5$ with M = Mo, W) and a mixed-valence, mixed oxo-hydroxo-bridged cluster,

$[(Cp^*Mo)_3(\mu\text{-}O)_2(\mu\text{-}OH)_4]^{2+}$ (previously serendipitously obtained and ill-characterized) has now been obtained by a designed synthetic procedure and fully characterized.

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.*

Many more examples of water soluble coordination compounds containing an intact white phosphorus molecule as a ligand have been synthesised in Florence. The chemistry of these amazing compound is still under investigation. Remarkably, the coordinated phosphorus molecule easily reacts with water undergoing in very smooth conditions (neutral pH and room temperature) a complete hydrolysis affording phosphine, PH_3, coordinated to the metal. Hypophosphorous acid, is also formed together with variable amounts of H_3PO_3. The mechanism of these intriguing reactions is under investigation.

The activation of the C-S bond in thioglycolic acid upon interaction with $Cp^*{}_2Mo_2O_5$ has been studied and reported by the CNRSLCC/b group. The extension to other compounds containing the C-S bond and to compounds containing C-halogen bonds is planned for Year 3.

The activation of NO by transition metal complexes has been studied in detail by the UEN group, and the mechanistic understanding of such processes is well advanced. On the basis of this understanding it is now possible to continue further work on the activation of inorganic and organic peroxides for the oxidation of substrate molecules. The applied techniques include 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/INEOSexperimental/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.

Ruthenium hydrides synthesised in Florence (CNR) have been studied by IR methods in Moscow (INEOS) to understand the influence of the solvent, including water, on the hydrogen bonding interaction. Theoretical methods have been used to investigating the hydrogen bonding established between an octahedral classical ruthenium(II) dihydride and a molecule of weak proton donor such as alcohol or water.

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 trans labilizing 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.

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 (HUJ) 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 [AD. Modestov, J. Gun, I. Savotin and O. Lev "On-line Electrochemical – mass spectrometry study of the mechanism of oxidation of N,N-dimethyl-p-phenylenediamine in aqueous electrolytes" J Electroanal. Chem. 565, 7-19

(2004) ; AD. Modestov, A. Mudrove J. Gun and O. Lev "Radial flow electrochemical flow cell for on-line coupling with mass spectrometry: Theory and electro-oxidation of dimethylaminomethyl ferrocene" Electroanalysis 16, 367-378 (2004)]

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**.**

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 theoretical study aimed at understanding the mechanism of the hydrogenation of α,β-unsaturated aldehydes by hydrosoluble Ru(II) complexes have been carried out by the UAB and UD teams. Both the reaction in acid and base media have been studied. The factors governing the selectivity (C=C or C=O hydrogenation), have been explained. Water molecules play an active role in the process.

A DFT study of the water coordination to a $CpMo^{VI}$ model system reveals that the $[CpMoO_2(H_2O)]^+$ system is more stable than the sum of $[CpMoO_2]^+$ and H_2O supporting the experimental study of the protonation kinetics.

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.

Objective 7: *Catalytic studies in aqueous or biphasic media at different pH: CO_2 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 aromatic sulfides to sulfones has been continued to be studied and the remarkable studies which provided good results in organic phase by using the Ru(II) complexes synthesised in Florence have been extended to water phase/biphasic conditions. Disappointingly, the catalytic activity drops to zero under these environmentally benign conditions. The premature end of the grant assigned to Dr Landaeta did not allow however to investigate further this system thus leaving the solution of the problem unanswered.

The intriguing oxidation of cycloalkanes to cycloalkanols and cycloketones (for example cyclohexane to cyclohexanol and cyclohexanone) has been accomplished by peroxidative oxidation, using aqueous H_2O_2, under mild conditions (room temperature), in biphasic aqueous/organic medium. The method developed by IST partener represents an intriguing and unprecedented use of inorganic Re coordination compounds as catalysts in alkane functionalization. Moreover, some new copper self-assembled complexes were shown to be highly active catalysts, acting as models of particulate methane monooxygenase.

The discovery that $Cp'_2Mo_2O_5$ is active in the cyclooctene epoxidation in an aqueous system with ^tBuOOH, but not with H_2O_2, requires additional stoichiometric investigations of the $Cp'_2Mo_2O_5/H_2O_2$ interaction at different pH, which is planned for year 3.

A first "hit" concerning the catalytic activity in biphasic media using a water-soluble first generation dendrimer has been identified: this dendrimer catalyses the isomerization of an allylic alcohol into a ketone. This work will be expanded to test the ability of the corresponding monomer and higher generations of the dendrimer. Other types of catalyses implying dendrimers will be tested.

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

The Jerusalem team (HUIJ) 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 in Florence and Almeria is currently under scrutiny.

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.

Photochemical studies promoted by solar light have been continued to be investigated by UAL. Extension of these studies to ruthenium complexes with WSP is showing an intriguing behaviour which may be ascribed to the irradiation conditions.Substitution reactions on WS Ru complexes are able driven by solar irradiation to give non classical substitution products. The kinetic and rules on the substiturion reaction modified by solar light are under progress.

➢ B.2 **Work Plan**

B.2.1 *Schedule and Milestones*

Network Meetings and publications: During 2005 the first year meeting was held in Lisbon hosted by IST on February 4 – 5. The program of the meeting and the minutes are available on-line in the intranet AQUACHEM web page (http://www.iccom.cnr.it/aquachem/). The meeting was attended by about 30 scientists from all the partners. The second year meeting, coinciding with the mid-term review meeting was held in Almeria (Spain) hosted by partner UAL on December 18 – 21, 2005. The meeting was named *Andalusia meets Europe II* and it was expanded to the size of a scientific workshop (AQUACHEM workshop) by inviting external experts from either Spain and abroad and was again expanded to the twin COST D29 working group (*Green Chemistry through Aqueous Organometallic Catalysis*), which has started almost at the same time (October 2003) of the AQUACHEM network and which gathers four of the partners participating in the AQUACHEM MC-RTN (UD, CNR, CNRS, UAL). The meeting was attended by more than 70 Senior and Junior scientists from 16 countries.

Training milestones: We have had a slow start in recruiting Young Researchers. However, the slowness at the beginning of the project may be considered not surprising to a certain extent and easily correctable. We foresee to improve the delay accumulated in the first two years and think that it will not be difficult to maintain the target of 326 man-months months by the end of the contract. 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. During the mid term review a plan has been madeto correct the distribution of the man-months in case some partners will not be on track in their recruitment policy.

B.2.2 *Research Effort of the Participants*

During the first two years of activity (January 1, 2004 – December 31, 2005) the research effort of the participants in the AQUACHEM MC-RTN has been as follows:

Participant	ESR (Early stage researchers; person-months)		ER (Experienced researchers; person-months)	
	Consumed	Expected	Consumed	Expected
1. [CNR-ICCOM]	0	0	12	12
2. [CNRS-LCC/a]	16	16	0	11
2. [CNRS-LCC/b]	14	16	0	0
3. [UD]	0	0	6	18
4. [HUJI]	0	0	6	6
5. [UAB]	0	0	12	12
6. [YoK]	0	0	15	18

7. [UEN]	13	18	0	0
8. [IST]	14	24	0	9
9. [UAL]	16	15	0	0
10. [INEOS]	0	0	0	0
Totals	73	89	51	85

The use of the assigned number of person-months within CNRSLCC will change. CNRSLCC/b will shift 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. The one residual ER person-month that is unused by CNRSLCC/b will be consumed by CNRSLCC/a.

These efforts deviate to some extent from the original plan and as it has agreed upon during the second year and mid-term review meeting will be corrected during the second part of the project. 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-ICCOM; Ms Inocenta Ayala (Peru) 16 months at UAL), Mr Yauhen Karabach (Belarus) 6 months at IST, and Dr Petr Prikhodcenko (Russia) 6 months at HUJI summing up a total of 40 person-months. This corresponds to ca. 32% of the overall person-months so far recruited, which is practically in line with the EC rule fixing to 30% the limit of the funded research-months for Third Country Researchers. Care will be taken during the project development to reassess this small deviation from the EC limit.

➢ B.3 **Organisation and Management**

B.3.1. Management of the Network has strictly followed the plan outlined in Annex I and already established during the first year running of this project. The coordination of the network has been under the responsibility of the Network Coordinator, Dr. M. Peruzzini, who has been helped in fulfilling this job by Dr L. Gonsalvi who has taken the role of Network Manager.

Exchange of information, drafts of joint papers and, in general, communications concerning the Network has been assured by a wide and continuous use of E-mail which has represented a fast and reliable method of communication.

In agreement with the management planning done during the negotiation of the project and the Kick-off meeting (Florence 2004), two additional meetings have been held during 2005. The First Annual Meeting has been done at the beginning of February at IST (Lisbon, Portugal). The meeting has been hosted by Prof. Armando Pombeiro and has included scientific presentations by all the recruited AQUACHEM ESR/ER researchers. The meeting 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 social activity organised in such occasion was also pleasant and helped to socialise.

The organization of the second year meeting, originally planned to be held in Barcelona (UAB), has been moved to the Almería team (UAL). The organization of this meeting took place in coincidence with the first AQUACHEM workshop. Prof. Antonio Romerosa (UAL team leader) and his team have organised the meeting. It has been attended not only by the AQUACHEM partners and the ESR/ER grant holders within the network, but also by external experts active in the areas of interest for the AQUACHEM consortium as well as by other several Spanish and foreign scientists and students (Morocco, Tunisia, Peru, Serbia, Mexico). The conjoint meeting of the Working Group 0009/03 of COST Action D29 has positively contribute to strength the scientific relatioinships between these two EC sponsored activities. A booklet including the abstracts presented at the meeting has been prepared by the Almeria's team and published under the sponsorship of the University of Almeria (2 plenary lectures; 32 oral communications; 17 posters). University of Almería, Bruker S. A., Afora S. A., Dicsa S. A., CTAP and have allowed the local Organizers to invite external lecturers and arrange a pleasant and intense social activity.

Also, some of the Network participants have met during the year 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. During these events chemical samples for collaborative studies have been transferred between the partners. Samples have been also sent to partner laboratories by courier service.

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 taken the duty to regularly place all the Network activities on the Network website (http://www.iccom.cnr.it/aquachem/)

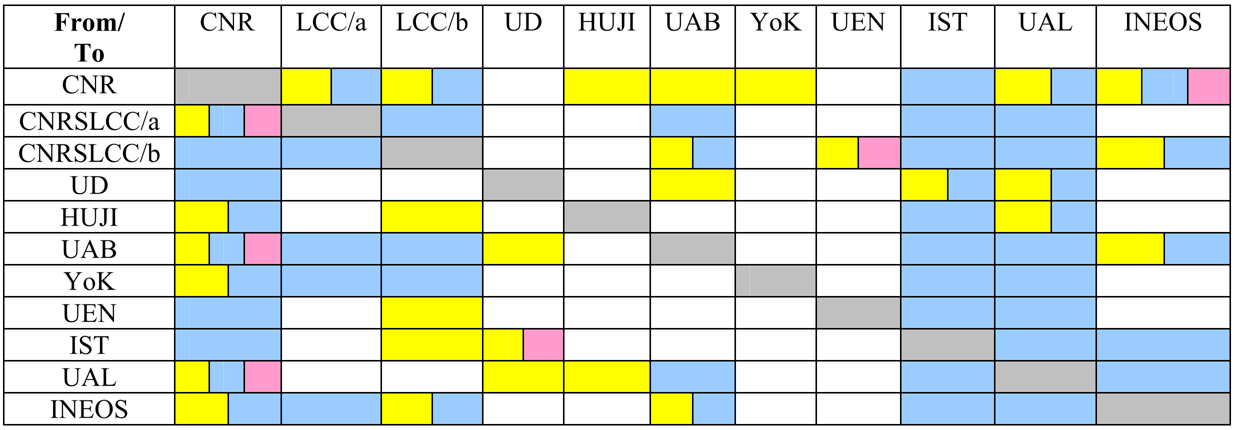
B.3.2. Major Network Meetings:

a. Kick-off meeting, Florence, Italy, 12-13 February 2004.
b. First Annual Meeting, Lisbon, Portugal, 4-5 February 2005 (host Prof. Pombeiro, IST, Lisbon).
c. Second Year Meeting, Almeria, Spain, 18 – 20 December 2005 (host Profs. A. Romerosa, UAL. Almeria, Spain and Prof. A. Lledos, UAB, Barcelona, Spain)
d. Mid-Term review meeting, Almeria, Spain, 21 december 2005 (host Profs. A. Romerosa, UAL. Almeria, Spain)

The Minutes of the meetings are available on the Intranet part of the Network's web site.

B.3.3. Networking

All network activities during the first two 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	HUJI	UAB	YoK	UEN	IST	UAL	INEOS
CNR	▨	🟨🟦	🟨🟦		🟨	🟨	🟨		🟦	🟨🟦	🟨🟦🟥
CNRSLCC/a	🟨🟦🟥	▨	🟦			🟦			🟦	🟦	
CNRSLCC/b	🟦	🟦	▨			🟨🟦		🟨🟥	🟦	🟦	🟨🟦
UD	🟦			▨		🟨			🟨🟦	🟨🟦	
HUJI	🟨🟦		🟨		▨				🟦	🟨🟦	
UAB	🟨🟦🟥	🟦	🟦	🟨		▨			🟦	🟦	🟨🟦
YoK	🟨🟦	🟦	🟦				▨		🟦	🟦	
UEN	🟦		🟨					▨	🟦	🟦	
IST	🟦		🟨	🟨🟥					▨	🟦	🟦
UAL	🟨🟦🟥			🟨	🟨	🟦			🟦	▨	🟦
INEOS	🟨🟦	🟦	🟨🟦			🟨🟦			🟦	🟦	▨

Colour Code:

🟨 Collaboration
🟦 Visit
🟥 Secondment

Secondments visits (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	14-2606/2005	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 lavoratory for synthesis
C. Dinoi	CNRSLCC/b	UEN	01-30/11/2005	Mechanistic and speciation studies involving high oxidation state organometallic oxo complexes

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] J.P. MAJORAL	CNRSLCC/a	UAB	19-21/09/04	Visit: discussions, attendance of bilateral (Midi-Pyrénées – Catalogne) scientific event
R. POLI [f]	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 2nd annual meeting of RTN HYDROCHEM; planning of research activities within the framework of the AQUACHEM project
T. CAMPOS [i]	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 [j]	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 [l]	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 [j]	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 PhDThesis
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]

[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 Eiencia. 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] Vist 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)

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

Sustainable / Green Chemistry and Chemical Technology Workshop, Venice, Italy, 20-21 February 2004. Participants were L. Gonsalvi (CNR), F. Joó (UD).

"*Modern trends in organoelement and polymer chemistry. International conference dedicated to 50th anniversary of A.N. Nesmeyanov Institute of Organoelement Compounds (INEOS)*", Moscow, Russia, 30-05/4-06-2004: participants were M. Peruzzini (CNR), R. Poli (CNRSLCC/b), A. Romerosa (UAL) and P. Revin, E. Gutsul, P. Dub, N. Belkova, E. Shubina, and L. Epstein (INEOS).

ICPC XIV, 16th International Conference on Phosphorus Chemistry; Birmingham, England, UK, 04-09/07/04: participants were M. Peruzzini (CNR), A.M. Caminade and J.-P. Majoral (CNRSLCC/a)

ISHC XIV, 14th International Symposium on Homogeneous Catalysis, Munich, Germany, 5-9 July 2004: participants were L. Gonsalvi (CNR), F. Joó, Á. Kathó, J. Kovács, I. Jószai, P. Csabai, G. Kovács (UD)

"*XXII Meeting of the Grupo Especializado de quimica organometalica (GEQO)*", Ciudad Real, Spain, July 12-14, 2004: participants were R. Poli and M. Baya (CNRSLCC/b) and A. Lledós and A. Nova (UAB), A. Romerosa, T. Campos, C. Ciardi (UAL)

Green Solvents for Synthesis, Bruchsal, Germany, 3/6-10-2004: participants were F. Joó (UD), A. Romerosa (UAL) and **V. Landaeta** (CNR).

"XVI FECHEM Conference on Organometallic Chemistry", Budapest, Hungary, 3/8-09-2005: participants were A.M. Caminade (CNRSLCC/a), F. Joó (UD), A. Lledós (UAB).

"5th International School of Organometallic Chemistry", Camerino, Italy, 10-14 September, 2005: participants were R. Poli, M. Baya, R. Malacea, J. Houghton, **C. Dinoi** (CNRSLCC/b), M. Peruzzini, S. Bosquain, E. Le Roux, D. Yakhvarov (CNR), S. Duckett, J. Lopez Serrano, P. Caldwell (YORK), N. Belkova, E. Gutsul, P. Revin (INEOS).

"Third Annual Meeting of 5th RFP RTN-HYDROCHEM.", Camerino, Italy, 14-15, September, 2005: participants were R. Poli, M. Baya, R. Malacea, J. Houghton, **C. Dinoi** (CNRSLCC/b), M. Peruzzini, S. Bosquain, E. Le Roux, D. Yakhvarov (CNR), S. Duckett, J. Lopez Serrano, P. Caldwell (YoK), A. Lledós, G. Ujaque, M. Besora (UAB), N. Belkova, E. Gutsul, P. Revin (INEOS).

"33rd Congresso di Chimica Inorganica della Società Chimica Italiana" Siena, Italy, July 11-16th 2005: M. Peruzzini, (CNR), **A. Rossin** (UAB)

"ISHHC-XII; International Symposium on the Relations between Homogeneous and Heterogeneous Catalysis" Firenze, Italy, July 18-22, 2005: M. Peruzzini, **V. Landaeta**, L. Gonsalvi, S. Bosquain, E. Le Roux, (CNR), **A. Rossin** (UAB)

XXth International Union of Crystallography; Firenze (Italy), August 21-28th 2005: M. Peruzzini, C. Mealli, A. Ienco (CNR), S. Manas, **I. Mallqui** (UAL), C. Daran (CNRS), Y. Antipin (INEOS).

➢ B.4 **Training**

B.4.1. As already reported for the first 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. A Network-wide advertisement has been posted on the Network's website and on the CORDIS website. Posting on other web pages has been done by each Network participant on an individual basis. It is believed that personal contacts and advertisements as well as direct e-mailing of colleagues has hade the highest impact in terms of generating applications from qualified candidates.

B.4.2. Recruitment has been as follows:

Participant	***Contract deliverable of Young Researchers to be financed by the contract (person- months)***			***Young Researchers financed by the contract so far (person-months)***		
	ESR (a)	***ER (b)***	***Total (a+b)***	***ESR (c)***	***ER (d)***	***Total (c+d)***
1. [CNR]	18	12	30	0	12	12
2. [CNRS] (a)	59[a]	11[a]	70	16	0	16
2. [CNRS] (b)				14	0	14
3. [UD]	0	36	36	0	6	6
4. [HUJI]	0	24	24	0	6	6
5. [UAB]	0	24	24	0	12	12
6. [YoK]	0	18	18	0	15	15
7. [UEN]	24	12	36	13	0	13
8. [IST]	36	9	45	13	0	13
9. [UAL]	33	10	43	16	0	16
10. [INEOS]	0	0	0	0	0	0
TOTAL	170[b]	156[c]	326	72	51	123

[a] The use of the assigned number of person-months within CNRSLCC will change. CNRSLCC/b will shift 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 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. The one residual ER person-month that is unused by CNRSLCC/b will be consumed by CNRSLCC/a. [b] Originally 165. [c] Originally 161

Partners CNR, CNRS (both a and b teams), HUIJ, UAB, YoK, UEN and UAL are more or less on schedule Other partners like UD and IST are slightly behind schedule, but this should not represent a problem as the total number of their allotted person-months is lower than the remaining two years duration of the project. If necessary a redistribution of person-months from the delayed partners to other participants in the network will be taken into consideration before the third year meeting. Such possibility was discussed during the mid-term review meeting a it was agreed upon the partners.

B.4.3. All ESR/ER have been integrated into the research programme according to plans. Below is the situation after second year of the project:

CNR: V. Landaeta has been mentored by Dr. M. Peruzzini.
CNRSLCC/a: P. Servin is mentored by Dr. A.M. Caminade
The recruitment of the ER has been postponed by CNRSLCC/a for the following reason: It appeared rapidly after the recruitment of the ESR (Paul Servin) that the early recruitment of an ER would not be judicious, because we had to find the right ways to combine the water-solubility and the catalytic properties in a single dendrimer, and this was not trivial. Now we have found a way, thus it is the right time to recruit the ER for the best efficiency and the best synergy between the ESR and the ER. The ER is already found (Maria del Mar Tristany) from Barcelona (Spain). She is recruited since January 15th 2006 by CNRSLCC/a for 11 months (10 month from LCC/a + 1 month left from LCC/b).
CNRSLCC/b: C. Dinoi is mentored by Prof. R. Poli
UD: W.Woitkow is mentored by Prof F. Joo
HUJI: P. Prikhodechenko is mentored by Dr. J. Gun.
UAB: A. Rossin has been mentored by Dr. G. Ujaque
YoK: N. Reddig is mentored by Prof. R. Perutz, Dr. A.-K. Duhme-Klair and Dr. S. B. Duckett
UEN: Ms R. Urpi-Bertran has been supervised by Prof. R. van Eldik
IST: Silvia Mazzega Sbovata has been mentored by Prof. A. J. L. Pombeiro

IST: : Yauhen Yu. Karabach is mentored by Prof. A. J.L. Pombeiro and by Dr. M.F.C.Guedes da Silva
UAL: I. M. Mallqui Ayala has been mentored by Dr. Antonio Romerosa
INEOS: No young researcher was to be recruited

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 (CNRSLCC/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)

Chiara Dinoi (CNRSLCC/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 Perklin-Elmer Spectrum GX FT-IR spectrophometer: 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)

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

Nicole Reddig (YoK) already trained in:
-Schlenk-Techniques; Operation of UV/Vis and cyclic voltammetry instrumentation; -Synthesis of transition metal complexes; Single Crystal structure determination (solution and refinement)
Received training in York as follows:
-Luminescence spectroscopy including work on Fluorimeter (8 h training by Dr. L. Abbott and H. Batey).
-Operation of IR instrumentation (4 h training by Prof. Perutz and Dr. N Jasim)
-Acquisition and processing of ^{1}H-,^{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 diffratometer (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)

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

Inocenta Mery Mallqui Ayala (UAL):
- Inert atmosphere synthesis and handling techniques (40 h training by M. Serrano Ruiz)
- Synthesis of ruthenium water soluble complexes (25 h training by A. Romerosa)
- Operation of IR and UV instrumentation (2 h by T. Campos, M. Serrano Ruiz)
- Acquisition and processing of ^{1}H, ^{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)

Petr Prikhodchenko (HUJ)
- 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).

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.

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):
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 a studying the catalytic hydrogenation of ketones and imines under biphasic aqueous conditions.
- Basic operations of Gas Chromatography (GC): 4 h (training by L. Gonsalvi)
- High pressure reactions ("autoclave"): 6 h (training by L Gonsalvi)

Yauhen Yu. Karabach (IST)
The ESR Y. Karabach (IST) spent 11 days (June 16th-26th) in Prof. Ferenc Joo's laboratory (UD), where he tested the use of a few copper complexes he had prepared in Lisbon as catalysts for the hydrogenation of 1-octen-3-ol to 1-octane-3-ol (see task 6d). The reactions were monitored by ^{1}H NMR. Hence, the ESR got training on the use of H_2 gas, on experiments of olefin hydrogenation and on reaction monitoring by NMR.

Paul Servin (CNRSLCC/a):
Mr Paul Servin, currently doing his PhD in Tolouse (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)

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 (CNRSLCC/b)
Ms Dinoi is doing her PhD in Tolouse under the supervision of Prof. Rinaldo Poli. As secondment activity, she has been in Erlangen (team of Prof Rudi Van Eldik) for one month. In the secondment period she has been trained in 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).

B.4.4.3 Complementary training
Vanessa Landaeta (CNR):
- Attended the Conference *Green Solvents For Synthesis,* Bruchsal, Germany, 3/6-10-2004 (http://events.dechema.de/gsfs2004.html) The participation of Dr Landaeta to this conference was encouraged as the aim of the meeting was quite in line with the AQUACHEM training activity of the ER. The aim of the Bruchsal meeting was indeed to highlight innovative concepts for the substitution of volatile organic solvents in solution phase synthesis in academia and industry. Emphasis were given to the development and application of alternative reaction media and phase-separable reagents (aqueous phase, ionic liquids, supercritical media, fluorinated phases, thermoregulated systems, soluble polymers etc.) in all areas of chemical synthesis.
- Attending/attended several CNR and University seminars given by Senior and Junior scientists.
- Preparation and revision of two scientific manuscripts (discussion and training by Dr. M. Peruzzini)
- Attended the NMR basic course on the use of BRUKER NMR spectrometers held in Milan (Bruker, May 2005, 3 days intensive course). The course included both practical and theoretical training on new generation spectrometers.
- Attended the 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: 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):

- 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.

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).

Wojciech Wojtkov (UD)

- Hungarian language coures, 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)

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)

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 six group meetings
- *"Towards phosphaadamantane (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

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)
"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

International conferences:

Paul Servin (CNRSLCC/a) has presented two oral communications:
"Synthesis of PTA bearing phosphorus dendrimers", *Journées Jeunes Chercheurs de la SFC*, Toulouse, France, April 7-8, 2005

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

Chiara Dinoi (CNRSLCC/b) has presented two posters:
"Réactions des complexes hémimétallocéniques de molybdène(VI) avec des composés souffrés", *GECOM-CONCOORD 2005*, Autrans, France, June 5-10, 2005
"Reactions of Hemimetallocenic Molybdenum(VI) Complexes with Sulfur Compounds", *5th International School of Organometallic Chemistry (ISOC)*, Camerino, Italy, Sept 10-14, 2005

Vanessa Landaeta (CNR) has presented two contributions
"Oxidación catalítica selectiva de aril tiofenos utilizando complejos de rutenio y H_2O_2", *VII Congreso Venezolano de Quimica,* Merida**,** Venezuela, 6/10-11-2005, *in Spanish.* Abstract CA35 (oral presentation).
"Ruthenium – Catalyzed Selective Oxidation of Aryl Thiophenes Using H_2O_2" *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-unsatured 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-unsatured 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-cynnamaldehyde to cynnamyl 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.

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 second year of the project, the ratio male/female was 5/6, 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. For example, CNR has signed a bilateral agreement with a Dutch company (THERMPHOS International BV, Vlissingen, NL; web page: http://www.thermphos.com/) to study new protocols for functionalising white phosphorus including the possible functionalization of elemental phosphorus in water. UEN has a standing collaboration and contract with Henkel GmbH to study the catalytic activation of peroxides

➢ B.5 **Difficulties**

Late recruitment from some of the partners was due to the need to stay within the quota for non-EU and associate state citizens. Some difficulties were encountered by several partners due to the late payment of the first year payment. Particularly, this delay has been particularly serious for those partners who could not borrow funds from their institutions or other sources to cover costs directly related to AQUACHEM during year 2005.