

# Inorganic and Organometallic Chemistry

The activities of the group comprise the synthesis, characterization and reactivity studies of inorganic, organometallic and intermetallic compounds of **actinides** and **lanthanides** in order to understand the influence of the electronic configuration and of the size of these elements in the chemical behaviour of their compounds. Reactivity properties are assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas phase ion-molecule reactions with the same elements and the study of the energetics of f-element compounds are also made with the same objective.

Although the dominant research activity of the group has a fundamental nature, the type of chemistry we are dealing with allowed us to envisage applications either in nuclear sciences or in catalysis and materials science. Whereas we intend for example to extend the gas phase chemistry of U and Th to the more toxic actinides, we are at the same time trying to explore the very interesting catalytic properties of some uranium and lanthanide compounds.

As it is well known, inorganic chemistry has been a driving force to the development of radiometal agents either for diagnostic or for therapy. As some of the **lanthanides** and **rhenium** have radionuclides which are suitable to be used in radiopharmaceuticals and can be produced in the Portuguese Research Reactor, the research of this group has been extended to the chemistry of rhenium. The idea was to design compounds which can be models for complexes with  $^{99m}\text{Tc}$  to be used as radiopharmaceuticals. The previous experience on lanthanide chemistry can also be applied to the synthesis of radiopharmaceuticals based on radiolanthanide compounds.

In the end of 1999, with our support, some researchers of the Inorganic and Organometallic Chemistry Group formed an **independent research group, Inorganic and Radiopharmaceutical Chemistry**, to apply their knowledge in inorganic chemistry to radiopharmaceutical investigation. This new group integrated also the former researchers from the radiopharmacy team who had already experience in  $^{99m}\text{Tc}$  radiochemistry.

# Reactivity of Lanthanide Compounds\*

Irene Lopes<sup>1</sup>, Ângela Domingos, Noémia Marques

## Objectives

The organometallic chemistry of the lanthanide elements has witnessed an explosive development since the introduction of the pentamethylcyclopentadienyl ligand system to this area of chemistry. The  $(C_5Me_5)_2LnR$  ( $R=H$ , alkyl) compounds have been shown to be exceptional catalysts, while, the arene soluble  $(C_5Me_5)_2Sm(THF)$  and its solvent free parent  $(C_5Me_5)_2Sm$  can affect unique organic transformations, which have been attributed to the strong reducing ability of  $Sm(II)$  and to the coordinative unsaturation of the metal center. However, the number of mono-ligated  $Ln$  complexes with cyclopentadienyls or other ligands remains surprisingly small, as the complexes tend toward ligand redistribution. In this project, we intend to study the reactivity of lanthanide compounds stabilized by hydrotris(pyrazolyl)borate ligands and to verify if these ligands which, by virtue of the wide range of available substituents, allow for tuning the steric size and electronic properties of the ligands, can lead to reactivity patterns different of those observed for the pentamethylcyclopentadienyl compounds.

## Results

The reactivity of the compound  $Sm(Tp^{Me_2})_2$  (**1**) ( $Tp^{Me_2} = HB(3,5-Me_2pz)_3$ ) has been tested with several unsaturated organic substrates. **1** undergoes readily one-electron transfer reactions with a variety of reagents. Reactions with ketones lead to  $Sm(Tp^{Me_2})_2X$  compounds in which  $X$  is the radical anionic form of the benzophenone or fluorenone or to dimeric compounds with two  $Sm$  centres bonded by a bridging dianionic ligand (quinone). In the reactions with benzaldehyde a ketyl complex is formed but this is unstable leading to a dimeric compound with two  $Sm$  centres bridged by the dianionic ligand  $(OCH(Ph)-CH(PhO))$  due to C-C coupling of two radical anions  $OCH(Ph)$ . **1** cleaves the E-E bonds of  $E_2R_2$  reagents ( $E = O, S, Se, R = C_5H_5N$ ) yielding the  $Sm(Tp^{Me_2})_2(ER)$  compounds. The compounds present the same coordination geometry (DD) in the solid state, but in solution the behaviour is different due to metal-centered rearrangements.[1] **1** reacts with  $TiCp$  to yield the first mixed  $Tp/Cp$  compound,  $Sm(Tp^{Me_2})_2(Cp)$ . The thermolysis of this compound in the solid leads to a compound in which the  $Sm$  is coordinated to a  $Tp$  ligand and to a novel, dianionic ligand,  $HB(3-5Me_2pz)_2(C_3H_4)$ , due to C-H activation mediated by the metal centre[2].

The synthesis of mono-ligated  $Yb(II)$  compounds has been achieved by using a  $Tp$  ligand with bulky mesityl substituents in the 3 position of the pyrazolyl rings. The synthesis of this ligand leads to two isomers:  $HB[(3-Mespz)_3]$  ( $Tp^{Mes}$ ) and  $HB[(3-Mespz)_2(5-Mespz)]$  ( $Tp^{Mes*}$ ). Ytterbium diiodide reacts with both ligands yielding  $YbI(Tp^{Mes})(THF)_2$  (**2**) and  $YbI(Tp^{Mes*})(THF)_2$  (**3**), respectively. **2** is unstable in THF solution leading to **3** due to isomerization of the ligand. The hydrocarbyl derivative  $YbI(Tp^{Mes*})[CH(SiMe_3)_2]$  was prepared. To hinder the isomerization of the ligand the new ligands  $HB[(3-Mes,5-Mepz)_3]$  ( $Tp^{Mes,Me}$ ) and  $HB[(3-Mes,5-Mepz)_2(3-Me,5-Mespz)]$  ( $Tp^{Mes,Me*}$ ) were prepared. In this case, due to the additional inductive effect of the methyl substituents, the isomerization reaction was not observed and the two compounds ( $YbTp^{Mes,Me}(THF)_2$ ) (**4**) and  $YbI(Tp^{Mes,Me*})(THF)_2$  (**5**) were isolated.

## References

1. Lopes, I., Domingos, A., Galvão, A., Solid State Structure and Solution Behaviour of Eight-Coordinate  $Sm(III)$  Poly(pyrazolyl)borate Compounds, Abstracts Book of the XIII<sup>th</sup> FECHM Conference on Organometallic Chemistry, Lisboa, Portugal, 1999. (poster)
2. Lopes, I., Lin, G. Y., Domingos, A., Marques, N., Takats, J., Unprecedented Transformation of a Hydrotris(pyrazolyl)borate Ligand at a Metal Center: Synthesis and Rearrangement of the First Mixed  $Tp/Cp$  Lanthanide Complex,  $Sm(Tp^{Me_2})_2(Cp)$ , *J. Am. Chem. Soc.* **121** (1999) 8110-8112.

## Further work

To test the reactivity of **1** in the polymerization of ethylene and to complete the characterization of the compounds formed in the reactions of **1** with isocyanate, di-*t*-butylperoxide, phenanthraquinone, benzaldehyde azine, etc. To synthesize the hydrocarbyl and hydride derivatives of **3**, **4**, and **5** and to test the reactivity of the hydrocarbyls with organic substrates.

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<sup>1</sup> PRAXIS PhD student.

# Compounds of f-Elements: Synthesis, Characterization and Reactivity Studies\*

Leonor J. Maria<sup>1</sup>, Ângela Domingos, J. Collin<sup>2</sup>, N. Giuseppone<sup>1</sup>, Isabel Santos

## Objectives

As an alternative to cyclopentadienyls, we have been exploring the chemistry of the poly(pyrazolyl)borates. These supporting ligands are very interesting for transition elements, as their steric and electronic properties can be easily modified by changing the number of pyrazolyl rings coordinated to the boron and by introducing various sterically bulky pyrazolyl ring substituents (Santos, I. *et al*, *New J. Chem.* **19** (1995) 551). This project explored the chemistry of U(IV) with [B(pz)<sub>4</sub>], and of U(III) with [Ph<sub>2</sub>B(pz)<sub>2</sub>], [H<sub>2</sub>B(<sup>i</sup>Pr<sub>2</sub>-pz)<sub>2</sub>], [H<sub>2</sub>B(3<sup>t</sup>Bu,5Me-pz)<sub>2</sub>], [HB(<sup>i</sup>Pr<sub>2</sub>-pz)<sub>3</sub>] and [H<sub>2</sub>B(SImz)<sub>2</sub>], to evaluate the type of complexes that can be stabilized and their behaviour in stoichiometric and catalytic reactions.

## Results

Using the monoanionic [B(pz)<sub>4</sub>]<sup>-</sup> we stabilized the complex {UCl<sub>2</sub>[B(pz)<sub>4</sub>]<sub>2</sub>} (**1**), which was fully characterized. The reactivity of **1** has been evaluated in stoichiometric reactions, and compared with the analogous, previously characterized, {UCl<sub>2</sub>[HB(pz)<sub>3</sub>]<sub>2</sub>} (**2**). Complexes **1** and **2** are very similar in terms of solid state structure and solution behaviour. However, the derivative chemistry of **1** is much more limited, specially when alkyl groups are involved. EHMO calculations were used to get a better insight into the properties of the [B(pz)<sub>4</sub>]<sup>-</sup> and [HB(pz)<sub>3</sub>]<sup>-</sup> ligands. The analysis of the frontier orbitals did not show any significant differences but the calculations indicate that stereochemical interactions condition the reactivity, by imposing unfavourable coordination geometries.<sup>1</sup> With U(III) we observed the formation of species UL<sub>3</sub>, when L=[Ph<sub>2</sub>B(pz)<sub>2</sub>] (**3**) and [H<sub>2</sub>B(<sup>i</sup>Pr<sub>2</sub>-pz)<sub>2</sub>] (**4**). These coordinatively saturated complexes are not promising for further reactivity studies (L. Maria, I. Santos, manuscript in preparation). Using the more bulky [H<sub>2</sub>B(3<sup>t</sup>Bu,5Me-pz)<sub>2</sub>], the first monodihydrobis(pyrazolyl)borate U(III) complexes, [U{H(μ-H)B(3<sup>t</sup>Bu,5Me-pz)<sub>2</sub>}<sub>2</sub>(THF)<sub>2</sub>] (**5**) and [U{H(μ-H)B(3<sup>t</sup>Bu,5Me-pz)<sub>2</sub>}<sub>2</sub>(OPPh<sub>3</sub>)<sub>2</sub>] (**6**) were completely characterized. The ligand is tridentate due to an agostic B...U interaction.<sup>2</sup> Catalytic studies were undertaken for UI<sub>3</sub>(THF)<sub>4</sub> and for **5**. UI<sub>3</sub>(THF)<sub>4</sub> is an efficient Lewis acid catalyst for Diels-Alder reactions and has a higher activity than samarium diiodide and other lanthanide complexes.<sup>3,4</sup> However, the use of the **5** has shown that the replacement of one iodide by a dihydrobis(pyrazolyl)borate decreases the activity and does not increase the selectivity (L. Maria, J. Collin, manuscript submitted). Some other studies involving [HB(<sup>i</sup>Pr<sub>2</sub>-pz)<sub>3</sub>] and [H<sub>2</sub>B(SImz)<sub>2</sub>] were also undertaken and the species formed are tentatively formulated as {UI<sub>2</sub>[HB(<sup>i</sup>Pr<sub>2</sub>-pz)<sub>3</sub>](THF)<sub>x</sub>} (**7**) and {UI[H<sub>2</sub>B(SImz)<sub>2</sub>]<sub>2</sub>(THF)<sub>x</sub>} (**8**).

## Further work

- Studies involving **1** will not be continued, due to the limited chemical interest of this complex.
- Complete the characterization of **7** and **8** and start the synthesis of heterobimetallic complexes of U and Re.

## References

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4. Giuseppone, N., Collin,\* J., Santos, I., "Enantioselective Diels-Alder Reactions Catalyzed by Samarium Iodo Binaphthoxides", *Tetrahedron Lett.*, in press.

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<sup>1</sup> PRAXIS PhD student.

<sup>2</sup> Laboratoire de Catalyse Moléculaire, UPRESA 8075, ICMO, Université de Paris Sud.

# Synthesis and Characterization of Lanthanide Alkoxides and Aryloxides\*

José Carretas, Joaquim Branco, João Paulo Leal, Joaquim Marçalo,  
Ângela Domingos, António Pires de Matos

## Objectives

The use of the cyclopentadienyl ligand  $C_5R_5^-$  ( $R = H, Me$ ) has been a crucial factor in the development of organolanthanide chemistry. Recently, there has been a growing interest toward the search for alternative ligands, in particular alkoxides and aryloxides. In part this is motivated by their potential use as precursors for pure oxide materials, which have currently considerable importance in the electronics, ceramics, glass and optical materials. In this project we intend to study the reactivity of lanthanide metals toward several alcohols and phenols, using several methods, in order to verify different patterns of reactivity.

## Results

We have been exploring the direct reactions of alcohols (phenols) with lanthanide metals, either using the metal vapour synthesis (MVS) technique (Carretas, J. M. and Pires de Matos, A., *Mater. Chem. Phys.*, 31 (1992) 123) or by dissolution of europium and ytterbium pieces in liquid ammonia (Carretas, J. M., Branco, J. W. A., J. Marçalo, J. C. Marques, N. and Pires de Matos, A., *Journal of alloys and compounds*, 275-277 (1998) 841). In this work we report the synthesis and characterization of lanthanide aryloxides. The reactions of samarium, europium and ytterbium metals with 2,6-di-tert-butylphenol, 1-naphthol, 2-naphthol and 2-aminophenol were studied. In general, the reactions involving samarium were made by MVS whereas the others were realized by dissolution in ammonia. The compounds obtained were characterized by elemental analysis, IR and NMR spectroscopies and x-ray crystallographic studies.

The monomeric complexes  $[Eu(OC_6H_3Bu^t_{2-2,6})_2(thf)_3]$  and  $[Yb(OC_6H_3Bu^t_{2-2,6})_2(CH_3CN)_4]$  were obtained with both the MVS technique and the dissolution in ammonia, using europium and ytterbium metal pieces and 2,6-di-tert-butylphenol as reagents. The above formulations were confirmed by x-ray diffraction.

The reactions of samarium, europium and ytterbium metals with 1-naphthol gave the following compounds ( $R = C_{10}H_7$ ): a samarium (III) aryloxide not fully characterized,  $[Eu_4(OR)_8(thf)_{10}].2thf$  and  $[Yb_2(OR)_6(thf)_2(CH_3CN)_2]$ . The europium and the ytterbium compounds were characterized by x-ray crystallographic studies. We did not yet succeed to obtain single crystals from the products of the reaction with 2-naphthol so no comparison could be made with the 1-naphthol derivatives.

Although the reaction products from the reactions of samarium, europium and ytterbium metals with 2-aminophenol were not completely characterized, these type of compounds have the following formulations ( $R = C_6H_4NH_2$ ):  $Sm(OR)_3$ ,  $Eu(OR)_2$  and  $Yb(OR)_3$ .

## Further Work

The main task of future work will be to complete the characterization of some of the compounds referred above. In the cases where no single crystals can be obtained we will try to use EXAFS to characterize them. Access to a Synchrotron radiation facility was possible through a collaboration already established with researchers from the University of Hamburg. Preliminary results with alkoxides were obtained.

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## Gas Phase Ion Chemistry of Lanthanides and Actinides \*

Joaquim Marçalo, António Pires de Matos, José Manuel Carretas,  
A. G. Marshall,<sup>1</sup> M. A. Freitas<sup>1</sup>, W. J. Evans<sup>2</sup>, S. Gérialdi<sup>3</sup>, N. Marchandé<sup>3</sup>

### Objectives

As a contribution to a better knowledge of the chemistry of the lanthanide (Ln) and actinide (An) series elements, we have been studying the gas phase reactivity with organic molecules of ions of metals, metal oxides, metal oxide clusters, intermetallic and organometallic compounds of these elements. Special attention has been given to the kinetics, mechanisms and energetics of the reactions, that we have tried to correlate with the electronic structure of the ions and to compare with analogous processes occurring in condensed phases. The experimental work has been based on the use of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS), a technique that is specially suited for the study of the chemistry of ion-molecule systems in the gas phase. We have also been exploring, through international collaborations, the use of electrospray ionisation (ESI) coupled to FT-ICR/MS to study different aspects of the gas phase chemistry of Ln and An compounds, taking advantage of the ability of ESI to transfer solution species to the gas phase.

### Results

Gas phase reactions of the rare earth metal cations  $Y^+$  and  $Ln^+$  ( $Ln = La-Lu$ , except Pm) with trimethylorthoformate and of  $Y^+$  and  $Lu^+$  with triethyl and tripropyl orthoformates were studied. The results obtained showed that, in the gas phase, trialkylorthoformates can be good alkoxy group suppliers, and that these reactions could be a route for the gas phase synthesis of neutral rare earth metal alkoxides [1].

As an extension of recent gas-phase ion chemistry experiments on Ln/substituted cyclopentadienyl systems, we performed gas phase reactivity studies of the  $Ln^+$  metal cations ( $Ln = La-Lu$ , except Pm) with cyclooctatetraene, and related the product distributions and the kinetics along the Ln series to the accessibility of reactive excited state electron configurations of the metal ions [2].

Several Ln and An compounds were studied by ESI-FT-ICR/MS and the relative metal-adduct bond energies in  $Eu(HBpz_3)_2$ (adduct) complexes were determined by photodissociation with a  $CO_2$  laser [3].

Studies on speciation of uranium in aqueous solutions using ESI-FT-ICR/MS were continued, namely of  $UO_2(ClO_4)_2$  solutions from which the gas phase species  $UO_2(H_2O)_3ClO_4^+$  could be identified.

### References

1. Marchandé, N., Breton, S., Gérialdi, S., Carretas, J. M., Pires de Matos, A., Marçalo, J., Gas Phase Reactivity of Rare Earth Metal Cations with Trialkylorthoformates: Synthesis of Neutral Rare Earth Alkoxides, *Int. J. Mass Spectrom.*, in press.
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### Further work

We intend to explore the gas phase ion chemistry of the lanthanide and actinide elements in systems which are progressively closer to condensed phases, namely clusters and coordination/organometallic complexes, trying to get more information about the mechanisms of chemical processes occurring in solution and on solid/gas interfaces. The use of ESI will be pursued to access less stable lanthanide and actinide complex species and to study their gas phase chemistry, and also to develop methods for uranium speciation in aqueous phase.

In the case of the actinides, we will also expand the work, until now limited to Th and U, to the more radioactive members of the series, and perform gas phase ion chemistry studies with Np, Pu, Am and if possible Ac, Pa and Cm, trying to gain insight on a potential 5f electron contribution to chemical reactivity.

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<sup>1</sup> National High Magnetic Field Laboratory, Tallahassee, Florida.

<sup>2</sup> Department of Chemistry, University of California-Irvine, Irvine, California.

<sup>3</sup> Groupement de Recherches en Chimie Fine Organique, Université de Nice-Sophia Antipolis, Nice, France.

# Energetics of f- Element Compounds\*

J. P. Leal, H. Raminhos<sup>1</sup>

## Objectives

The main objective of the project is to foster the knowledge of energetics on f-element compounds (both on solid state and in solution). To achieve this goal both lanthanide and actinide, organometallic and intermetallic compounds were studied. Also alkaline and alkaline-earth compounds (alkoxides, phenoxides, tiolates and cyclopentadienyls) will be addressed in order to provide adequate models that allow a deeper understanding and improve our capability of prediction of properties.

## Results

During 1999 the work follows different paths to achieve the stated objectives. The determination of bond enthalpies in Uranium organometallic compounds [ $U_2X\{HB(Me_2-pz)_3\}$ , X = OR, I and Cl] was made by a reaction-solution calorimeter (Fig. 1). The enthalpies of formation of Europium alkoxides [ $Eu(OR)_2$  (R= Me, Et)] were measured using the same technique. To develop a large enough database of alkaline and alkaline-metal compounds that permit to predict, with an accurate precision, enthalpies of formation for new lanthanide alkoxides, some additional enthalpies of formation of Potassium, Rubidium, Caesium, Magnesium and Calcium alkoxides [MOR (M=K, Rb, and Cs; R= Hex; M= Rb; R= Et, M(OR)<sub>2</sub> (M = Mg, Ca; R=Me, Et and Bu)] were determined. Also some alkaline metal tiolates and cyclopentadienyls [MSR (M=Li, Na and K; R= Et and Bu ); MCp (M = Li, Na, K and Tl)] were studied. These values would be used to check if it is possible to use a previously developed model (J. P. Leal, J. A. Martinho Simões, *Organomet. Chem.* **1993**, 460, 131) to estimate the enthalpies of formation of organometallic species.

In addition, the enthalpy of formation of the  $UFe_2$  intermetallic compound was measured by reaction-solution calorimetry. The obtained value is not in perfect agreement with literature values derived by high temperature measurements (M. P. Antony, R. Babu, C. K. Mathews, U. V. Varada Raju, *J. Nuclear Mat.* **1995**, 223, 213). Some effort is being made to understand the observed discrepancy. It is believed that a clear insight on this, could clarify the role of the f-element on this kind of compounds.

Finally, some development of equipment was made (calibration automated reaction-solution calorimeter) that will lead to easier and more reliable measurements on future.

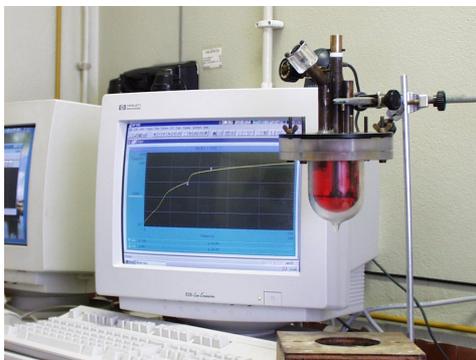


Figure 1 – Reaction-solution calorimeter cell

## References

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## Further work

In the future we intend to make a strong effort on lanthanide and actinide compounds (both organometallics and intermetallics). Some new ligands will be explored for uranium organometallic compounds and the metal alkoxide study will be enlarged to new lanthanide metals. We will keep also some interest on alkaline and earth-alkaline compounds because they show to be very good models to understand more complicated compounds, in this particular case f-elements ones.

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<sup>1</sup> Graduate student, Faculdade de Ciências da Universidade de Lisboa.

## Chemical Behaviour in the Heterogeneous Phase of Compounds of the *f*-Elements\*

António Pires de Matos, Carlos Henriques<sup>1</sup>, Helena Vasques<sup>2</sup>, João Silva<sup>2</sup>, Joaquim Branco, José M. Lopes<sup>1</sup>, Noémia Marques, Teresa Almeida Gasche

### Objectives

The main goal of this project is to study different compounds containing lanthanides and actinides in order to understand the influence of the electron configuration and the variation in size of the *f* block elements, in particular across the lanthanide series, in the chemical behaviour of those compounds. The chemical behaviour is probed through the reactivity of these compounds with organic substrates, in heterogeneous phase.

### Results

The work here reported include reactivity studies of intermetallic compounds containing a *d* element and a *f* element and modified zeolites by impregnation of rare earth nitrates.

The behaviour of LnNi (Ln=Pr, Gd, Tm) and UNi<sub>2</sub> as catalysts for the hydrogenation of isoprene (2-methyl-1,3-butadiene) was studied. Comparison was made with nickel metal and a commercial catalyst (5%Pt/Al<sub>2</sub>O<sub>3</sub>). For the Pd and Pt catalysts the products of reaction are the three methylbutene isomers: 2-methyl-1-butene, 3-methyl-1-butene and 2-methyl-2-butene, in an approximate ratio 1:1:2. With the compounds studied a different selectivity was observed and all of them present a better activity than the nickel metal catalyst. Within the lanthanide compounds TmNi presents the best activity. Surprisingly the uranium catalyst is the most active in the hydrogenation of isoprene.

Preliminary studies (J. Branco, A. Gonçalves, A. Pires de Matos, Communication, "4<sup>o</sup> Encontro da Divisão de Catálise", SPQ, 1999, Aveiro) were made on the hydrogenation of toluene with the same intermetallic compounds. The only reaction product observed was methylcyclohexane. No difference in activity for this reaction was observed among the lanthanide intermetallics and all of them are less active than nickel. Again UNi<sub>2</sub> displays a better activity than nickel.

Studies of the basic-acid properties of the NaX zeolite modified by impregnation with several rare earth nitrates were made. By further thermal treatment rare earth oxides were obtained deposited in the microporous structure of the zeolite. The modified zeolite was tested in the gas phase isomerization of the butene-1 double bond position and in the cracking of n-heptane. Concerning the isomerization reaction it was observed that the initial catalytic activity did not change significantly with the lanthanides tested with exception of YbNaX which showed a very marked increase. Small variations in the acid-basic character of the impregnated zeolite depended on temperature and at 250°C the basic character seems to decrease slightly along the series, except for YbNaX which displays a basic character. In the cracking of n-heptane, the main effect of the modification of the NaX zeolite by impregnation of rare earth nitrates is a loss of activity for Ce, Nd, Eu, Dy, Er and an increase of activity for Yb.

### Further Work

Concerning the different behaviour of the intermetallics, all the lanthanides in the series (except promethium) should be tested. XPS surface studies will be made to compare some of the catalysts. In view of the interesting results obtained for UNi<sub>2</sub> we are planning to test also ThNi<sub>2</sub>. In general further physical-chemical characterisation of the compounds is needed.

In order to obtain catalysts with a possible commercial interest we intend to impregnate alumina with ammonia solutions of europium and ytterbium metals. By this process we expect to achieve very large surface areas.

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<sup>1</sup> Instituto Superior Técnico.

<sup>2</sup> Instituto Superior de Engenharia de Lisboa.

# Rhenium Complexes with Nitrogen Donor Ligands\*

Raquel Garcia<sup>1</sup>, António Paulo, Ângela Domingos, Isabel Santos

## Objectives

There has been a renewed interest on the nature and chemical behaviour of rhenium oxides due to their potential relevance in several stoichiometric and catalytic transformations. In the major part of these transformations it is well accepted that the electronic and coordinative saturation of the metal center plays a crucial role, and this is controlled by using ligands with different stereochemical and electronic properties. In this project, we are studying the chemistry of rhenium oxocomplexes (Re(V) and Re(VII)) stabilized by polypyrazolylborates with different steric and electronic properties.

## Results

The coordination chemistry of rhenium with dihydrobis(pyrazolyl)borates and with tetrakis(pyrazolyl)borate continued to be explored during this year.<sup>1-4</sup> With the ligands  $[H_2B(pz^*)_2]^-$  ( $pz^*=pz$ , 3,5-Me<sub>2</sub>pz) polyhydrides or dioxocomplexes were synthesized, depending on the reaction conditions and on the electronic properties of the Re(V) starting materials.<sup>1,2</sup> In the case of  $[B(pz)_4]^-$ , we have continued to study the reactivity of Re(V) oxocomplexes.<sup>3,4</sup> The reactivity of *trans*- $[ReO_2\{\kappa^2-B(pz)_4\}(L)_2]$  was evaluated towards ClSiMe<sub>3</sub>, leading to  $[ReO(OSiMe_3)\{\kappa^2-B(pz)_4\}(L)_2]Cl$  (L= py (**1**), 4-NMe<sub>2</sub>py (**2**), 1-Meimz (**3**)) and  $[ReO(OSiMe_3)\{\kappa^2-B(pz)_4\}(dmpe)]Cl$  (**4**), respectively. Anions *trans*- $[ReO_2\{\kappa^2-H_2B(pz)_2\}_2]^-$  ( $pz^*=pz$  (**5**), 3,5-Me<sub>2</sub>pz (**6**)) also display a notorious nucleophilic character and their treatment with trimethylsilyl chloride gave quantitatively new oxo-siloxyde derivatives:  $[ReO(OSiMe_3)\{\kappa^2-H_2B(pz^*)_2\}_2]$  ( $pz^*=pz$  (**7**), 3,5-Me<sub>2</sub>pz (**8**)). In solution, cations **1-4** are unstable species and those with unidentate nitrogen ligands (**1-3**) tend to transform into the neutral derivatives  $[ReO(Cl)(OSiMe_3)\{\kappa^2-B(pz)_4\}(L)]$  (L= py (**9**), 4-NMe<sub>2</sub>py (**10**), 1-Meimz (**11**)). In contrast, **7** and **8** can be kept in solution for long periods of time without detectable decomposition. Compounds **1-11** have been characterized by the usual spectroscopic techniques, including X-ray crystallographic analysis for some of them.

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## Further work

- Screening of the catalytic activity of the already available rhenium oxocomplexes stabilized with  $[B(pz)_4]^-$ , namely in aldehyde olefination. This work will be done in collaboration with ITQB<sup>2</sup> which participates in this project.
- Synthesis and characterization of five-coordinated Re(VII) trioxides with ligands of the type  $[R_2B(pz^*)_2]^-$  (R = alkyl, aryl) and evaluation of their reactivity, namely in oxygen transfer reactions.

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<sup>1</sup> PRAXIS Graduate student.

<sup>2</sup> Grupo de Química Organometálica e Catálise, ITQB, Quinta do Marquês, Oeiras.

# Re and Tc Complexes with Phosphine Containing Ligands for the Labelling of Biomolecules

João D. G. Correia<sup>1</sup>, Ângela Domingos, Isabel Santos

## Objectives

This project is being developed in the context of the COST Action B12 "Radiotracers for *in vivo* Assessment of Biological Functions". New heterofunctionalized phosphine ligands are being developed, and their utility as chelating agents for the stabilization of the  $[M=O]^{3+}$ ,  $[M(CO)_3]^+$ , and  $[M\equiv N]^{2+}$  (M=Re, Tc) cores is being studied. The main goal of the work is to use the isolated complexes for the labeling ( $^{99m}\text{Tc}$ ,  $^{186/188}\text{Re}$ ) of biomolecules available within the COST B12 action.

## Results

New heterofunctionalized phosphine ligands, with the donor atom sets  $PN_2$ ,  $PNO$  and  $PNS$ , have been synthesized and fully characterized (J.D.G. Correia, I. Santos, manuscript submitted). The capacity of these ligands to stabilize Re(V) in the form of the well known  $[Re=O]^{3+}$  moiety was studied. The  $PN_2$  and  $PNO$  systems coordinate to the metal as neutral and bidentate, leading to complexes of the type  $[Re(O)Cl_3(\eta^2-L)]$  ( $L=H_2PNO$  (1),  $H_3PN_2$  (2)) (J.D.G. Correia, I. Santos, manuscript submitted). However, choosing properly the experimental conditions, the  $PNO$  and  $PNS$  systems can also coordinate to the metal as tridentate and dianionic. Several complexes were isolated and fully characterized:  $[Re(O)(\eta^3-PNO)(\eta^2-DPPBA)]$  (3) or  $[Re(O)(\eta^3-PNO)(\eta^2-H_2PNO)Cl]$  (4),  $[Re(O)(\eta^3-PNO)(\eta^1-SR)]$  (5),  $[Re(O)(\eta^3-PNS)(\eta^1-HPNS)]$  (6) and  $[Re(O)(\eta^3-PNS)(\eta^1-SR)]$  (7) (J.D.G. Correia, I. Santos, manuscript in preparation). On the other side, with the  $PN_2$  system the only complex isolated was  $[Re(O)(\eta^3-H_2PN_2)(OMe)(Cl)]$  (8), where the ligand acts as tridentate and monoanionic. Complexes 5 and 7 (R = alkyl, aryl) are obtained in relatively high yield in a *one pot reaction*. These results indicate that these systems can be used at the non carrier added (n.c.a.) level for conjugation with receptor binding molecules. The preparation of these complexes uses the so called "3+1" approach, developed originally by Johannsen et al.. As shown by other research groups, this approach is relatively flexible, but these five-coordinate species are sometimes reactive, not only because they still have an available coordination site, but also because the SR groups are easily displaced *in vivo*. To prevent some of these disadvantages, the six-coordinate  $[Re(O)(\eta^3-PNO)(\eta^2-DPPBA)]$  (3) (3+2 approach) is also promising since the coordination of the biomolecule can be done through the bidentate and monoanionic co-ligand, DPPBA.

## References

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## Further work

- Complexes 3, 5 and 7 will be prepared at the *n.c.a.* level. The stability *in vitro* and *in vivo* of the species will be evaluated. The lipophilicity of  $PNO$  and  $PNS$  type ligands will be modified and their suitability for complexes of the type 3, 5 and 7 tested.
- The utility of these ligands, in organic and aqueous media, for stabilizing complexes with the core  $[M(CO)_3]^+$  will be evaluated.

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<sup>1</sup> PRAXIS Post-Doctoral.

## Organometallic Re and Tc Complexes for the Labelling of Biomolecules

Raquel Garcia<sup>1</sup>, António Paulo, Ângela Domingos and Isabel Santos

### Objectives

This project is being developed in the context of the COST Action B12 "Radiotracers for in vivo Assessment of Biological Functions". Boron containing ligands, monoanionic and tri or bidentate, of the type ( $R_2BR'_2$ ) and ( $RBR'_3$ ) ( $R'$ =sulphur or nitrogen donor groups) are being evaluated for the stabilization of complexes with the core  $[M(CO)_3]^+$  ( $M=Re, Tc$ ). The main goal is to develop model complexes suitable for the labeling ( $^{99m}Tc, ^{186/188}Re$ ) of biomolecules available within the COST B12 Action. The biologically active molecule will be linked to derivatized tridentate ligands ( $RBR'_3$ ) or to a monodentate co-ligand ( $L'$ ) when the anchor is bidentate ( $R_2BR'_2$ ) (2+1 approach).

### Results

Reaction of  $[ReBr(CO)_5]$  or  $(NEt_4)_2[ReBr_3(CO)_3]$  with  $Na[HB(Simz)_3]$  or  $Na[H_2B(Simz)_2]$ , in organic or aqueous medium, gave  $[Re\{\eta^3-HB(Simz)_3(CO)_3\}]$  (**1**) and  $[Re\{\eta^3-H(\mu-H)B(Simz)_2(CO)_3\}]$  (**2**), respectively. In complex **1**, the Re-H-B agostic interaction can be cleaved by nitrogen, phosphorous or carbon donors, leading to complexes of the type  $[Re\{\eta^2-H_2B(Simz)_2(L)(CO)_3\}]$  ( $L=PPh_3$  (**3**),  $tBuNC$  (**4**), 4-NMe<sub>2</sub>py (**5**), imzH (**6**), histamine (**7**)). Compounds **1-7** were characterized by IR,  $^1H$ ,  $^{13}C$  and  $^{11}B$  NMR spectroscopies and, in some cases, by X-ray crystallographic analysis. The mixed complexes (**3-7**) can be seen as valuable models for the development of  $^{99m}Tc$  and  $^{186/188}Re$  specific radiopharmaceuticals based on the [2+1] approach. This is valid, in particular, for complexes **6** and **7**, since imidazole is present in histidine and histamine residues of many relevant biologically active molecules.

### Further work

- The basic knowledge developed with Re will be extended to  $^{99}Tc$  and to the n.c.a. level.
- The most promising compounds will be used for the labelling of biomolecules.

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<sup>1</sup> PRAXIS Graduate student.

## Chemical Identification of $^{99m}\text{Tc}$ -Peptide Complexes

Célia Fernandes,<sup>1</sup> Maria Paula Campello, Isabel Santos

### Objectives

Previous studies on  $^{99m}\text{Tc}$  oxocomplexes have shown that it was possible to label small peptides functionalized with a sulphur donor group, using the so called “3+1” approach (Célia Fernandes, Master Thesis, Universidade de Lisboa, 1999)<sup>1</sup>. From the dipetides studied only three were selected for biodistribution studies, due to the yield of labelling and radiochemical purity. For these  $^{99m}\text{Tc}$ -dipeptides no specific uptake in organs or tissues was found but a different biological behaviour was observed, in terms of blood clearance and urinary versus hepatobiliary excretion, that, apparently, can not be directly related with the lipophilicity of the species. This work was done in order to establish the chemical structure of these two compounds.

### Results

As above referred the synthesis of the  $^{99m}\text{Tc}$ -dipeptides was done using the so called “3+1” approach, introduced by Johannsen *et al.* The tridentate ligand is the commercially available 2-mercaptoethyl sulphide and the co-ligands were Gly-Gly, AlaGly and PheGly, previously functionalized with a thiol group. The previously described,  $[\text{ReOLCl}]$  (**1**) (L= 2-mercaptoethyl sulphide) has been synthesized by reacting  $[\text{ReOCl}_4]^-$  with 2-mercaptoethyl sulphide in methanol/dichloromethane. Complex **1** reacts with HS-Gly-Gly, in acetonitrile in the 1:1 molar ratio in the presence of  $\text{NEt}_3$ , leading to a species that by IR and  $^1\text{H}$  NMR spectroscopies was formulated as  $[\text{ReOL}(\text{S-Gly-Gly})]$  (L= 2-mercaptoethyl sulphide) (**2**). The X-ray structural analysis of this compound and their characterization by HPLC are underway.

### Further work

This work intended to introduce Célia Fernandes on the chemical characterization of the  $^{99m}\text{Tc}$ -peptides, that she previously prepared.<sup>1</sup> However, this work will not be carried out with the above referred chelate ligand. Célia Fernandes will follow with her PhD research work just submitted to CD/ITN

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<sup>1</sup> Célia Fernandes joined the group on September 1999, after her Master thesis, to initiate a PhD work.

