

# Inorganic and Organometallic Chemistry

## Introduction

The activities of the group comprise the synthesis, characterization and reactivity studies of inorganic, organometallic and intermetallic compounds of **actinides and lanthanides** and gas phase ion-molecule reactions with the same elements, 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, by homogeneous and heterogeneous catalytic studies and also by surface techniques. Due to the type of chemistry we are dealing with, and 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, we started by extending our research 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. Experience on  $^{99m}\text{Tc}$  radiochemistry exists already in the Radiopharmacy Group. Having rhenium a quite rich chemistry, research has also been directed to the development of compounds that could be used as intermediates in reactions useful to organic synthesis.

During 1998 studies on the chemistry of uranium(III) and the lanthanides continued. Several polypyrazolyl borate ligands with different electronic and steric properties have been evaluated. Relevant results are the stabilization of the first monodihydrobis(pyrazolyl)borate uranium(III) compound,  $[\text{U}\{\text{H}_2\text{B}(3^t\text{Bu}, 5\text{Me-pz})_2\}_2(\text{THF})_2]$ , the stabilization of a benzophenone ketyl complex,  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\eta^1\text{-OCPh}_2)$  and a unprecedented transformation of a hydrotris(pyrazolyl)borate ligand at a metal center by the synthesis and rearrangement of the first mixed Tp/Cp lanthanide complex,  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{Cp})$ . The bond dissociation enthalpies in some uranium(IV) compounds have been measured.

Research on coordination chemistry of rhenium chemistry has continued using mainly polydentate ligands. Using the chelating and reducing properties of the polypyrazolylborates a new route has been found to enter into rhenium(III) and rhenium(V) hydrides. It has been also shown that polydentate oxygen donor ligands are able to stabilize Re(V) nitrido complexes. New ligands were made in order to use the mixed-ligand approach (the so called  $3+1$ ) for the development of new radiopharmaceuticals. Some of these ligands started to be evaluated towards different rhenium starting complexes in order to specifically target biological “locks” (e.g. receptors).

During 1998 the setup of experimental conditions to study the catalytic properties of f element compounds continued. Preliminary studies included the use of uranium and thorium compounds as catalytic precursors in the polymerization of ethylene, oxidative carbonylation of methanol by  $\text{CO}_2$  using lanthanide compounds as catalysts, the hydrogenation of toluene using U/Ni and Ln/Ni intermetallic compounds and the study of the base and acid properties of zeolites impregnated with Ln compounds. Surface studies on the adsorption of small molecules on intermetallic compounds were also continued.

Gas phase chemistry studies were continued using the existing Fourier Transform Ion Cyclotron Resonance Spectrometer. An upgrade of the equipment was made with a new data station. Gas phase studies included reactions of lanthanide and actinide ions with ferrocene, the reactivity of some transition metal oxide cluster anions towards methanol and the gas phase synthesis of neutral rare earth metal alkoxides. Having in mind the implementation of the electrospray ionization in our equipment, some experiments using this type of ionization were made in the NHMFL, Florida, using several uranium and lanthanide compounds.

## Research Team

Researchers –	10	( 9 PhD + 1 research assistant)
Post-Doctoral -	2	
Research Students –	2	(PhD Students)
Technicians –	2	

## Publications

Journals –	7	and 5 in press
Proceedings –	1	and 8 in press
Conf. Commun.:	17	
PhD Theses -	2	

	10 <sup>3</sup> PTE
<b>Expenditure:</b>	<b>31 109</b>
Missions:	672
Other Expenses:	8 869
Hardware & Software:	129
Other Equipment:	21 439

		10 <sup>3</sup> PTE
<b>Funding:</b>		<b>30 789</b>
OE/ITN	OF	4 302
External	1997	1 234 <sup>(1)</sup>
Projects:	1998	24 359
Others		894

<sup>(1)</sup> Funding not used in 1997

**f-ELEMENT CHEMISTRY****Synthesis and Structure of U(III) Complexes with Dihydrobis(Pyrazolyl)Borates**

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**Abstract**

The synthesis of the U(III) complexes  $[U\{H_2B(3^tBu,5Me-pz)_2\}I_2(THF)_2]$  (**1**),  $[U\{H_2B(3^tBu,5Me-pz)_2\}I_2(OPPh_3)_2]$  (**2**) and  $[U\{Ph_2B(pz)_2\}_3]$  (**3**) are reported. The molecular structures have been determined by single crystal X-ray diffraction: **1** is monomeric and crystallizes in the orthorhombic space group  $P2_12_12_1$  with cell parameters  $a = 10.386(1)$ ,  $b = 13.115(1)$ ,  $c = 26.556(2)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 3617.3(5)$  Å<sup>3</sup>,  $Z = 4$ ; **2** is monomeric and crystallizes in the monoclinic space group  $P2_1/n$  with cell parameters  $a = 17.950(3)$ ,  $b = 19.866(3)$ ,  $c = 18.793(2)$  Å,  $\beta = 96.894(12)$ ,  $V = 6653(2)$  Å<sup>3</sup>,  $Z = 4$ ; **3** is monomeric and crystallizes in the triclinic space group  $P1$  with cell parameters  $a = 13.565(1)$ ,  $b = 15.715(2)$ ,  $c = 15.929(2)$  Å,  $\alpha = 118.957(9)$ ,  $\beta = 92.650(11)$ ,  $\gamma = 97.36(2)$ ,  $V = 2923.7(6)$  Å<sup>3</sup>,  $Z = 2$ . In complexes **1** and **2** the U(III) is seven coordinated by the two pyrazolyl nitrogens, the two iodides and two oxygen atoms of the neutral ligands and by an agostic B-H...U interaction. In **3** the uranium is six-coordinated by the nitrogen atoms of the chelating  $[Ph_2B(pz)_2]$  ligands which are arranged in a trigonal prismatic geometry around the uranium center.

Submitted to *J. Chem. Soc., Dalton Trans.*

**Trapping of Anionic Organic Radical by (TpMe<sub>2</sub>)<sub>2</sub>Sm: Solid State Structure and Solution Behavior of a Sm(III)-Benzophenone Ketyl Complex**

*I. Lopes,<sup>†</sup> G.Y. Lin,<sup>‡</sup> A. Domingos,<sup>†</sup> N. Marques,<sup>\*†</sup> and J. Takats<sup>\*</sup>*

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**Abstract**

Addition of stoichiometric amount of benzophenone to a toluene slurry of  $Sm(Tp^{Me_2})_2$  (**1**) forms the stable and structurally characterizable benzophenone ketyl complex,  $Sm(Tp^{Me_2})_2(\eta^1-OCPh_2)$  (**2**) in good yield. The samarium centre is seven-coordinate with two tridentate ligands staggered with respect to each other and the benzophenone oxygen occupying the seventh site. The steric protection provided by the two- $Tp^{Me_2}$  ligands prevents pinacol formation by C-C coupling and is responsible for the solution rigid structure of complex **2**.

submitted to *Inorg. Chem.*

## Unprecedented Transformation of a Hydrotris(pyrazolyl)borate Ligand at a Metal Center: Synthesis and Rearrangement of the First Mixed Tp / Cp Lanthanide Complex, Sm(TpMe<sub>2</sub>)<sub>2</sub>(Cp)

*I. Lopes,<sup>†</sup> G.Y. Lin,<sup>‡</sup> A. Domingos,<sup>†</sup> N. Marques,<sup>\*†</sup> and J. Takats<sup>\*‡</sup>*

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### Abstract

The reaction of Sm( $\eta^3$ -TpMe<sub>2</sub>)<sub>2</sub> (**1**) (TpMe<sub>2</sub> = HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>) with the stoichiometric amount of TICp affords Sm( $\eta^3$ -TpMe<sub>2</sub>)( $\eta^2$ -TpMe<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) (**2**). Thermolysis of **2** proceeds via hydrogen abstraction from the cyclopentadienyl ligand to give Sm[HB(3,5-Me<sub>2</sub>pz)<sub>2</sub>( $\eta^1$ : $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)]( $\eta^3$ -TpMe<sub>2</sub>)(**3**) and Sm( $\eta^3$ -TpMe<sub>2</sub>)<sub>2</sub>( $\eta^2$ -3,5-Me<sub>2</sub>pz) (**4**). The compounds were characterized by conventional methods including X-ray diffraction.

submitted to *J. Am. Chem. Soc.*

## Synthesis and Structural Comparison of a Series of Divalent Ln(TpR,R')<sub>2</sub> (Ln=Sm, Eu, Yb) and Trivalent Sm(TpMe<sub>2</sub>)<sub>2</sub>X (X = F, Cl, Br, I, BPh<sub>4</sub>) Complexes

*XingWang Zhang,<sup>†</sup> Graham H. Maunder,<sup>#</sup> Sung Ying Liu,<sup>#</sup> Todd A. Eberspacher,<sup>‡</sup> Angela Domingos,<sup>§</sup> Noémia Marques,<sup>§</sup> Victor W. Day<sup>\*‡</sup> Andrea Sella<sup>\*,#</sup> and Josef Takats<sup>\*†</sup>*

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### Abstract

Reaction of LnI<sub>2</sub> (Ln = Sm, Yb) with two equivalents of NaTpMe<sub>2</sub> or reduction of Eu(TpMe<sub>2</sub>)OTf gives good yields of the highly insoluble homoleptic Ln(II) complexes, Ln(TpMe<sub>2</sub>)<sub>2</sub> (Ln = Sm (**1a**), Yb (**2a**), Eu (**3a**)). Use of the additionally 4-ethyl substituted TpMe<sub>2,4-Et</sub> ligand produces the analogous, but soluble Ln(TpMe<sub>2,4-Et</sub>)<sub>2</sub> (**1-3b**) complexes. Soluble compounds are also obtained with the Tp<sup>Ph</sup> and Tp<sup>Tm</sup> ligands, Ln(Tp<sup>Ph</sup>)<sub>2</sub> (Ln = Sm, **1c**; Yb, **2c**) and Ln(Tp<sup>Tm</sup>)<sub>2</sub> (Ln = Sm, **1d**; Yb, **2d**). To provide benchmark parameters for structural comparison the series of Sm(TpMe<sub>2</sub>)<sub>2</sub>X complexes (X = F, **1e**; Cl, **1f**; Br, **1g**; I, **1h**; BPh<sub>4</sub>, **1i**) were prepared either via oxidation of the Sm(TpMe<sub>2</sub>)<sub>2</sub> or salt metathesis from SmX<sub>3</sub> (X = Cl, Br). The solid state structures of **1-3a**, **1-2c** and **1e-1i** were determined by single crystal X-ray diffraction. The homoleptic bis-Tp complexes are all six-coordinate with trigonal antiprismatic geometries, planes of the  $\kappa^3$ -Tp ligands are parallel to one another. In the series of Sm(TpMe<sub>2</sub>)<sub>2</sub>X complexes the structure changes from seven-coordinate molecular compounds, with intact Ln-X bonds, for X = F, Cl, to six-coordinate ionic structures [Sm(TpMe<sub>2</sub>)<sub>2</sub>]<sup>+</sup>X<sup>-</sup> (X = I, BPh<sub>4</sub>), the bromide compound exhibits schizophrenic behavior. The

dependence of the structures on the size of X is understandable and provides an empirical definition of the size of the cleft that the "Sm(III)(Tp<sup>Me2</sup>)<sub>2</sub>" fragment can make available to coordinate reactive one-electron ligands and/or radical anionic species.

submitted to *Inorg.Chem.*

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## Current Work

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### Solid State Structure and Solution Behaviour of Eight-Coordinate Sm(III) Poly(pyrazolyl)borate Compounds

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<sup>‡</sup>*Christopher Ingold Laboratories, Dept. of Chemistry; UCL, 20 Gordon Street, London, WC1H 0AJ, U.K.*

Reaction of two equivalents of Sm(Tp<sup>Me2</sup>)<sub>2</sub> with 2,2'-dipyridyl disulfide or 2,2'-dipyridyl diselenide give good yields of Sm(Tp<sup>Me2</sup>)<sub>2</sub>X compounds (X=2-SC<sub>5</sub>H<sub>4</sub> (**1**), 2-SeC<sub>5</sub>H<sub>4</sub>N (**2**)). Salt metathesis of Sm(Tp<sup>Me2</sup>)<sub>2</sub>Cl with the sodium salt of the hydroxypyridine affords Sm(Tp<sup>Me2</sup>)<sub>2</sub>(2-OC<sub>5</sub>H<sub>4</sub>N) (**3**). [Sm(Tp<sup>Me2</sup>)<sub>2</sub>](S<sub>2</sub>CNEt<sub>2</sub>) (**4**) has been isolated from reaction of {Et<sub>2</sub>NC(S)S}<sub>2</sub> with Sm(Tp<sup>Me2</sup>)<sub>2</sub>. The solid state structures of **1-4** have been investigated by single-crystal X-ray diffraction analysis and revealed that the metal centres are eight-coordinate, with the samarium atoms bound in tridentate fashion to two pyrazolylborate ligands and in bidentate fashion to the thio-, seleno-, oxo-pyridine or dithiocarbamate ligands.

*manuscript in preparation*

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### Ytterbium (II) Hydrotris(mesitylpyrazolyl)borate Compounds

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Reaction of YbI<sub>2</sub> with one equivalent of Tl[HB(3-Mespz)<sub>3</sub>] or Tl[HB(3-Mespz)<sub>2</sub>(5-Mespz)], at room temperature, gives good yields of YbI[HB(3-Mespz)<sub>2</sub>(5-Mespz)](THF)<sub>2</sub> (**1**). The solid state structure of **1** was determined by single crystal X-ray diffraction. The three nitrogen atoms of the chelating [HB(3-Mespz)<sub>3</sub>] ligand, the iodine atom and the two oxygen atoms of the THF molecules are arranged in an octahedral geometry. Reaction of YbI<sub>2</sub> with one equivalent of Tl[HB(3-Mespz)<sub>3</sub>], at 0 °C, affords YbI[HB(3-Mespz)<sub>3</sub>](THF)<sub>2</sub> (**2**). Attempts to recrystallize **2** from THF, diethyl ether and toluene were unsuccessful. In THF the compound isomerizes readily to give **1**. In diethyl ether **2** gives [Yb(μ-I){HB(3-Mespz)<sub>2</sub>(5-Mespz)}(THF)]<sub>2</sub> (**3**) and in toluene crystals of [Yb(μ-I){HB(3-Mespz)<sub>2</sub>(5-Mespz)}(MespzH)]<sub>2</sub> (**4**) were obtained. The compounds were characterized by means of X-ray diffraction analysis. **3** and **4** were also obtained when **1** was recrystallized from the same solvents. **1** reacts with K[CH(SiMe<sub>3</sub>)<sub>2</sub>] to yield Yb[CH(SiMe<sub>3</sub>)<sub>2</sub>][HB(3-Mespz)<sub>2</sub>(5-Mespz)]

(5). Hydrogenolysis of **5** yields  $\text{YbH}[\text{HB}(\text{3-Mespz})_2(\text{5-Mespz})]$  (**6**). Crystals of **5** and **6** suitable for X-ray diffraction analysis could not be obtained due to the instability of the compounds. In order to get more stable compounds the synthesis of the new ligands  $\text{Ti}[\text{HB}(\text{3-Mes},\text{5-Mepz})_3]$  and  $\text{Ti}[\text{HB}(\text{3-Mes},\text{5-Mepz})_2(\text{5-Mes},\text{3-Mespz})]$  has been achieved. Reaction of  $\text{YbI}_2$  with one equivalent of  $\text{Ti}[\text{HB}(\text{3-Mes},\text{5-Mepz})_2(\text{5-Mes},\text{3-Mespz})]$  yielded  $\text{YbI}[\text{HB}(\text{3-Mes},\text{5-Mepz})_2(\text{5-Mes},\text{3-Mepz})](\text{THF})_2$  (**7**). Derivative chemistry of **7** proved to be easier than with **1**.

## Synthesis and Characterization of Thorium and Uranium Tetraphenylimidophosphinates Complexes: The Crystal and Molecular Structures of $\text{Th}(\text{tpip})_4$ , $\text{U}(\text{tpip})_4$ and $\text{UCl}(\text{tpip})_3$

A. Carvalho,<sup>†</sup> A. Domingos,<sup>†</sup> R. Cea-Olivares,<sup>§</sup> N. Marques,<sup>†</sup> A. Pires de Matos<sup>†</sup>

<sup>†</sup>Departamento de Química, ITN, Estrada Nacional 10, P-2686 Sacavém Codex, Portugal

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The compound  $\text{Th}(\text{tpip})_4$  (**1**), tetra(tetraphenylimidophosphinato)thorium, was obtained from  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  and Ktpip in aqueous medium. Recrystallization of **1** from THF solution yielded crystals suitable for X-ray diffraction analysis. The metal centre is eight-coordinate, with the thorium atom bound in bidentate fashion through the oxygen atoms to four imidophosphinate ligands. The metal coordination geometry is best described as being square antiprismatic (SAP). The analogous uranium compound,  $\text{U}(\text{tpip})_4$  (**2**), has been prepared by reacting  $\text{UCl}_4$  with Ktpip in the stoichiometric ratio 1:4, in THF solution. X-ray diffraction analysis showed that compounds **1** and **2** were isostructural. Uranium tetrachloride reacts with 3 equivalents of Ktpip in THF affording  $\text{UCl}(\text{tpip})_3$  (**3**). The crystal and molecular structure of **3** has been determined and showed that **3** is monomeric with the six oxygen of the three chelating ligands and the chlorine atom arranged in a pentagonal bipyramidal geometry around the metal. The analogous thorium compound could not be obtained. Due to the larger ionic radius of the Th ion, only compound **1** was obtained. The compounds were also characterized by infra-red and  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopies.

*manuscript in preparation*

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## Synthesis, Characterization and Fluorescence Studies of Bis(Hydrotris(pyrazolyl)borate) Europium Complexes

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Reaction of  $\text{EuI}_2$  with two equivalents of  $\text{KHBpz}_3$  gives good yield of  $\text{Eu}(\text{HBpz}_3)_2(\text{THF})_2$ . The THF molecules can be readily replaced by other donor ligands. A series of compounds  $\text{Eu}(\text{HBpz}_3)_2\text{L}_2$  (L=triphenylphosphineoxide (TPPO), diphenylsulfoxide (DPSO), bis(pentamethylene)urea ( $\text{OC}(\text{NC}_5\text{H}_5)_2$ ), azocyclonane ( $\text{C}(\text{O})(\text{NH}(\text{CH}_2)_7$ ) and  $\epsilon$ -caprolactama ( $\text{OCO}(\text{CH}_2)_5$ ) have been synthesized and characterized by elemental analysis and IR spectroscopy. Complexes have been further characterized by X-ray diffraction analysis. The fluorescence properties of the compounds are being investigated.

## Dimethyl Carbonate Synthesis via Oxidative Carbonylation of Methanol by $\text{CO}_2$ using Lanthanide Alkoxides and Iodides as Catalysts

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There is a growing interest in the direct conversion of carbon dioxide to more valuable products. Carbon dioxide is a cheap material and can be transported and handled without problems. Our interest concerns the use of  $\text{CO}_2$  as a functionalization agent, namely for the synthesis of carbonates. Dimethylcarbonate (DMC) is an important agent for carbonylation (it can replace phosgene in many industrial applications) and methylation in fine chemistry. Nevertheless, until now there are no relevant results concerning the catalytic production of carbonates via oxidative carbonylation of methanol by  $\text{CO}_2$ . Results reported in the literature indicate that this reaction gives less than 4 TON (turnover number) when dialkyl tin dialkoxides, tin or titanium tetraalkoxides, a mixture of palladium (II) chloride and copper acetate, and mixtures of thallium hydroxide and alkali metal iodides are used as catalysts.

We tested the lanthanide alkoxides  $[\text{Eu}(\text{OMe})_2]$ ,  $[\text{Eu}(\text{OC}_6\text{H}_4\text{-2-OCH}_3)_2]$ ,  $[\text{Yb}(\text{OC}_6\text{H}_4\text{-2-OCH}_3)_3]$ ,  $[\text{Ln}(\text{OC}_6\text{H}_2\text{N}(\text{CH}_3)_2\text{-2-Me-4,6})_3]$  (Ln=Eu, Yb), and the lanthanide iodides,  $\text{EuI}_2 \cdot 2\text{thf}$  and  $\text{SmI}_2 \cdot 2\text{thf}$ , as precursors for the catalytic carboxylation of methanol by  $\text{CO}_2$ . The iodide compounds only gives rise to the formation of dimethyl carbonate in stoichiometric amounts (TON=1 for the samarium compound), but  $[\text{Eu}(\text{OC}_6\text{H}_4\text{-2-OCH}_3)_2]$  catalyses the reaction with a TON=11. The results of this study indicate that a good activity for the synthesis of DMC using lanthanide alkoxides as catalysts can be achieved.

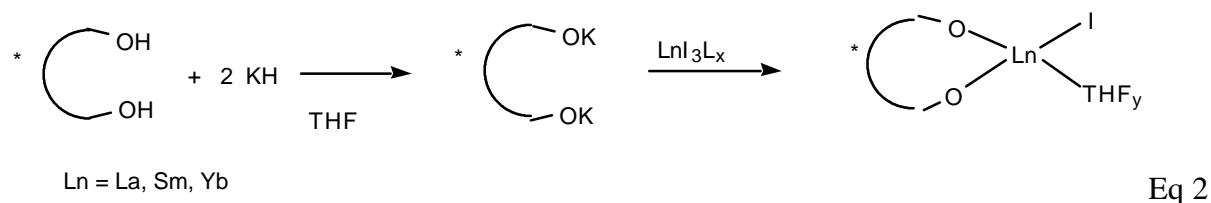
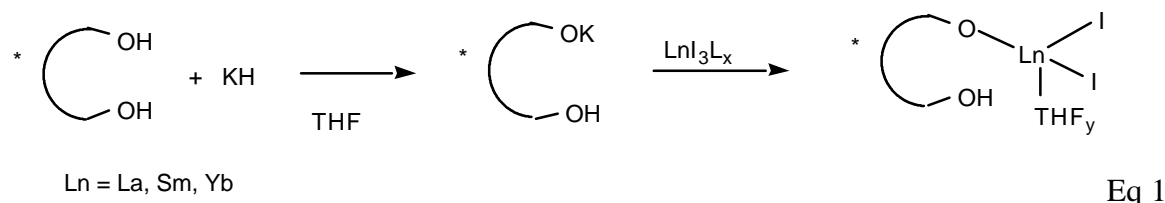
## Synthesis and Characterization of Asymmetric Lanthanide Complexes

Nicolas Giuseppone,<sup>b</sup> Jacqueline Collin,<sup>b\*</sup> Ângela Domingos,<sup>a</sup> Isabel Santos<sup>a\*</sup>

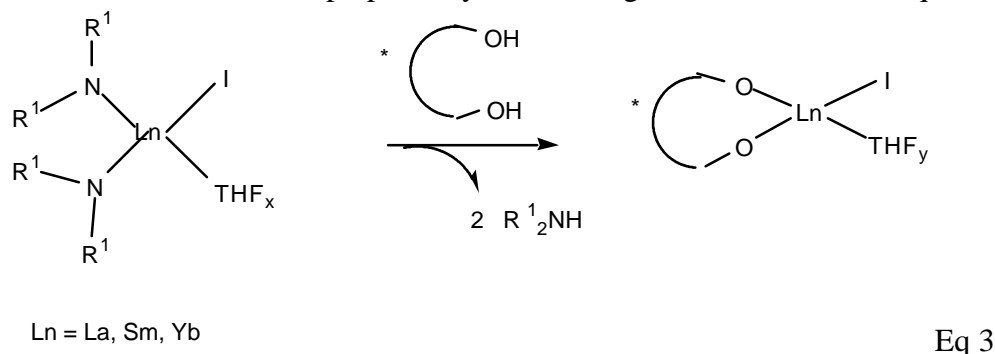
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<sup>b</sup>Laboratoire de Synthèse Asymétrique, URA 1497, ICMO, Université Paris-Sud, 91405 Orsay, France

In order to prepare enantioselective Lewis acid catalysts we have been studying the possibility of preparing lanthanide complexes stabilized by an asymmetric diol. We observed that  $\text{LnI}_3$  ( $\text{Ln}=\text{La, Sm, Yb}$ ) reacts with asymmetric diolates leading to mono (eq 1) or bis (eq 2) alkoxide derivatives



The bis alkoxides have also been prepared by the exchange reaction shown in equation 3.



The synthesis of a new asymmetric diol with additional chelating groups have also been developed and the coordinating possibilities of this new ligand is under investigation, as well as the utility of the complexes already characterized for enantioselective catalysis.

## Uranium and Thorium Compounds as Catalytic Precursors

Rui Dias, Noémia Marques, A. Pires de Matos

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The compounds  $\text{MX}_2(\text{HBpz}_3)_2$  ( $\text{M}=\text{Th, U}$ ;  $\text{X}=\text{Cl, CH}_2\text{SiMe}_3$ ) were synthesized and were tested as catalytic precursors in the polymerization of ethylene. The experiments were made in homogeneous phase and the complexes showed a very weak activity. Experimental conditions are now being studied to support these precursors on silica or alumina. It is known that compounds of the type  $\text{MX}_2\text{Cp}^*_2$  only showed activity in the polymerization of ethylene when supported in these materials.



## The Hydrogenation of Toluene over LnNi (Ln=Pr, Gd, Yb) and UNi<sub>2</sub> Intermetallic Compounds

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The hydrogenation of toluene over *f*-element binary intermetallic compounds: LnNi (Ln=Pr, Gd, Yb) and UNi<sub>2</sub> has been studied. The only product of these reactions is methylcyclohexane. We observed that the lanthanide intermetallic compounds are 10 to 20 less active than Ni and no variation of the activity was found along the Ln series.

UNi<sub>2</sub> showed the same activity as found for Ni due to a segregation of the d transition element to the surface.

Future work will be based on a new reaction: the hydrogenation of isoprene (2-methyl-2,3-butadiene). The higher activity referred in the literature for this reaction has been found over large palladium particles. The reaction in solution or in the gas phase proceeds under near ambient conditions to give three methylbutene isomers: 2-methyl-1-butene, 3-methyl-1-butene and 2-methyl-2-butene in an approximate ratio 1:1:2. The reaction is structure sensitive.

We intend to test the above mentioned intermetallic compounds in this reaction as the large particle size and the low intrinsic area (<1m<sup>2</sup>/g) of these compounds can lead to a better activity and regioselectivity in the hydrogenation of isoprene.

## Study of Base and Acid Properties of Zeolites after Impregnation with Rare Earth's Salts

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In this work we studied the basic-acid properties of the NaX zeolite modified by impregnation with different rare earth nitrates. The modified zeolite was tested in the gas phase isomerization of the butene-1 double bond position. The preliminary results show that the catalysts acid properties are important, but that there is an important contribution of the basic properties of the modified zeolite. This contribution increases from yttrium to ytterbium. This behaviour is different from the results reported in the literature where the major contribution arises from the acidic properties of the catalysts.

## RHENIUM CHEMISTRY

### Rhenium Complexes with Poly(pyrazolyl)borates

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#### Abstract

This paper presents an overview on the coordination chemistry of Re with poly(pyrazolyl)borates of the type  $[R_2B(pz^*)_2]$  ( $R=H, Ph, \text{pyrazolyl}$ ;  $pz^*=$ pyrazolyl or 3,5-dimethylpyrazolyl). This includes a variety of compounds like trioxo, dioxo, oxo, and hydrides with the metal in different oxidation states. Synthetic, spectroscopic, structural and other relevant aspects are reviewed.

*Trends in Inorganic Chemistry* (in press).

### Synthesis and Characterization of a New Re(V) Nitrido Complex with Iminobis(diphenylphosphine oxide): $[ReN\{N(OPPh_2)_2\}_2(PPh_3)]$

J. D. G. Correia<sup>1</sup>, A. Domingos<sup>1</sup>, A. Paulo<sup>1</sup>, I. Santos<sup>1</sup>, V. G. Montalvo<sup>2</sup>, R. C. Olivares<sup>2</sup>

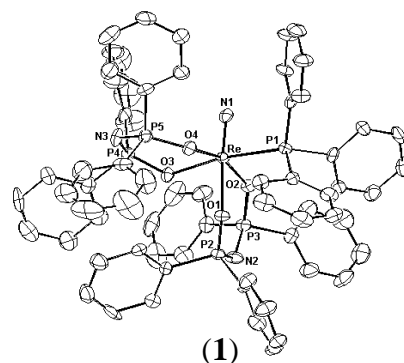
<sup>1</sup>Departamento de Química, ITN, Estrada Nacional 10, 2686 Sacavém Codex, Portugal

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#### Abstract

In the present work we describe the preparation of  $[ReN\{N(OPPh_2)_2\}_2(PPh_3)]$  (**1**) by reaction of  $[ReNCl_2(PPh_3)_2]$  with  $K[N(OPPh_2)_2]$  in  $CH_2Cl_2$ . Compound **1**, a brown-reddish solid, was spectroscopically characterized, including by X-ray crystallography (Figure 1). **1** crystallizes from  $CH_2Cl_2$ /hexane in the triclinic space group  $P\bar{1}$  with cell parameters  $a=11.261(2)$ ,  $b=14.114(2)$ ,  $c=22.311(3)\text{\AA}$ ,  $\alpha=83.67(1)^\circ$ ,  $\beta=75.06(1)^\circ$ ,  $\gamma=71.03(1)^\circ$ ,  $V=3239(1)\text{\AA}^3$ ,  $Z=2$ . In this bis-chelate, the rhenium atom is six-coordinate in a distorted octahedral configuration with the nitrido function *trans* to one oxygen atom of the chelate. Selected bond distances ( $\text{\AA}$ ) are: Re-N 1.606(10), Re-O(*trans*) 2.252(7). The N-Re-O(*trans*) angle is  $175.4(4)^\circ$ .

To have a better insight on the coordination ability of the  $PPh_3$  compared to other  $\sigma$ -donating ligands (e.g. pyridine,  $PEt_3$ ),  $^{31}P$ -NMR studies were undertaken, and are presented.



(1)

Communication to: *5th International Symposium on Technetium in Chemistry and Nuclear Medicine*, Bressanone, Italy (1998).

## Stability of Neutral *trans*-Dioxo Rhenium Complexes with Poly(pyrazolyl)borates

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### Abstract

[ReO<sub>3</sub>{η<sup>3</sup>-HB(pz)<sub>3</sub>}] (**1**) is reduced by PPh<sub>3</sub> in the presence of pyridine (py) and dimethylphosphinoethane (dmpe) affording neutral *trans*-[ReO<sub>2</sub>{η<sup>2</sup>-HB(pz)<sub>3</sub>}(py)<sub>2</sub>] (**2**) and *trans*-[ReO<sub>2</sub>{η<sup>2</sup>-HB(pz)<sub>3</sub>}(dmpe)] (**3**), respectively. The hydrotris(pyrazolyl)borate in **3** is easily displaced by dmpe and the formed complex is *trans*-[ReO<sub>2</sub>(dmpe)<sub>2</sub>][HB(pz)<sub>3</sub>] (**4**). As shown by X-ray crystallographic analysis, in these complexes the poly(pyrazolyl)borate is bidentate lying in the equatorial plane with the neutral ligands. **2** and **3** are the first examples of Re(V) complexes with {η<sup>2</sup>-HB(pz)<sub>3</sub>} and are rare examples of neutral *trans*-dioxo complexes.

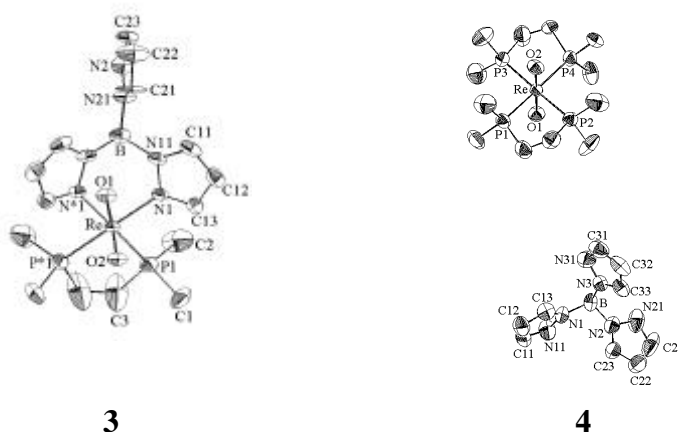


Figure 1. ORTEP diagrams of **3** and **4**.

Communication to: *5th International Symposium on Technetium in Chemistry and Nuclear Medicine*, Bressanone, Italy (1998).

## A New Route to Rhenium(III) and Rhenium(V) Hydrides

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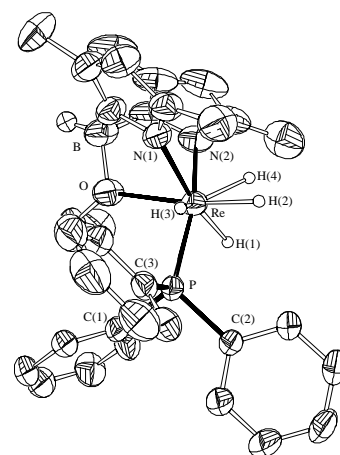
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### Abstract

The reaction of  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  with  $\text{Na}[\text{H}_2\text{B}(\text{pz})_2]$  or  $\text{Na}[\text{H}_2\text{B}(3,5\text{-Me}_2\text{pz})_2]$  in alcohols (ROH, R= Me, Et) allowed the direct synthesis of the hydride complexes  $[\text{ReH}_2\{\kappa^3\text{-(OR)}(\mu\text{-OR})\text{B}(\text{pz})_2\}(\text{PPh}_3)_2]$  (R=Me (**1**), Et (**2**)) and  $[\text{ReH}_4\{\kappa^3\text{-(H)}(\mu\text{-OR})\text{B}(3,5\text{-Me}_2\text{pz})_2\}(\text{PPh}_3)]$  (R=Me (**3**), Et (**4**)). The spectroscopic properties of **1-4** indicated a classical nature for these complexes, as it will be discussed. For **1** and **4** X-ray diffraction studies associated to Molecular Orbital Calculations of the type Extended Hückel and *ab initio* will also be reported.

Communication to: XXXIII International Conference on Coordination Chemistry, Florence, Italy (1998).



(4)

## Current Work

### Rhenium (V) Dioxocomplexes with Dihydrobis(pyrazoly)borates: Synthesis and Reactivity Towards Electrophilic Substrates

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The complex  $[\text{ReO}_2(\text{py})_4]\text{Cl}$  reacts with  $\text{K}[\text{H}_2\text{B}(\text{pz}^*)_2]$  and  $\text{K}[\text{B}(\text{pz})_4]$  leading to *trans*- $[\text{ReO}_2(\text{py})_4][\text{ReO}_2\{\text{H}_2\text{B}(\text{pz}^*)_2\}_2]$  ( $\text{pz}^* = \text{pz}$  (**1**), 3,5-Me<sub>2</sub>pz (**2**)) and *trans*- $[\text{ReO}_2(\text{py})_4][\text{B}(\text{pz})_4]$  (**3**), respectively. Complexes **1** and **2** react with electrophilic substrates ( $\text{ClSiMe}_3$ ,  $\text{ClSnMe}_3$ ) yielding  $[\text{ReO}(\text{OSiMe}_3)\{\text{H}_2\text{B}(\text{pz}^*)_2\}_2]$  ( $\text{pz}^* = \text{pz}$  (**4**), 3,5-Me<sub>2</sub>pz (**5**)) and  $[\text{ReO}(\text{OSnMe}_3)\{\text{H}_2\text{B}(\text{pz})_2\}_2]$  (**6**), regenerating  $[\text{ReO}_2(\text{py})_4]\text{Cl}$ . This is an unprecedented synthetic process, as it allows direct access to the chemistry of monoxocomplexes with dihydrobis(pyrazoly)borates, what is impossible by a direct method due to the reducing properties of these ligands. Complex **1** crystallizes in the triclinic space group  $P\bar{1}$ , with cell parameters  $a=9.419(1)$  Å,  $b=9.584(1)$  Å,  $c=12.652(1)$  Å,  $\alpha=89.03(1)$ ,  $\beta=82.41(1)$ ,  $\gamma=72.75(1)$ ,  $V=1080.9(2)$  Å<sup>3</sup>,  $Z=$  ; **3** crystallizes in the monoclinic space group  $C2/c$ , with cell parameters  $a=14.730(3)$  Å,  $b=13.3261(8)$  Å,  $c=17.368(3)$  Å,  $\beta=101.20(2)$ ,  $V=3344.4(8)$  Å<sup>3</sup>,  $Z=4$ ; **4** crystallizes in the monoclinic space group  $P2_1/n$ , with cell parameters  $a=10.785(2)$  Å,  $b=17.680(2)$  Å,  $c=11.971(2)$  Å,  $\beta=98.67(1)$ ,  $V=2256.5(6)$  Å<sup>3</sup>,  $Z=4$ .

*manuscript in preparation*

### Rhenium (V) Oxo-Siloxides Stabilized with Tetrakis(pyrazoly)borate: The First Cationic Rhenium Oxocomplex Structurally Characterized

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Cationic oxo-rhenium(V) complexes with poly(pyrazoly)borates are reactive species which have been used to promote relatively rare chemical transformations, such as thermal migration of alkyls from the metal center to oxo ligands. However, until now none of these cationic species was unambiguously identified by X-ray crystallographic analysis.

We found that was possible to stabilize the cationic complexes  $[\text{ReO}(\text{OSiMe}_3)\{\kappa^2\text{-B}(\text{pz})_4\}(\text{py}^*)_2]^+$  ( $\text{py}^* = \text{py}$  (**1**), 4-NMe<sub>2</sub>py (**2**)) and  $[\text{ReO}(\text{OXMe}_3)\{\kappa^2\text{-B}(\text{pz})_4\}(\text{dmpe})_2]^+$  ( $X = \text{Si}$  (**3**),  $\text{Sn}$  (**4**)), by reacting *trans*- $[\text{ReO}_2\{\kappa^2\text{-B}(\text{pz})_4\}(\text{py}^*)_2]$  ( $\text{py}^* = \text{py}$ , 4-NMe<sub>2</sub>py) and *trans*- $[\text{ReO}_2\{\kappa^2\text{-B}(\text{pz})_4\}(\text{dmpe})]$  with electrophilic substrates

Complexes **1** and **2** are very reactive and are easily transformed into the neutral oxocomplexes  $[\text{ReO}(\text{Cl})(\text{OSiMe}_3)\{\kappa^2\text{-B}(\text{pz})_4\}(\text{py}^*)]$  ( $\text{py}^* = \text{py}$  (**5**), 4-NMe<sub>2</sub>py (**6**)). The crystal and molecular structures of **3** and **6** were determined by X-ray crystallographic analysis, being the structure of **3** the first example described for a cationic oxorhenium complex containing a poly(pyrazoly)borate.

## **Oxorhenium (V) Complexes with Pyridine-2-thiolate Ligands**

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*Departamento de Química e Radioisótopos, ITN, 2686 Sacavém Codex, Portugal*

### **Abstract**

Pyridine-2-thiolate ligands can coordinate to metal centers through the sulphur atom or through the sulphur and nitrogen atoms. We have been evaluating the reactivity of rhenium(V) oxocomplexes towards pyridine-2-thiolate ligands, in order to control the coordination mode of these ligands. In fact, choosing properly the starting oxorhenium complex, we were able to modulate the denticity of pyridine-2-thiolate ligands. The complexes  $[\text{ReO}\{\kappa^3\text{-B(pz)}_4\}(\text{S-py})_2]$  (**1**) and  $[\text{ReO}\{\kappa^2\text{-B(pz)}_4\}(\text{S-py})_2(\mu\text{-O})]$  (**2**) were obtained when  $[\text{ReO}(\mu\text{-O})\{\kappa^3\text{-B(pz)}_4\}]_2$  reacted with pyridine-2-thiol (py-SH) and  $[\text{ReO}\{\kappa^2\text{-B(pz)}_4\}(\kappa^2\text{-py-S})(\text{OMe})]$  (**3**) was obtained by reacting  $[\text{ReO}\{\kappa^3\text{-B(pz)}_4\}(\text{OMe})_2]$  with py-SH. The crystal and molecular structure of **1** was determined by X-ray crystallographic analysis, and confirmed the monodentate coordination of the pyridine-2-thiolate ligand. The analogous reactions with 5-Me<sub>3</sub>Si-py-2-SH are currently under study, in order to evaluate the effect of the bulkyness of the substituents in the coordination versatility of pyridine-2-thiolates in these rhenium complexes.

## **Research on Peptide Based Radiopharmaceuticals**

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The mixed-ligand approach (the so called *3+1*) for the development of new radiopharmaceuticals is accepted as an easy access to a large variety of different Tc and Re complexes potentially useful to specifically target biological “locks” (e.g. receptors). Using this approach a large variety of complexes can be prepared and their structural and chemical properties modulate and related with their biological behaviour.

### **Part I : Synthesis and Characterization of New Chelate Ligands**

New tridentate chelate ligands, potentially monoanionic and dianionic, suitable for coordination to Rhenium and Technetium have been synthesized and characterized. These ligands, which contain nitrogen, phosphorous, oxygen and/or sulphur atoms, have been fully characterized by elemental analysis, IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopies and by X-ray crystallography.

### **Part II: Evaluation of the new ligands towards different rhenium starting materials**

The stabilizing properties of the above mentioned ligands have been evaluated towards different rhenium starting materials under different reaccional conditions. Some of those reactions allowed the isolation and characterization of new Re (V) oxocomplexes.

## GAS PHASE CHEMISTRY

### Formation of Some Transition Metal Oxide Cluster Anions and Reactivity Towards Methanol in the Gas Phase

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<sup>2</sup> *Departamento de Química, Instituto Tecnológico e Nuclear, 2686 Sacavém Codex, Portugal*

<sup>3</sup> *Departamento de Química, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Ed. C1 - 5º Piso, 1700 Lisboa, Portugal*

#### Abstract

Negative cluster ions of transition metal oxides ( $[M_xO_y]^-$ ;  $M = \text{Mn, Fe, Co, Ni, Cu}$ ) have been generated by laser desorption/ionisation from metal oxide pellets and studied using Fourier transform ion cyclotron resonance mass spectrometry. For the same metal, the stoichiometrically different oxides yield similar collections of anions, with small differences in the ion intensity distributions. The most intense transition metal anions were isolated and their reactivity towards methanol was investigated. The  $[MO_2]^-$ ,  $[M_2O_3]^-$  and  $[M_2O_4]^-$  anions react exothermically with methanol leading to  $[MO_2H_2]^-$ ,  $[M_2O_3H_2]^-$  and  $[M_2O_4H_2]^-$  as primary products, respectively. The  $[MO_3]^-$  anions are unreactive towards methanol. The rate constants determined for the various reactions suggest that the  $[MO_2]^-$  and  $[M_2O_3]^-$  anions react more efficiently with methanol than the  $[M_2O_4]^-$  cluster anions. The reaction efficiencies decrease when the metal varies from manganese to copper indicating that the number of electrons in the  $d$  shell of the metal atom appears to be an important factor on reactivity.

*International Journal of Mass Spectrometry*, in press.

### Reactivity in the Gas Phase of Lanthanide and Actinide Ions with Ferrocene

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#### Abstract

The volatile iron compound ferrocene,  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , was used as a possible alternative to iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , for the gas phase synthesis of intermetallic ions  $M\text{Fe}^+$  by reaction of the complexes with  $M^+$  ions [1-2], in which  $M$  is a lanthanide ( $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$ ), Th or U. All the experiments were performed in a Fourier transform ion cyclotron resonance mass spectrometer Finnigan FT/MS 2001-DT, equipped with a 3 Tesla superconducting magnet and with a Spectra-Physics Nd:YAG laser operated at the fundamental wavelength (1064nm).

We observed that, for the majority of the  $M^+$  ions, metal exchange reactions occurred, with formation of  $M(\text{C}_5\text{H}_5)_2^+$  ions. This type of reaction was previously observed by Freiser and co-workers in systems involving only  $d$  transition metals [3]. In some cases these authors also observed electron transfer reactions, but in our case the ionisation energy of ferrocene is higher than the ionisation energies of thorium, uranium and all the lanthanide metals, and accordingly, we did not observe any electron transfer reactions. In the case of the less reactive

lanthanide cations,  $\text{Sm}^+$ ,  $\text{Eu}^+$ ,  $\text{Tm}^+$  and  $\text{Yb}^+$  [4-5,7], we observed the formation of  $\text{MFe}(\text{C}_5\text{H}_5)_2^+$  ions, that is the adduct species. The relative rate constants obtained in kinetic studies were also in agreement with the known relative reactivity of the  $\text{M}^+$  ions.

The formation of  $\text{M}(\text{C}_5\text{H}_5)_2^+$  ions in the reactions of  $\text{M}^+$  with  $\text{Fe}(\text{C}_5\text{H}_5)_2$  corresponds to a new way of synthesizing in the gas phase lanthanide and actinide metallocenes, systems that have been studied recently [6-7].

Finally, we studied the possibility of formation of  $\text{MFe}^+$  ions from  $\text{MFe}(\text{C}_5\text{H}_5)_2^+$  species, using Tm as a test element. We conducted argon collision induced dissociation (CID) experiments with the  $\text{TmFe}(\text{C}_5\text{H}_5)_2^+$  ion, but we only observed the formation of  $\text{Tm}^+$  and  $\text{Tm}(\text{C}_5\text{H}_5)_2^+$  ions, observations that ruled out ferrocene as an adequate reagent for the gas phase synthesis of  $\text{MFe}^+$  intermetallic ions. The differences in the CID products obtained in the case of the reactions with  $\text{Fe}(\text{C}_5\text{H}_5)_2$  and  $\text{Fe}(\text{CO})_5$  are probably a consequence of the differences in the binding modes of the the  $\text{M}^+$  ions to the two iron complexes.

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Communication to: Meeting "Quarenta Anos de Investigação em Espectrometria de Massa" - Jubilee of Professor Maria Alzira Bessa Almostr Moura Ferreira, Faculdade de Ciências-Universidade de Lisboa (1998).

## Gas Phase Synthesis of Neutral Rare Earth Metal Alkoxides as Intermediates of "High-Tech" Materials

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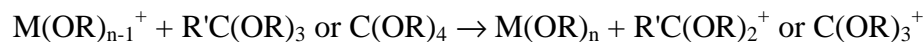
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### Abstract

In recent years, the studies concerning chemical, structural and energetic aspects of alkoxo and aryloxo chemistry of lanthanides, yttrium and scandium have been greatly boosted, not only because of the exploitation of these metal alkoxides or aryloxides in new synthetic reactions, but also because of their application in high-tech materials often using gas phase processes.<sup>1</sup> In this way, efforts have been made to elaborate new synthetic methods, particularly in the gas phase.<sup>2</sup>

The aim of the present work is to propose and to test a new concept of gas phase synthesis of rare earth alkoxides  $\text{M}(\text{OR})_n$  ( $n = 2$  or  $3$ ) not based on the reaction of the atomic form  $\text{M}$  of rare earth metals with oxygenated precursors but based on the reaction of the monovalent ion  $\text{M}^+$  with potential alkoxy or aryloxy group suppliers such as alkyl orthoesters  $\text{R}'\text{C}(\text{OR})_3$  or carbonates  $\text{C}(\text{OR})_4$ .





In order to test our concept of gas phase generation of rare earth metal alkoxides  $M(OR)_n$ , the cell of a Fourier transform mass spectrometer is used as a micro reactor,  $M^+$  ( $M = Sc, Y, Ln$ ) being generated by laser/ desorption ionization from high purity foils.

The relative reactivity of the rare earth metal cations is discussed in terms of factors like the ground-state electronic configuration of each metal ion and like the relative magnitude of the excitation energies to reactive configurations with two non f-electrons.

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Communication to: *NATO ASI on Energetics of Stable Molecules and Reactive Intermediates*, Castelo Branco (1998).

## **Current Work**

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### **Electrospray Mass Spectrometry of Uranium and Lanthanide Species**

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We have been investigating the use of electrospray ionization for the analysis of organocompounds of f block elements using Fourier Transform Ion Cyclotron Mass Spectrometry. This technique seemed to be quite adequate for compounds sensitive to the water and oxygen, provided an adequate solvent could be found. The electrospray tip was protected with a blanket of nitrogen avoiding any product decomposition. We are studying this type of ionisation method as we expect to access less stable lanthanide and actinide organometallic species and study their gas phase chemistry. To evaluate the usefulness of this technique a few compounds were electrosprayed.

UCl(tpip), tpip= tetraphenylimidophosphinate and U(tpip)<sub>4</sub> gave mass spectra identical showing a very strong peak due to U(tpip)<sub>3</sub><sup>+</sup> ion. In both cases a very small peak due to [UCl(tpip)<sub>3</sub>-H]<sup>+</sup> was also observed.

A sample of UCl<sub>2</sub>(HBPz<sub>3</sub>)<sub>2</sub> dissolved in THF gave no spray current. Using acetonitrile, where the compound is slightly soluble, a very complex spectra was obtained, and a peak corresponding to the UCl(HBPz<sub>3</sub>)<sub>2</sub><sup>+</sup> ion could barely be seen. This is surprising as laser desorption gives a good spectrum.

The ionic compound Sm[HB(3,5Me<sub>2</sub>Pz)<sub>3</sub>]<sub>2</sub>I<sup>-</sup> gave a very negligible peak of the molecular species Sm[L]<sub>2</sub><sup>+</sup>. Electrospray seemed to decompose the product and a very intense peak of a dimer of the ligand [LH]<sub>2</sub>H<sup>+</sup> was observed. Photodissociation of this species with a CO<sub>2</sub> laser gave LH<sub>2</sub><sup>+</sup>.

Eu(HBPz<sub>3</sub>)<sub>2</sub>.2DPPA in THF solution; DPPA = diphenylphosphineamine (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>O NH<sub>2</sub> P was analysed. A very good spectrum was obtained showing a very strong peak corresponding to the molecular species with the two ligands. Photodissociation with a CO<sub>2</sub> laser was used and species without DPPA or with one or two molecules of this ligand were identified in the gas phase.

Sm[HB(3,5Me<sub>2</sub>Pz)<sub>3</sub>]<sub>2</sub> is almost insoluble in THF. A solution in THF was made and electrosprayed immediately after preparation. The molecular species Sm[HB(3,5Me<sub>2</sub>Pz)<sub>3</sub>]<sub>2</sub><sup>+</sup> was easily identified. Electrospray of a solution in CH<sub>2</sub>Cl<sub>2</sub> of this compound showed oxidation and both the molecular species and SmO[HB(3,5Me<sub>2</sub>Pz)<sub>3</sub>]<sub>2</sub><sup>+</sup> could be identified.

### **Equilibrium Studies of Phenols in Gas Phase**

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The gas phase acidity of Vitamin E (α-Tocopherol) was determined by bracketing method using FT-ICR mass spectrometry. The electroaffinities of PhOH, p-t-BuPhOH and Vitamin E (α-Tocopherol) were also measured using the same method.

## Uranium Speciation by Electrospray Mass Spectrometry

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The ability of electrospray ionization to transfer solution species to the gas was explored. Preliminary results obtained with solutions of uranyl perchlorate\* were studied by Fourier Transform Ion Cyclotron Mass Spectrometry and indicated the species listed in the following table:

	Uranium ( $10^{-3}$ M); F ( $10^{-3}$ M); pH=4	Uranium ( $10^{-3}$ M); F ( $10^{-4}$ M); pH=4
Species	Relative abundance	Relative abundance
$\text{UO}_2(\text{OH})^+(\text{?})$	7.2	1.6
$\text{UO}_2(\text{H}_2\text{O})_3(\text{OH})^+$	47.7	62
$\text{UO}_2(\text{H}_2\text{O})_3\text{F}^+$	100	-
$\text{UO}_2(\text{H}_2\text{O})_4(\text{OH})^+$	-	15.8
$\text{UO}_2(\text{H}_2\text{O})_4\text{F}^+$	39	5.2
$\text{UO}_2(\text{H}_2\text{O})_3(\text{OH})\text{FNa}^+$	31.9	100
$\text{UO}_2(\text{H}_2\text{O})_5(\text{OH})^+$	-	3.8
$\text{UO}_2(\text{H}_2\text{O})_5\text{F}^+$	-	1.7
$\text{UO}_2(\text{H}_2\text{O})_3\text{ClO}_4^+$ (2 peaks due to the $^{35}\text{Cl}$ and $^{37}\text{Cl}$ )	24.6; 6.8	44.6; 12.9

Whereas these are preliminary results they are encouraging and a more systematic work is in progress. The species obtained in the gas phase depend on the fluoride ion concentration in the solution. The existence of the ion  $\text{UO}_2(\text{H}_2\text{O})_3\text{ClO}_4^+$ , which depicts a non coordinating anion  $\text{ClO}_4^-$ , has still to be proved. More experimental work has to be made in the ICR cell to confirm the structure listed.

\* The solutions used in this work were provided by the Group of Prof. G. R. Choppin, Florida State University.

## THERMOCHEMISTRY

### Current Work

#### Standard Molar Enthalpies of Formation of Mg and Ca Alkoxides

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Alkaline and alkaline-earth metal compounds have a major importance in synthetic chemistry. However their energetics are still mostly unknown. The energetics of alkaline-earth alkoxides were studied and enables the extension of a previously developed model (1,2), allowing for the prediction of the enthalpy of formation of some unmeasured Be, Sr and Ba alkoxides.

Compound	$\Delta_f H_m^\circ$ (kJ/mol)
Mg(OMe) <sub>2</sub>	-792.6±1.2
Mg(OEt) <sub>2</sub>	-847.9±2.7
Ca(OMe) <sub>2</sub>	-890.8±6.4
Ca(OEt) <sub>2</sub>	-924.5±2.6
Ca(OBu) <sub>2</sub>	-989.8±5.4

1. J.P. Leal, A. Pires de Matos, J.A. Martinho Simões, *J. Organomet. Chem.*, 403 (1991) 1.
2. J. P. Leal, J. A. Martinho Simões, *J. Organomet. Chem.*, 460 (1993) 131.

*manuscript in preparation*

#### Standard Enthalpies of Formation of Lithium, Sodium, and Potassium Cyclopentadienyls

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The enthalpies of formation of lithium, sodium and potassium cyclopentadienyls were measured using a reaction-solution calorimeter.

Compound	$\Delta_f H_m^\circ$ (kJ/mol)	Reaction studied
LiCp	-76.3±2.3	with water
LiCp	-77.2±4.4	with HCl (0.1 N)
NaCp	-36.0±2.5	with water
NaCp	-39.8±2.9	with water
NaCp	-40.0±4.7	with ethanol
NaCp	-41.8±9.0	with ethanol in toluene
NaCp	-43.4±1.9	with HCl (0.1 N)
KCp	-85.4±2.7	with water
KCp	-74.8±6.1	with HCl (0.1 N)

As the crystal structures of these compounds are known it is possible to relate the structural parameters with the distances metal-Cp ring calculated from the derived thermodynamic data. Based on a previously model (1,2) it is possible to estimate the enthalpies of formation of other cyclopentadienyl salts.

1. J.P. Leal, A. Pires de Matos, J.A. Martinho Simões, *J. Organomet. Chem.*, 403 (1991) 1.
2. J. P. Leal, J. A. Martinho Simões, *J. Organomet. Chem.*, 460 (1993) 131.

*manuscript in preparation*

## Bond Dissociation Enthalpies in U(IV) Complexes. An Integrated View

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The enthalpies in uranium compounds reported in the literature had been measured using two different approaches, one anchored on the bond dissociation enthalpy of U-Cl in the gas phase and another based on the bond dissociation enthalpy of U-I in solution. Whereas the relative scales are comparable the absolute values are different.

Bond dissociation enthalpies for  $UTp^{Me_2}I_2X$  ( $Tp^{Me_2} = HB(3,5-Me_2Pz)_3$ , X = oxygen ligand, chloride and iodide) were measured. Based on the data obtained it was possible to list all the existing uranium bond dissociation enthalpies literature values in one single scale.

Compound	X	D(U-X) (kJ/mol)	Reaction studied
$Tp^{Me_2}UI_3$	I	263±12	$Tp^{Me_2}UI_2(thf)_2 + I_2$
$Tp^{Me_2}UI_2(O-t-Bu)$	O-t-Bu	304±11	$Tp^{Me_2}UI_2(thf)_2 + t-BuO-O-t-Bu$
$Tp^{Me_2}UI_2Cl$	Cl	329±12	$Tp^{Me_2}UI_2(thf)_2 + C_5H_{11}Cl$
$Tp^{Me_2}UCl_3$	Cl	344±12	$Tp^{Me_2}UI_2(thf)_2 + Cl_2$

*manuscript in preparation*

## Enthalpy of Formation of Alkaline Metal Thiolates

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Some new enthalpies of formation of alkaline metal thiolates, MSR (M=Li, R=Et; M=Li, Na, R=Bu), were measured by reaction solution calorimetry.

## SURFACE STUDIES

### Photodissociation of Condensed Carbon Dioxide Below the Gas Phase Threshold

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#### Abstract

We have investigated photodesorption from condensed carbon dioxide for photon energies ranging from 13 to 35 eV using synchrotron radiation. We report the desorption of O<sub>2</sub><sup>+</sup> ions at energies as low as 13 eV and discuss this behaviour in terms of ion-molecule reactions. The desorbed CO<sup>+</sup> ion yield shows resonances at ~ 15.4 eV and 17 eV, below the gas-phase thermodynamic threshold for CO<sup>+</sup> formation. These peaks are also assigned to a two-step process, in which the photodissociation of CO<sub>2</sub> leads to neutral CO production.

*Chem. Phys. Letters.* **287** (1998) 742-745.

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### UHV Sample Holder for Fast Heating and Cooling Cycles

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#### Abstract

We describe a UHV sample holder that allows fast heating and cooling between 77 K and 1300 K. The system allows us to performed thermal treatment of a sample. The samples are heated by electron bombardment and the cooldown is achieved by liquid nitrogen. The sample holder is designed to be assembled in a multitechnique surface analysis apparatus that performs AES, SIMS, TDS and XPS analysis.

*Vacuum* **52** (1999) 23-26.

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## Current Work

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### Azides on Polycrystalline Ni: SIMS and XPS Studies

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We have investigated the adsorption of 2-Azidoacetic Acid (  $\text{N}_3\text{CH}_2\text{COOH}$  ) on Ni polycrystalline surface. XPS and SIMS were the techniques used. The adsorption took place at room temperature. XPS spectra of O1s and N1s showed a broad peak with a maximum at 531.98 and 398.6 eV, respectively. The C1s orbital spectrum showed two peaks at 283.6 and 286.56 eV. For the Ni 2p spectrum, the orbitals  $2p^{1/2}$  and  $3p^{3/2}$  were observed at 871.75 and 854.51 eV, respectively. The positive and negative SIMS spectra obtained shows that the NI contribution increases with azide dosage. The most important ion contribution was given by:  $\text{NO}^+$ ,  $\text{Ni}^+$ ,  $\text{NiO}^+$ ,  $\text{CN}^-$ ,  $\text{O}^-$ ,  $\text{OCN}^-$ .

*manuscript in preparation*

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## OTHER WORKS

### Dépot Chimique en Phase Vapeur à Basse Température de Revêtements dans le Système V-C-N à Partir de Bis(Arene)Vanadium

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#### Abstract

Low temperature chemical vapour deposition of V-C-N type coatings using bis(arene)vanadium. Vanadium carbide coatings V8C7 have been deposited on steel substrates by MOCVD using bis(arene)vanadium as precursors at temperatures lower than 550°C. Addition of C<sub>6</sub>Cl<sub>6</sub> in the gas phase allows to reduce the carbon content of the films to 13 at. %. These metal coatings exhibit the features of a metastable carbon rich solid solution. Carbonitride V(C,N) and nitride δ-VN layers with only 5 at. % carbon have been deposited in the presence of NH<sub>3</sub>. These reactive gas phases allow to grow almost all the phases of the V-C-N ternary diagram.

*Ann. Chim. Sci. Mat.* **23** (1998) pp. 695-706.

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### Multilayer Surface Coating of Glass with Metal Oxides: Characterization by Rutherford Backscattering, X-ray Fluorescence and FTICR Mass Spectrometry

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Dichroic glass samples made by multilayer deposition of two different metal oxides onto glass were analysed by different techniques. Whereas X-ray fluorescence and Fourier transform ion cyclotron resonance mass spectroscopy gave elemental analysis of the major oxides deposited, Rutherford Backscattering Spectroscopy (RBS) combined with Particle Induced X-ray Emission (PIXE) analysis allowed to determine the composition and thickness of the different layers. In this work the results obtained on the correlations between modulation period, composition and spectral response (i.e. colour) in transmission modes of different n-fold double layered structures are reported. Samples with double layered structures with colours covering the full wavelength range of the optical spectrum were studied. Vacuum deposition of multilayers was achieved by vaporising the metal oxides with an electron beam.

*Proceedings of XVII International Congress on Glass*, San Francisco, California, USA, July 5-10, 1998. [Westerville, Ohio, USA]: The American Ceramic Society, principal editors M.K.Choudhary, N.T. Huff and C.H. Drummond III, 1998. "C4:pp.13-18, Coatings, Surfaces and Surface Analysis".[cd-rom]

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## Analysis of the Program “CACHe for Windows”

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### Abstract

The Program CACHe® for Windows (Computer Aided Chemistry) is commercialized by Oxford Molecular Ltd. and works both on Microsoft Windows 95® and on Microsoft Windows NT 4.0® systems. It allows to draw and modelling molecules as well as perform some calculations over the molecules predicting molecular properties and energetics. It is sold at different levels of power skills/functionalities/prices from the basic one *Personal CACHe* to the more elaborated one *CACHe WorkSystem*. For using over local nets it is also available the version *CACHe Satellite* allowing multiusers. The version analyzed on this paper was *Quantum CACHe version 3.0*.

Some properties like enthalpies of formation, infrared spectra and molecular orbital energies were calculated for different kind of molecules [organic (polar and apolar) and inorganic] and compared with experimental values to have an idea of the program quality.

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