

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 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. Due to the type of chemistry we are dealing with, we extended our work to the chemistry of **rhenium**, with the aim of developing compounds that could be used as intermediates in reactions directed to organic synthesis and that can be models for compounds with ^{99m}Tc to be used as radiopharmaceuticals. These activities are supported by X-ray diffraction analysis for structural studies and thermochemical studies for determination of metal-ligand bond disruption enthalpies. The gas-phase reactions of metallic, intermetallic and oxide ions involving lanthanides and actinides with organic substrates are studied by means of Fourier transform ion cyclotron resonance spectroscopy.

During 1997 a new NMR multinuclear spectrometer has been installed.

The work done during the last year in the domain of organometallic compounds allowed to accomplish the study of the reactivity of the system $\text{UCl}_2(\text{Bpz}_4)_2$. Studies on the reactivity of σ -hydrocarbyl derivatives of $\text{UCl}_3[\text{HB}(3,5\text{-Me}_2\text{pz})_3]$ towards unsaturated organic substrates has proceeded. The use of more sterically hindered polypyrazolylborate ligands, such as $[\text{H}_2\text{B}(3\text{-}t\text{Bu},5\text{-Mepz})_2]$, $[\text{HB}(3\text{-}t\text{Bu},5\text{Mepz})_3]$ and $[\text{HB}(3\text{-Mespz})_3]$, allowed the synthesis of new systems of U(III) and Ln(II). The reactivity of the new systems is under study.

The development of structural facilities for catalytic studies has been implemented. Activation tests of $\text{Yb}[\text{OC}_6\text{H}_2(\text{CMe}_3)_2\text{-}2,6\text{-Me-}4]_2(\text{THF})_2$ with H_2 , CO_2 and MeOH have been performed in batch conditions (50 °C / 50 bar). No formation of dimethylcarbonate, formate or carbonate type complexes has been observed, but insertion of CO_2 into the M-O bond had occurred.

The steric/electronic properties of polypyrazolylborate ligands of the type R_2Bpz_2 (R=H, pz) allowed the synthesis of polyhydrides and *cis* or *trans*-dioxo complexes of rhenium.

The work in the gas-phase included studies of the reactivity of lanthanide and actinide metal and oxide ions with hydrocarbons, alcohols and phenols. The studies undertaken provided further examples confirming the relevance of the accessibility of reactive electronic configurations to the reactivity of lanthanide and actinide ions with organic molecules. Formation of *f-d* intermetallic ions was achieved and the reactivity of these species with organic molecules was tested. Reactivity of several lanthanide and actinide oxide and chloride cluster ions with organic molecules was also studied. Collaborative work has been carried out on the gas-phase reactivity of transition metal oxide ions.

The method for determination of the enthalpy of formation of binary intermetallic compounds of transition metal-lanthanide/actinide was clarified and tested with a known compound (UFe_2). This method will allow the determination of some more values for this family of compounds.

Research Team

Researchers –	13	*	(10 PhD)
Research Students –	3		(2 PhD Students)
Undergraduate Students –	3		
Technicians –	1		

* 2 Post-Doctoral + 2 Assistant Researchers from other groups of ITN.

Publications

Journals –	6	(one in press)
Special Publ. –	3	
Conf. Commun. –	30	
Internal Reports –	2	
Theses:		
Lic. –	1	

	10 ³ PTE
Expenditure:	82.739
Missions:	2.081
Others Expenses:	12.933
Hardware & Software:	1.110
Other Equipment:	66.615 ⁽¹⁾
⁽¹⁾ Includes the Nuclear Magn. Reson. Spectrometer	

		10 ³ PTE
Funding:		83.971
OE/ITN	OF	58.206 ⁽¹⁾
External Projects:	1997	24.753
Others		1.012
⁽¹⁾ Nuclear Magnetic Resonance Spectrometer		

f-ELEMENT CHEMISTRY

The “Dissolution” of Europium and Ytterbium in Alcohols

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Abstract

Direct “dissolution” of metallic europium and ytterbium in alcohols, without the use of a catalyst, was studied. In this work we report the reactions with methanol, ethanol and isopropanol. The Mössbauer spectra of the europium compounds indicated that the element in the obtained products is in the oxidation state II whereas for the ytterbium compounds the oxidation state of the element is III. Some of the compounds were also prepared by the metal vapour synthesis technique for comparison.

J. Alloys Comp. (in press)

Organocompounds of *f*-Elements with Hydrotris(pyrazolyl)borate Ligands

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Abstract

The large ionic radii of the *f*-elements associated with its strong ionic character usually lead to the formation of complexes with high coordination numbers and with variable coordination geometries. In order to get stable complexes of these ions with a low coordination number it is necessary to use sterically demanding ligands. The hydrotris(pyrazolyl)borate ligands are a unique set of tripodal ligands, with different steric and electronic requirements, due to the large amount of substituents which can be introduced in the pyrazolyl rings.

In this work we will describe the syntheses of uranium (IV) and lanthanide (II) compounds with hydrotris(pyrazolyl)borate ligands and we will show how the structure and the reactivity of these compounds can be modulated by the steric and electronic requirements of the ligands.

Communication to: *3º Encontro de Química Inorgânica da Soc. Portuguesa de Química, Fátima (1997).*

Chemical and Structural Aspects of Uranium Compounds with the Fragment " $U\{B(pz)_4\}_2$ "

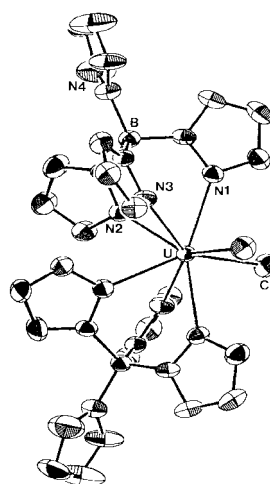
M. Paula C. Campello, Ângela Domingos, A. Pires de Matos and Isabel Santos

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Abstract

Previous studies of $[UCl_2\{HB(pz)_3\}_2]$ (**1**) have shown that this complex is a good starting material for the synthesis of derivatives with U-O, U-N, U-S and U-C bonds¹ However, the stability of the U-C bonds depends significantly of the nature of the alkyl group².

In this communication we will present some chemical and structural results which were obtained when we used the $\{B(pz)_4\}^-$ ligand to stabilize U(IV) complexes. This ligand, as $\{HB(pz)_3\}^-$, is monoanionic and potentially tridentate and stabilizes $[UCl_2\{B(pz)_4\}_2]$ (**2**). **1** and **2** are eight-coordinated but the structure and the chemistry of the compound with the fragment " $U\{B(pz)_4\}_2$ " seems to be dominated by the presence of the fourth pyrazolyl ring (Figure 1).



1 (bite 2,98)

Fig. 1 Molecular Structure of **2**

1. I. Santos, N. Marques, *New J. Chem.* **19** (1995) 551.
2. M. P. C. Campello, M. J. Calhorda, A. Domingos, A. Galvão, J. P. Leal, A. Pires de Matos, I. Santos, *J. Organomet. Chem.* **538** (1997) 223.

Communication to: 3^a Encontro de Química Inorgânica da Soc. Portuguesa de Química, Fátima (1997).

Crystal Structure of the Complex $\{YbCl_3[HB(3,5-Me_2Pz)_3]\}(Me_2PzH_2)$

Ângela Domingos, Noémia Marques and José M. Carretas

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Abstract

The compound $\{YbCl_2[HB(3,5-Me_2Pz)_3]\}(THF)$ (**1**) was synthesised by reacting $YbCl_3$ with $K[HB(3,5-Me_2Pz)_3]$ in THF solution, and its monomeric structure has been assigned by means of X-ray analysis.

In one attempt to obtain crystals of **1**, with the same experimental conditions, we got crystals of the complex $\{YbCl_3 [HB(3,5-Me_2Pz)_3]\}(Me_2PzH_2)$. The structural characterisation of this compound by X-ray diffraction analysis showed that the compound crystallises in the monoclinic space group $P2_1/c$, with $a=16.489(2)$, $b=10.141(1)$, $c=17.185(2)$ Å, $\beta=105.27(1)^\circ$, $V=2772.2(5)$ Å³, $Z=4$. The molecular structure of the anion has an octahedral geometry, as shown in Figure 1.

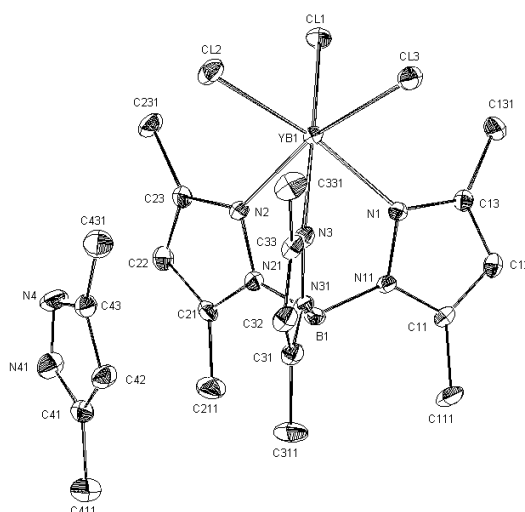


Fig. 1 - Molecular diagram of $\{YbCl_3 [HB(3,5-Me_2Pz)_3]\}(Me_2PzH_2)$

Communication to: 3^o Encontro de Química Inorgânica da Soc. Portuguesa de Química, Fátima (1997).

Carboxylation of Methanol to Dimethyl Carbonate using CO₂ as Starting Material

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Abstract

There is a growing interest in the direct conversion of carbon dioxide to more valuable products. Carbon dioxide is a cheap material and from the safety aspect it can be transported and handled without problems¹.

Our interest concerns the use of CO₂ 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 chemistry². Nevertheless, until now there are no relevant results concerning the catalytic production of carbonates via carboxylation of methanol with CO₂.

In this work we used alloys containing f-elements as catalysts. We described here some of the preliminary results obtained with YbNi alloys synthesized in a slurry form using metal vapor synthesis techniques (MVS).

This study pointed out a good activity and selectivity of the YbNi alloys for the synthesis of DMC.

Communication to: *3º Encontro da Divisão de Catálise da SPQ, IST, Lisboa (1997).*

X-Ray Structure of The Lanthanide (III)Complex [YbCl₂(THF)₂](μ-Cl)₂Li(THF)₂]

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Abstract

The [YbCl₂(THF)₂](μ-Cl)₂Li(THF)₂] complex (**1**) was isolated during an attempted preparation of YbCl₂(pyr*) (pyr* = NC₄H₂¹Bu₂-2,5) from the reaction of YbCl₃ with Li(pyr*) in THF, and it was structurally characterized by single-crystal X-ray diffraction. Crystals of (**1**) are monoclinic, space group C2/c with a=21.163(4)Å, b=10.282(1)Å, c=22.475(4)Å, β=90.805(9)°, V=4890(1)Å³ and Z=8. The X-ray structure (Fig.1) showed the Yb and Li atoms in distorted octahedral and tetrahedral environments, respectively. M(μ-Cl)₂Li units have been observed in several structures of f-element complexes.

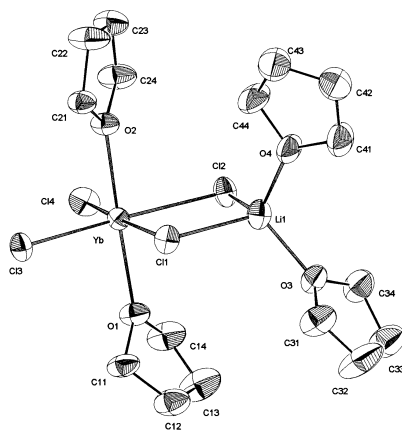


Fig.1 ORTEP diagram of 1

Communication to: *Seventeenth European Crystallographic Meeting, Lisboa (1997).*

Syntheses of Lanthanide Aryloxides

J. Branco¹, J. M. Carretas¹, A. Carvalho¹, A. Domingos¹, M. T. Duarte¹, J. Marçalo¹, N. Marques¹, A. Pires De Matos¹, J. C. Waerenborgh¹, M. Pissavini², S. Geribaldi²

¹. Departamento de Química, ITN, Estrada Nacional 10, 2686 Sacavém Codex

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Abstract

Alkoxides are known for almost all the elements, but the structural chemistry of these compounds is dominated by the formation of polymeric structures. Due to the large ionic radii of the lanthanides, the formation of multinuclear species is still more general for lanthanide alkoxides, leading to compounds with low solubility and reactivity.

In order to obtain low nuclearity bulky aryloxides have been used by several authors. A recent review lists the recent advances in alkoxo and aryloxo chemistry of the lanthanides¹. In this work we describe results obtained in our Laboratories using either conventional routes such as the alcoholysis of lanthanide tris[bis(trimethylsilyl)amido] compounds, the reaction between LnCl₃ and the potassium salts of phenoxo ligands in thf and the reaction of Yb or Eu metal in liquid ammonia at -78°C with the phenols, or the metal vapour synthesis and another method we have been developing by exploring the capability of metallic ytterbium and europium to be activated by ammonia gas in presence of the alcohols. We have been using phenoxo ligands and phenoxo ligands bearing an additional ether or amine function. In this work we describe the products obtained which were characterized by elemental analysis, infrared spectroscopy and in the case of europium also by Mössbauer spectroscopy. Most of the alkoxides of europium were in the oxidation state II, as confirmed by Mössbauer spectroscopy, while for the ytterbium alkoxides the elemental analysis indicated an oxidation state III for the metal. Full characterization of most of the compounds was not achieved due to the lack of crystals suitable for X-ray diffraction studies. However crystals of an ytterbium (III) species were obtained by recrystallization from thf/hexane mixtures of the products obtained by reacting YbCl₃ with KOC₆H₄-OCH₃-2 or by reacting ytterbium metal in liquid ammonia with HOC₆H₄-OCH₃-2. X-ray diffraction analysis showed that the compound was formulated as the polymeric species



1. L. G. Hubert-Pfalzgraf, *New J. Chem.* **19** (1995) 727.

Communication to: 3rd *International Conference on f Elements*, Paris (1997).

Hydrotris(Pyrazolyl)Borate Ligands In f-Element Chemistry

Ângela Domingos, Irene Lopes, Noémia Marques and Manuela Silva

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Abstract

This communication will focus on the synthesis and derivative chemistry of U(IV) and Ln(II) complexes stabilized with polypyrazolyl ligands.

Previous results have shown that the hydrotrispyrazolylborate ligands were able to stabilize σ -hydrocarbyl uranium (IV) complexes of general formula $UCl_2R[HB(3,5-Me_2pz)_3]$. The reactivity of these the compounds towards organic substrates has been studied and it was found that the reactivity patterns were dependent on the steric size of the R group. To probe the effect of the ancillary ligands the studies were extended to uranium compounds containing polypyrazolyl ligands with larger substituents in the 3-position of the pyrazolyl rings ($HB(3-Mspz)_3^-$, Ms = mesityl). The reactivity of both systems will be compared.

The larger size of the ligand $[HB(3-Mspz)_3^-]$ allowed the isolation of the “half-sandwich” complex $YbI[HB(3Ms-pz)_3](THF)_2$ which proved suitable for further derivatization chemistry. These results will be described.

It has been shown that the *tris*-dimethylpyrazolylborate ligand coordinates to lanthanide (II) yielding compounds of the type $Ln[HB(3,5-Me_2pz)_3]_2$ (Ln = Eu, Sm, Yb). We will show that the $Sm[HB(3,5-Me_2pz)_3]_2$ compound is able to reduce several substrates such as diaryl ketones, quinones and E_2R_2 (E = S, Se; R = C_5H_4N) reagents. The structure and the reactivity of the compounds will be discussed.

1. Takats, J.; Zhang, X. W.; Day, V. W.; Eberspacher, T.A. *Organometallics* **1993**, *12*, 4286.
2. Maunder, G. H.; Sella, A.; Tocher, D. A.; *J. Chem. Soc. Chem. Commun.* **1994**, 885

Communication to: 5th *Chemical Congress of North America*, Cancun (1997).

Current Work

Derivative Chemistry of $[UCl_2\{B(pz)_4\}_2]$: Stability of Complexes Containing the Fragments “ $[U\{B(pz)_4\}_2]$ ” and “ $[U\{HB(pz)_3\}_2]$ ”

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Abstract

Uranium tetrachloride reacts with two equivalents of $K[B(pz)_4]$ in THF leading to $[UCl_2\{B(pz)_4\}_2]$ (**1**) in 75% yield. **1** is monomeric and crystallizes in the monoclinic space group C2/c with cell parameters $a = 13.700(6)$, $b = 12.765(2)$, $c = 17.512(2)$ Å, $\beta = 101.37(2)$, $V = 3002.46$ Å³, $Z = 4$. The derivatives $[UCl(OR)\{B(pz)_4\}_2]$ (R = C_2H_5 (**2**), ^tBu (**3**), C_6H_4 -*o*-OMe (**4**) and C_6H_2 -2,4,6Me₃ (**5**)) were obtained by reacting **1** with sodium alkoxides in the 1:1 molar ratio (62%-80% yield). All the compounds are stable in the solid state or in solution and the solid state structure determined for **5** indicates that it crystallizes in the monoclinic space group C2/c with cell parameters $a = 30.575(3)$, $b = 9.929(1)$, $c = 24.884(3)$ Å, $\beta = 90.59(1)$, $V = 3446$ Å³, $Z = 8$. The complex $[U(O^tBu)_2\{B(pz)_4\}_2]$ (**6**) can also be obtained but in a very low yield (40%), and decomposes in solution. By reacting **1** with NaS^iPr in the molar ratio 1:2 it was isolated $[U(S^iPr)_2\{B(pz)_4\}_2]$ (**7**). **7** thermally unstable and crystallizes in the monoclinic space group C2/c with cell parameters $a = 24.286(7)$, $b = 9.471(2)$, $c = 16.076(32)$ Å, $\beta = 96.443$, $V = 3674(2)$ Å³, $Z = 4$. The attempts made to prepare

derivatives with metal-carbon bonds failed and $[\text{UCl}(\text{Me})\{\text{B}(\text{pz})_4\}_2]$ (**8**) is the only derivative isolated and fully characterized. Extended Huckel Molecular Orbital Calculations (EHMO) were used to explain the electronic properties of the ligands $[\text{B}(\text{pz})_4]$ and $[\text{HB}(\text{pz})_3]$ and the stability of complexes containing the fragments $[\text{U}\{\text{B}(\text{pz})_4\}_2]$ and $[\text{U}\{\text{HB}(\text{pz})_3\}_2]$.

To be submitted to *Journal of Organometallic Chemistry*.

Reactivity of $\text{UCl}_2\text{R}[\text{HB}(3,5\text{-Me}_2\text{pz})_3]$ ($\text{R}=\text{CH}_2\text{SiMe}_3, \text{CH}(\text{SiMe}_3)_2$) Towards Nitriles and Isonitriles

Ângela Domingos,^a Noémia Marques,^a Manuela Silva

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The reactivity of the σ -hydrocarbyl uranium (IV) complex, $\text{UCl}_2\text{RTp}^{\text{Me}_2}$ ($\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{pz})_3$) (**1**) towards nitriles and isonitriles has been investigated. **1** reacts with nitriles to give the corresponding azomethine compounds, $\text{UCl}_2\text{N}(\text{CR})(\text{CH}_2\text{SiMe}_3)\text{Tp}^{\text{Me}_2}$ ($\text{R}=\text{CH}_3$ (**2**), C_6H_5 (**3**)), due to insertion of the nitriles into the U-C bond. The X-ray molecular structure of **3** was studied by X-ray diffraction methods. **1** reacts with cyclohexylisonitrile to yield the corresponding iminoacyl uranium complex, which has been characterized by IR and ^1H NMR spectroscopies. Reactions of **1** with other isonitriles ($\text{R}=\text{CH}_2\text{C}_6\text{H}_5$, ^tBu) only yielded uncharacterizable products.

Reactivity studies of $\text{UCl}_3[(\text{HB}(3\text{-Mespz})_2(5\text{-Mespz}))]$

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^b E. I. Du Pont de Nemours & Company, Inc., Experimental Station, Wilmington, Delaware 19880-0302

During the last years we have been studying the reactivity of the U-C bond of σ -hydrocarbyl uranium (IV) complexes of general formula $\text{UCl}_2\text{RTp}^{\text{Me}_2}$ ($\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{pz})_3$). Since it was found that the reactivity patterns were dependent of the size of the R group, it will be of interest to determine which effect in the reactivity could be achieved by changing the steric and/or electronic requirements of the ancillary ligands. We have decided to use the ligand Tp^{Ms} ($\text{Tp}^{\text{Ms}} = [\text{HB}(3\text{-Mespz})_3]$). The reaction of UCl_4 with $\text{Ti}[\text{HB}(3\text{-Mespz})_3]$ when performed in CH_2Cl_2 or THF yielded the complex $\text{UCl}_3[(\text{HB}(3\text{-Mespz})_2(5\text{-Mespz}))]$ (**1**) ($[\text{HB}(3\text{-Mespz})_2(5\text{-Mespz})] = \text{Tp}^{\text{Ms}*}$) due to isomerization of the Tp^{Ms} ligand. **1** undergoes metathetical reactions with $\text{K}[\text{N}(\text{SiMe}_3)_2]$, $\text{LiC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ and $\text{LiCH}_2\text{C}_6\text{H}_4\text{NMe}_2$ to yield the corresponding $\text{UCl}_2\text{XTp}^{\text{Ms}*}$ compounds ($\text{X} = \text{N}(\text{SiMe}_3)_2$ (**2**), $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ (**3**), $\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2$ (**4**)). The crystal and molecular structures of **1** and **2** were determined by means of X-ray diffraction analysis. Due to the chelating nature of the hydrocarbyl ligand, **3** and **4** failed to insert nitriles and isonitriles into the U-C bond, as observed for $\text{UCl}_2(\text{CH}_2\text{SiMe}_3)\text{Tp}^{\text{Me}_2}$ (see above). The same holds for the reaction of **3** with acetone which did not yield the corresponding tertiary alkoxide. Instead formation of the uranium aldolate $\text{UCl}_2(\text{OC}(\text{Me}_2\text{CH}_2\text{C}(\text{O})\text{Me})\text{Tp}^{\text{Ms}*}$ (**5**) was observed due to C-C coupling of two acetone molecules.

U(III) Complexes: Synthesis, Characterization, Derivative Chemistry and Catalytic Studies

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During the last years we have been studying the chemistry of uranium (III) with the so-called 1st generation Trofimenko's poly(pyrazolyl)borates. With the ligands [R₂B(pz*)₂] (R=H and pz*=3,5Me₂pz; R=Ph, pz*=pz) the compounds isolated were the homoleptic derivatives [U{H₂B(3,5-Me₂pz)₂}₃]¹ and [U{Ph₂B(pz)₂}₃]². In these complexes the metal center is very congested, as indicated by X-ray crystallographic analysis, and its reactivity towards organic substrates is low. The electronic and/or steric properties of the poly(pyrazolyl)borate ligands can be changed by introducing different substituents in the pyrazolyl rings and they affect the nature of the complex that is possible to stabilize. We decided to use the more bulky K{H₂B(3-^tBu,5-Mepz)₂} to see whether it was possible to stabilize a less congested and more reactive complex. The reaction of [UI₃(THF)₄] with K{H₂B(3-^tBu,5-Mepz)₂} in THF yielded the complex [UI₂{H₂B(3-^tBu,5-Mepz)₂}(THF)₂] (**1**). **1** crystallizes in the orthorhombic space group P2₁2₁2₁ with cell parameters a=10.386(1), b=13.115(1), c=26.556(2) α=β=γ=90°, V=3617.3(5) Å³, Z=4. The reactivity of **1** in catalytic and stoichiometric reactions is being studied.

1. Adelaide Carvalho, Ângela Domingos, Paulo Gaspar, Noémia Marques, A. Pires de Matos, Isabel Santos, *Polyhedron*, 1992, **11**, 1481.
2. Sandra Jorge, Ângela Domingos, Isabel Santos, unpublished results.

Multinuclear NMR solution Structural Study of LnCp₃.TMU Compounds

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[§]*Departamento de Química, ITN, Estrada Nacional 10, 2686 Sacavém Codex*

[&]*Instituto de Química, Universidade de S. Paulo, Cx, Postal 20780, CEP 05599-970, São Paulo-SP, Brasil*

Abstract

In this contribution we report a multinuclear NMR study in solution of a series of organolanthanide compounds, the tetramethylurea adducts of the triscyclopentadienyllanthanide (III) complexes, LnCp₃.TMU. The diamagnetic La(III) member of this series was also studied using ¹³⁹La, ¹H and ¹³C NMR chemical shift and relaxation data, and compared with ¹H and ¹³C NMR data for the analogous Y(III) compound. The ¹H and ¹³C lanthanide induced shifts (LIS) of the paramagnetic members of the series (Ln = Ce, Nd, Sm, Eu, Yb) were separated into their contact and dipolar contributions. The latter contribution was used to determine the average solution molecular structure of these compounds through comparison of their experimental and calculated values using appropriate computational methods. This structure was compared with those obtained from the X-ray crystal structures of some of these compounds.

Chloro-Actinide and Lanthanide Complexes Containing the Hydrotris(3,5-dimethylpyrazol-1-yl)borate Ligand

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Abstract

Reaction of NpCl_4 with KTp^{Me_2} ($\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{pz})_3$) in THF afforded the complex $\text{NpCl}_3\text{Tp}^{\text{Me}_2}(\text{THF})$ (**1**), the crystal and molecular structure of which has been determined by single crystal X-ray diffraction. The THF could be removed by extraction with pentane to yield the complex $\text{NpCl}_3\text{Tp}^{\text{Me}_2}$ (**2**). The crystal structure of this compound has been determined. Reactions of PuCl_3 and LnCl_3 ($\text{Ln} = \text{Pr}, \text{Nd}$) with the stoichiometric amount of KTp^{Me_2} yielded the complexes $[\text{MCl}_2\text{Tp}^{\text{Me}_2}(3,5\text{-Me}_2\text{pzH})]_2$ ($\text{M} = \text{Pu}$ (**3**), Pr (**4**), Nd (**5**)). By contrast, the analogous reaction with YbCl_3 yielded the monomeric $\text{YbCl}_2\text{Tp}^{\text{Me}_2}(\text{THF})$ (**6**). The crystal structures of **4** and **6** have been assessed by means of X-ray single crystal diffraction analyses.

Ketyl Complexes of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ ($\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{pz})_3$)

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Abstract

Most of the chemistry of samarium (II) has been based on the bis(pentamethylcyclopentadienyl) ligand system. Since it is well known the importance of steric factors in lanthanide chemistry there has been increasing interest on extending the range of ancillary ligands beyond cyclopentadienyls and its analogues. Some of us have reported the synthesis and the X-ray crystal structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$.³

Herein, we report that $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ reacts with diaryl ketones to form ketyl complexes which have been structurally characterized. The reaction of one equivalent of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ (**1**) with benzophenone in toluene, yields the dark-blue compound $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OCPh}_2)]$ (**2**), in 75% yield. A similar procedure with fluorenone yields the dark green compound $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_{13}\text{H}_8)]$ (**3**), in 80% yield. **2** and **3** were characterized by infrared, UV-vis and ¹H NMR spectroscopies. In order to confirm the identity of the complexes single crystal X-ray diffraction studies were undertaken.

In both structures the samarium centre is seven-coordinate with the two tridentate Tp ligands staggered with respect to each other, with the benzophenone or the fluorenone units occupying the seventh site. The coordination geometries are best described as capped octahedron. The Sm-O distances in compounds **2** and **3** (2.201(3), 2.186(4) Å) are slightly longer than the similar distance in $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{OC}_6\text{Me}_4\text{H})$, and in five-coordinated Sm(III) alkoxides,

consistent with more congested nature of the Sm centre in the pyrazolylborate complex, but shorter than the Sm-O distances observed in the structures of Sm (II) aryloxides, such as in $[\text{Sm}(\text{OAr})_2(\text{THF})_3]$ (av. 2.304(8)Å). This suggests that the Sm(III) centre is in a trivalent state.

The C-O bond distances in the ketone ligands are 1.315(6) and 1.313(8) Å for **2** and **3**, respectively, and compare with the value of 1.313 (7) Å for the C-O bond distance of the fluorenone unit in the metal ketyl complex $\text{Sm}(\text{biphenyl-2,2'-diyl ketyl})(\text{OAr})_2(\text{THF})_2$ reported by Hou and in $\text{Sm}(\text{Tp}^{\text{Me}_2})_2[\text{OC}_6\text{H}_2(\text{tBu})_2\text{O}]$ (1.300(11)Å). The carbonyl carbon atoms of the ketones are all in sp^2 hybrid states, as can be seen in the sum of the angles around it (359.9(5), 359.9(7)° for **2** and **3**, respectively). These data indicate that compounds **2** and **3** can be formulated as Sm(III) ketyl complexes.

Reduction of organic substrates by $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ ($\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{pz})_3$)

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We have been studying the ability of $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$ ($\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{pz})_3$) to reduce organic substrates. The quinones can be reduced in two one-electron steps. $\text{SmTp}^{\text{Me}_2}$ react with 1,4-benzoquinone in the molar ratio 1:1 to yield the Sm(III) compound, $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_6\text{H}_4\text{O})$. However, this compound is unstable and react further with another molecule of $\text{SmTp}^{\text{Me}_2}$ to yield a dimeric compound, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2(\mu\text{-OC}_6\text{H}_4\text{O})$, in which the quinone is bridging the two Sm centres, as shown by X-ray diffraction analysis. $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$ is able to reduce E_2R_2 reagents ($\text{E}=\text{S}, \text{Se}$; $\text{R}=\text{C}_5\text{H}_4\text{N}$) to yield $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{ER})$ compounds. The crystal and molecular structure of the thiolate derivative has been determined and showed that the thiopyridine was coordinated to the metallic centre in an η^2 coordination mode.

The compound $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$ does not react with CpH or HCCPh, but it is readily oxidized by TlCp or AgCCPh . The compounds $\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{Cp}$ and $\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{CCPh}$ have been isolated. An X-ray diffraction study of the compound $\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{Cp}$ showed that the Cp ligand was η^5 coordinated to the metallic centre. While one of the Tp^{Me_2} ligands retains its η^3 coordination mode, the second Tp^{Me_2} ligand turns bidentate in order to decrease the steric saturation around the samarium ion.

$\text{Sm}(\text{Tp}^{\text{Me}_2})_2$ also reduce other organic substrates such as pyridazine, phenantraquinone, 2,2-bipyridyl to yield intensely coloured compounds, which need further characterization by X-ray diffraction analysis.

Synthesis and Reactivity of a New Class of Mixed-Ligand Yb(II) Complexes

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Ytterbium di-iodide reacts with the thallium salts of the ligands Tp^{Ms} ($\text{Tp}^{\text{Ms}} = [\text{HB}(3\text{-Mespz})_3]$) and Tp^{Ms^*} ($\text{Tp}^{\text{Ms}^*} = [\text{HB}(3\text{-Mespz})_2(5\text{-Mespz})]$) to yield the compounds $\text{YbI}[\text{HB}(3\text{-Mespz})_3](\text{THF})_x$ (**1**) and $\text{YbI}[\text{HB}(3\text{-Mespz})_2(5\text{-Mespz})](\text{THF})_2$ (**2**), respectively. The crystal and molecular structure of **2** has been determined by means of X-ray diffraction analysis. Complex **2** is coordinatively unsaturated and adds easily a neutral molecule of mesitylpyrazole

to yield the compound $[\text{Yb}(\mu\text{-I})\{\text{HB}(3\text{-Mespz})_2(5\text{-Mespz})\}(5\text{-MespzH})_2]$ (**3**). The dimeric nature of the compound has been established by X-ray diffraction analysis. **2** undergoes metathetical reaction with $\text{KN}(\text{SiMe}_3)_2$ to yield $\text{Yb}[\text{N}(\text{SiMe}_3)_2][\{\text{HB}(3\text{-Mespz})_2(5\text{-Mespz})\}]$ (**4**). The attempted recrystallization of **4** from a toluene solution in the presence of HCl, allowed to isolate a new dimeric species, $[\text{Yb}\{\text{HB}(3\text{-Mespz})_2(5\text{-Mespz})\}(\mu\text{-Cl})_2]$ (**5**). The determination of the X-ray crystal structure of **5** showed another way of the metallic centre to increase steric and electronic saturation through an additional interaction between a carbon atom of a mesilpyrazole ring of the ligand and the ytterbium atom. Compound **2** can be easily oxidized by iodine to yield $\text{YbI}_2[\{\text{HB}(3\text{-Mespz})_2(5\text{-Mespz})\}(\text{THF})]$, which will allow a new entry into Yb(III) chemistry. Attempts to obtain σ -hydrocarbyl derivatives of **2** are in course.

Catalytic studies using CO_2 as a raw material

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Starting from the well established complex $\text{Yb}(\text{OC}_6\text{H}_2(\text{CMe}_3)_2\text{-2,6-Me-4})$ we have performed several activation tests with H_2 , CO_2 and MeOH. No molecular lanthanide hydride was prepared by oxidative addition of H_2 to the metal center, but we have achieved the insertion of CO_2 in the Yb-O bond with the formation of a η^1 complex : $\text{Yb-O}(\text{CO})\text{-OC}_6\text{H}_2(\text{CMe}_3)_2\text{-2,6-Me-4}$, without the formation of dimethylcarbonate, formate or carbonate type complexes. Future work must be based on other well characterized compounds, namely homonuclear lanthanide and actinide complexes, i.e. hydrides and pyrazolyborate ligands.

RHENIUM CHEMISTRY

Structural Preferences of Rhenium Hydrides with Ligands of the Type Poly(pyrazolyl)borates

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Abstract

Rhenium complexes with poly(pyrazolyl)borates have been synthesized in the Chemistry Department of ITN and, when possible, characterized by X-ray diffraction analysis. This technique only in a few cases allows the definition of the structural parameters of hydrides coordinated to the metal. However, to define the coordination geometry of the complexes we need to know the structural parameters of all the atoms coordinated to the rhenium. In this work is presented an X-ray diffraction study associated to Extended Hückel Molecular Orbital Calculations (EHMO) for a rhenium polyhydride. All the structural parameters of the non-hydrogen atoms were determined based on the intensities diffracted by a single crystal. For the molecular geometry determined were made molecular orbital calculations by EHMO and the number of LUMO was in agreement with the number of hydrides expected for the molecule. Finally we have done a topological analysis of the electronic density corresponding to each molecular orbital and the structural parameters of each hydrogen coordinated to the metal was determined. As an example we present the molecular structure of a rhenium complex with four hydrides $[H_4Re\{HB(OEt)(3,5-Me_2pz)_2\}(PPh_3)]$ (**1**), figure 1, and the projection for $d(Re-H)=1.8$ of the electronic density map corresponding to the LUMO orbital, figure 2.

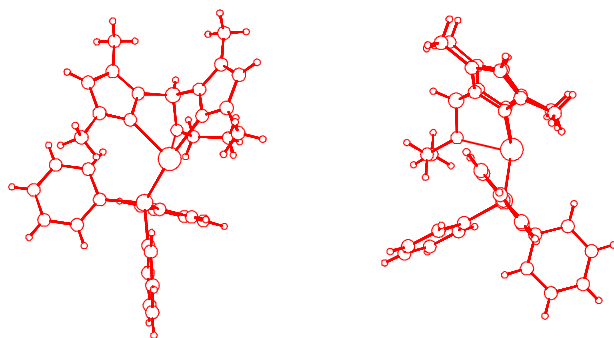


Fig. 1- Molecular Structure of **1**

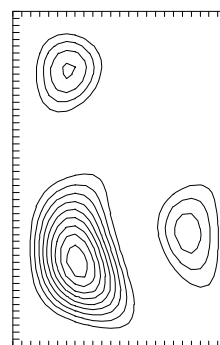


Fig. 2- LUMO electronic density map

Communication to: 3^a Encontro de Química Inorgânica da Soc. Portuguesa de Química, Fátima (1997)

Reactions of Oxocomplexes of Rhenium (V) with Poly(pyrazolyl)borates

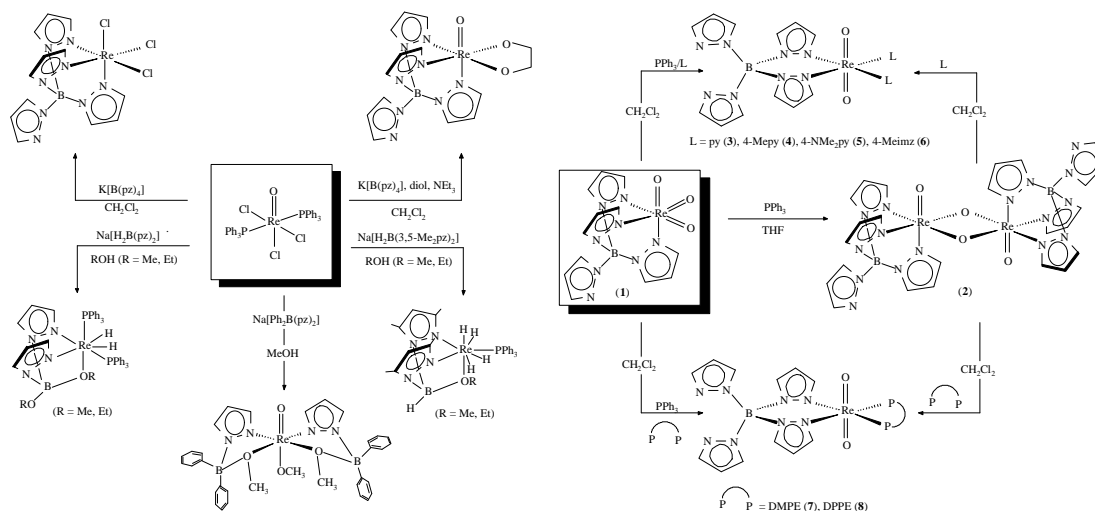
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Abstract

$[\text{ReOCl}_3(\text{PPh}_3)_2]$,¹ $\text{trans-}[\text{ReO}_2(\text{py})_4]\text{Cl}^2$ and $\text{cis-}[\text{ReO}_2(\text{PPh}_3)_2\text{I}]^3$ are important starting materials for the synthesis of oxo- and dioxo complexes of Rhenium (V).

The possibility of using $[\text{ReOCl}_3(\text{PPh}_3)_2]$, $\text{trans-}[\text{ReO}_2(\text{py})_4]\text{Cl}$ and $\text{cis-}[\text{ReO}_2(\text{PPh}_3)_2\text{I}]$ for the preparation of oxo-complexes with poly(pyrazolyl)borate ligands will be presented (Scheme 1). Some examples will be given in order to show that these materials are not an alternative to $[\text{ReO}_3\{\text{B}(\text{pz})_4\}]^4$ for the synthesis of dioxo-complexes (Scheme 2).



Scheme 1

Scheme 2

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Communication to: 3^a Encontro de Química Inorgânica da Soc. Portuguesa de Química, Fátima (1997).

NMR studies of Re (III) and Re(V) polyhydrides with modified poly(pyrazolyl)borates

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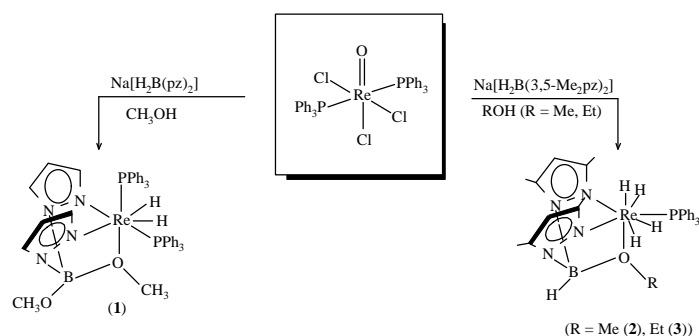
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Abstract

The rhenium is one of the transition metals for which has been described a larger number of polyhydrides, and most of these studies have been motivated by the activation of hydrocarbons.¹ Most of the rhenium polyhydrides have phosphines as co-ligands, being the compounds [LReH₆] and [LReH₄(PPh₃)] (L⁻ = Cp^{*}, [HB(pz)₃]) rare examples of hydrides stabilized by anionic and potentially tridentate ligands.²⁻⁴

As part of our ongoing work on the chemistry of rhenium with poly(pyrazolyl)borates we investigated reactions of [ReOCl₃(PPh₃)₂] with dihydrobis(pyrazolyl)borates (Scheme 1).



Scheme 1

The reducing properties of these ligands allowed the synthesis of the polyhydrides **1-3** in one step preparation. In this work we will present variable temperature ¹H, ³¹P and ³¹P-¹H(selective) NMR studies which allowed the determination of the number of hydrides coordinated to the metal center. T₁(min) measurements were also done and suggest a classical structure for the hydrides **1-3**.⁵

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Communication to: 3^a Encontro de Química Inorgânica da Soc. Portuguesa de Química, Fátima (1997).

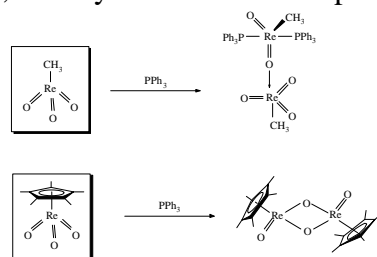
Synthesis and characterization of *trans*-[Re^VO₂{B(pz)₄}L₂] and *trans*-[Re^VO₂{B(pz)₄}(P[∧]P)]

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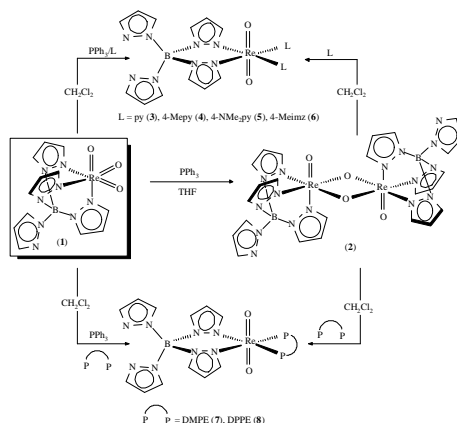
Abstract

The chemistry of rhenium oxocomplexes in high oxidation states, has called a lot of interest, and the organometallics (C₅Me₅)ReO₃ e CH₃ReO₃ are examples of that.¹ These compounds have a different chemical behaviour, namely in reactions with phosphines (Scheme 1).



Scheme 1

In our laboratory we have been studying the chemistry of oxocomplexes with the [B(pz)₄] ligand and, particularly, the chemistry of [ReO₃{B(pz)₄}] (**1**).² Depending on the conditions, **1** reacts with PPh₃ leading to results which are comparable to (C₅Me₅)ReO₃ or CH₃ReO₃ (Scheme 2).



Scheme 2

In this work we will describe the reduction of **1** in the presence or absence of neutral ligands, as well as reactions of *trans*-[ReO₂(py)₄]Cl and *cis*-[ReO₂I(PPh₃)₂] with K[B(pz)₄].

- (1) Herrmann, W.A.; Roesky, P.W.; Wang, M; Scherer, W.; *Organometallics* 1994, **13**, 4531; e referências aí citadas.
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Communication to: 3^a Encontro de Química Inorgânica da Soc. Portuguesa de Química, Fátima (1997).

Rhenium (III) and Rhenium (V) Hydride Complexes with Modified Poly(pyrazolyl)borates

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Abstract

Reactions 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) at room temperature give $[\text{ReH}_2\{\eta^3\text{-(OR)}(\mu\text{-OR})\text{B}(\text{pz})_2\}(\text{PPh}_3)_2]$ (R=Me (**1**), Et (**2**)) and $[\text{ReH}_4\{\eta^3\text{-(H)}(\mu\text{-OR})\text{B}(3,5\text{-Me}_2\text{pz})_2\}(\text{PPh}_3)]$ (R=Me (**3**), Et (**4**)), respectively; in ethanol and for $\text{Na}[\text{H}_2\text{B}(3,5\text{-Me}_2\text{pz})_2]$ the complex $[\text{ReO}(\text{H})\{\eta^2\text{-H}_2\text{B}(3,5\text{-Me}_2\text{pz})_2\}_2]$ (**5**) was also identified. The same type of reaction with $\text{Na}[\text{Ph}_2\text{B}(\text{pz})_2]$, using methanol as solvent, allowed to isolate $[\text{ReO}(\text{OMe})\{\eta^2\text{-Ph}_2\text{B}(\text{OMe})(\text{pz})_2\}_2]$ (**6**) in a very low yield. All the new compounds have been characterized by IR and ^1H NMR spectroscopies and for **1**, **3** and **4** ^{31}P - $\{^1\text{H}\}$ NMR, variable temperature ^1H and ^{31}P NMR studies and T_1 measurements have also been done. The characterization of **1**, **4** and **6** includes single-crystal X-ray diffraction analysis: **1** crystallizes in the triclinic space group $\text{P}\bar{1}$, with cell parameters $a=11.625(2)$ Å, $b=12.683(3)$ Å, $c=15.885(4)$ Å, $\alpha=96.65(2)^\circ$, $\beta=100.20(2)^\circ$, $\gamma=115.54(2)^\circ$, $V=2030.6(8)$ Å³, $Z=2$; **4** crystallizes in the triclinic space group $\text{P}\bar{1}$, with cell parameters $a=9.8554(7)$ Å, $b=11.035(1)$ Å, $c=14.868(2)$ Å, $\alpha=107.354(7)^\circ$, $\beta=91.229(5)^\circ$, $\gamma=100.002(5)^\circ$, $V=1515.3(3)$ Å³, $Z=2$; **6** crystallizes in the triclinic space group $\text{P}\bar{1}$, with cell parameters $a=11.274(1)$ Å, $b=13.007(1)$ Å, $c=13.350(1)$ Å, $\alpha=100.639(7)^\circ$, $\beta=100.376(8)^\circ$, $\gamma=108.309(7)^\circ$, $V=1766.1(2)$ Å³, $Z=2$. The classical nature of the compounds **1** and **4** and the structural parameters of the hydride ligands were defined by X-ray diffraction studies associated to Extended Hückel Molecular Orbital Calculations (EHMO).

Inorganic Chemistry, submitted.

Current Work

Neutral Trans-Dioxo Rhenium(V) Complexes with the Anionic Tetrakis(pyrazolyl)borate Ligand

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Abstract

Reduction of $[\text{ReO}_3\{\eta^3\text{-B}(\text{pz})_4\}]$ with triphenylphosphine in the presence of mono or bidentate neutral substrates gives *trans*- $[\text{ReO}_2\{\eta^2\text{-B}(\text{pz})_4\}(\text{L})_2]$ (L = pyridine (**3**), 4-methylpyridine (**4**), 4-dimethylaminopyridine (**5**), N-methylimidazole (**6**)) and *trans*- $[\text{ReO}_2\{\eta^2\text{-B}(\text{pz})_4\}(\text{P}^{\wedge}\text{P})]$ ($\text{P}^{\wedge}\text{P}$ =dimethylphosphinoethane (**7**), diphenylphosphinoethane (**8**)), respectively. The

analogous $[\text{ReO}_3\{\eta^3\text{-HB}(\text{pz})_3\}]$ is also reduced by PPh_3 in the presence of pyridine or dimethylphosphinoethane leading to *trans*- $[\text{ReO}_2\{\eta^2\text{-HB}(\text{pz})_3\}(\text{py})_2]$ (**9**) and *trans*- $[\text{ReO}_2\{\eta^2\text{-HB}(\text{pz})_3\}(\text{dmpe})]$ (**10**), respectively. Compounds **3-8** have been characterized by elemental analyses, IR, ^1H NMR spectroscopy, ^{31}P NMR (**7** and **8**) and X-ray diffraction (**5** and **7**). Compounds **9** and **10** are relatively unstable and their characterization was only done by IR and NMR spectroscopies and, in the case of **10**, by X-ray crystallographic analysis. Compound **5** crystallizes from dichloromethane/*n*-hexane as orange crystals containing three molecules of solvated CH_2Cl_2 (crystal data: triclinic space group P1, with cell parameters $a=10.907(2)$ Å, $b=11.113(1)$ Å, $c=16.922(2)$ Å, $\alpha=97.91(1)^\circ$, $\beta=102.37(1)^\circ$, $\gamma=94.21(1)^\circ$, $V=1973(1)$ Å³, $Z=2$). Compound **7** crystallizes from dichloromethane/*n*-hexane as yellowish crystals containing one molecule of solvated CH_2Cl_2 (crystal data: tetragonal space group $I4_1/a$, with cell parameters $a=19.413(1)$ Å, $b=19.413(1)$ Å, $c=32.186(5)$ Å, $\alpha=\beta=\gamma=90^\circ$, $V=12133(2)$ Å³, $Z=16$). Compound **10** crystallizes from dichloromethane/*n*-hexane as yellowish crystals containing one molecule of pzH (crystal data: orthorhombic space group Pnma, with cell parameters $a=18.422(2)$ Å, $b=11.850(1)$ Å, $c=11.434(1)$ Å, $\alpha=\beta=\gamma=90^\circ$, $V=2496.1(4)$ Å³, $Z=4$). The attempts made to prepare dioxocomplexes by reacting $[\text{ReO}_2(\text{py})_4]\text{Cl}$ with $[\text{KB}(\text{pz})_4]$ in dichloromethane failed and the species isolated were $[\text{ReO}(\eta^2\text{-}N,O)(\mu\text{-O})\text{B}(\text{pz})_3\{\text{pz}\}(\text{pzH})_2]$ (**11**) and $[\text{ReO}\{\eta^2\text{-}N,O)(\mu\text{-O})\text{B}(\text{pz})_3\}\text{Cl}(\text{py})_2]$ (**12**). **11** crystallizes from dichloromethane/*n*-hexane in the monoclinic space group $\text{P}2_1/n$, with cell parameters $a=10.890(1)$ Å, $b=15.162(1)$ Å, $c=14.137(2)$ Å, $\beta=102.07(1)^\circ$, $V=2282.6(4)$ Å³, $Z=4$. Extended Hückel molecular orbital calculations were performed on ReO_2 and ReO_3 fragments, as well as on selected Re compounds. ReO_2 is more stable in the *trans* arrangement and ReO_3 in the meridional one for d^2 species, while *cis* and *fac* are preferred for d^0 derivatives.

To be submitted to Inorganic Chemistry

Dioxo Rhenium(V) Complexes with Poly(pyrazolyl)borates.

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Abstract

By choosing properly the solvent and the ancillary ligand it is possible to prepare different dioxocomplexes. With dihydrobis(pyrazolyl)borates were prepared and fully characterized complexes of the type $[\text{ReO}_2\{\text{H}_2\text{B}(\text{pz}^*)_2\}]$ ($\text{pz}^*=\text{pz}$ (**1**) or 3,5-Me₂pz (**2**)) and with the tetrakis(pyrazolyl)borate it was stabilized $[\text{ReO}_2(\text{py})_4]\text{B}(\text{pz})_4$ (**3**). Compound **1** crystallizes in the triclinic space group P1 with cell parameters $a=9.422(1)$ Å, $b=9.579(1)$ Å, $c=7.998(1)$ Å, $\alpha=52.22(1)^\circ$, $\beta=73.62(1)^\circ$, $\gamma=72.72(1)^\circ$, $V=539.98(10)$ Å³, $Z=1$. Complex **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, $\beta=101.20(2)^\circ$, $V=3344.4(8)$ Å³, $Z=4$.

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Reactivity of $[\text{ReO}\{\eta^3\text{-B}(\text{pz})_4\}(\text{OMe})_2]$ with Heterocyclic Nitrogen Donor Ligands

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The reactivity of the complex $[\text{ReO}\{\eta^3\text{-B}(\text{pz})_4\}(\text{OMe})_2]$ (**1**) towards potentially bidentate protic substrates is well established.¹ By choosing properly the nature of the substrate it is possible to modulate the coordination mode of the tetrakis(pyrazolyl)borate. Deprotonation is always observed when protic oxygen donor ligands are used, but this not always happens with nitrogen donor ligands. These results led us to study the reactivity of **1** towards neutral heterocyclic nitrogen donor ligands, such as imidazoles and pyridines. The interaction of complex **1** with those substrates led to Re(V) adducts of the type $[\text{ReO}\{\eta^2\text{-B}(\text{pz})_4\}(\text{OMe})_2(\text{L})]$ (L = imzH, 1-Meimz, py, 4-Mepy, 4-NMe₂py) which, in solution, are in equilibrium with **1**. These equilibria depend on the basicity of the substrates and are under study by ¹H NMR spectroscopy.

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GAS PHASE CHEMISTRY

Reactivity of Lanthanide, Group 2, and Group 3 Metal and Metal Oxide Cations with Pentamethylcyclopentadiene: Gas Phase Synthesis of Cyclopentadienyl Cations

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Abstract

The gas phase reactivity of lanthanide ($\text{Ln}^+ = \text{La}^+ - \text{Lu}^+$), group 2 (Ca^+ , Sr^+ , and Ba^+), and group 3 (Sc^+ and Y^+) cations, and of their corresponding monoxide ions MO^+ , with pentamethylcyclopentadiene ($\text{C}_5\text{Me}_5\text{H}$) was studied by Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS). The reactivity of Eu^+ , Tm^+ , Yb^+ , and the alkaline earth metal ions was similar to that observed previously for Sm^+ , namely formation of the fulvenide ion $\text{M}(\text{C}_5\text{Me}_4\text{CH}_2)^+$ as main primary product and of the metallocene ion $\text{M}(\text{C}_5\text{Me}_5)_2^+$ as main secondary product. With Sc^+ , Y^+ , and the remaining lanthanide series ions, several other species were observed in the primary reactions, corresponding to single and multiple losses of neutral molecules such as H_2 and CH_4 . These differences in reactivity appear to correlate with the accessibility of reactive excited state electron configurations of the metal ions. In the case of the metal oxide cations MO^+ , the reactivity with pentamethylcyclopentadiene appears to be determined by the strength of the M^+-O bonds. The ions with the strongest bonds, LaO^+ , CeO^+ , PrO^+ , and NdO^+ formed $\text{M}(\text{C}_5\text{Me}_5)(\text{OH})^+$ as sole primary product, which reacted further, eliminating water, to give the metallocene ion $\text{M}(\text{C}_5\text{Me}_5)_2^+$. ScO^+ , YO^+ , and the lanthanide series ions SmO^+ , $\text{GdO}^+ - \text{TmO}^+$, and LuO^+ yielded $\text{MO}(\text{C}_5\text{Me}_4\text{CH}_2)^+$ and $\text{M}(\text{C}_5\text{Me}_4\text{CH}_2)^+$ as primary products in addition to $\text{M}(\text{C}_5\text{Me}_5)(\text{OH})^+$, and $\text{M}(\text{C}_5\text{Me}_4\text{CH}_2)_2^+$ and $\text{M}(\text{C}_5\text{Me}_5)_2^+$ as secondary products. The ions with the weakest $\text{M}^+ - \text{O}$ bonds, EuO^+ , YbO^+ , CaO^+ , SrO^+ , and BaO^+ , formed MOH^+ as a primary product and $\text{M}(\text{C}_5\text{Me}_5\text{H})^+$ as a secondary product.

Organometallics **16** (1997) 3845.

Gas Phase Actinide Ion Chemistry: FT-ICR/MS Study of the Reactions of Thorium and Uranium Metal and Oxide Ions with Arenes

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Abstract

Gas phase reactions of M^+ , M^{2+} , MO^+ ($\text{M} = \text{Th}$ and U), and UO_2^+ with several arenes (benzene, naphthalene, toluene, mesitylene, hexamethylbenzene, and 1,3,5-tri-*t*-butylbenzene) have been studied by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS). For M^+ ions C–H and/or C–C bond activation was observed in the primary reactions for all of the arenes studied. MO^+ and UO_2^+ ions yielded the adduct species, with the exceptions of the

reactions of MO^+ with hexamethylbenzene and 1,3,5-tri-*t*-butylbenzene for which bond activation products also formed. In the M^{2+} reactions charge transfer products dominated but formation of doubly charged bond activation products was also observed with all the arenes. Product distributions and reaction rate constants are reported and related to the electronic configurations of the reacting ions, the polarizabilities of the arenes and the energetics of the different reactions.

Organometallics **16** (1997) 4581.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Abstract

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR/MS) is a mass analysis technique that consists in the trapping and detection of ions in a region of space defined by homogeneous magnetic and electrical fields, and that has applications in the areas of analytical chemistry and physical chemistry.

Química **66** (1997) 32.

Gas Phase Reactions of Lanthanide Ions with Alcohols

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Abstract

The gas phase reactions of the lanthanide series ions La^+ - Lu^+ (except Pm^+) with methanol, ethanol and isopropanol were studied by FTICR/MS. The metallic ions were produced by laser ionisation of the corresponding metals and thermalised by collisions with argon, which was introduced in the instrument through pulsed valves; the reagents were introduced through a "leak valve".

All the lanthanide ions react exothermically with the alcohols, with formation of MO^+ and MOH^+ ions as main primary products, which participate in subsequent reactions that lead to $\text{M}(\text{OR})_x(\text{HOR})_y^+$ species, where $x = 1-2$ and $y = 0-3$. The results obtained for some of the lanthanide series ions show close similarities with those obtained by Geribaldi and co-workers with group 3 metal ions [1-2]. The detailed study of the reaction sequences and of the corresponding kinetics showed the existence of important differences in the relative reactivity of the metallic ions, in agreement with the known data on the reactivity of the lanthanide series ions with other organic molecules [3-6].

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Reactivity of Lanthanide Cations with Indene: Gas Phase Synthesis of Metal(Indenyl)⁺ Ions

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Abstract

The gas phase reactivity of lanthanide metal cations with indene was studied by FTICR/MS. The metal ions were produced by laser desorption/ionization of metal pieces and the organic reagent was admitted to the instrument through a leak valve; argon, introduced through pulsed valves, was used for collisional cooling of the reagent ions.

In the case of the less reactive metal ions, a single primary product, the indenyl ion (C₉H₇)M⁺, was observed, and as secondary product only the condensation product (C₉H₈)(C₉H₇)M⁺ formed. In the case of the more reactive metal ions, the main primary product was due to dehydrogenation of indene, (C₉H₆)M⁺, which then yielded the bis(indenyl) ion (C₉H₇)₂M⁺ in a secondary reaction.

The reactivity of the lanthanide ions with indene shows similarities with that previously observed for pentamethylcyclopentadiene [1-2]. Differences in the reactivity and the kinetics along the lanthanide series can be related, in the case of indene as well as in the case of pentamethylcyclopentadiene and of other hydrocarbons [3-4], to the accessibility of reactive excited state electron configurations of the metal ions.

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Communication to: *14th International Mass Spectrometry Conference*, Tampere, Finland (1997).

Gas Phase Reactivity of Lanthanide Oxide Cluster Ions

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Abstract

The gas-phase reactivity of lanthanide oxide cluster ions of the type Ln_xO_y^+ ($\text{Ln} = \text{La} - \text{Lu}$) [1-3] with unsaturated hydrocarbons and with small oxygenated molecules was studied by FTICR/MS. The lanthanide oxide cluster ions were produced by direct laser desorption/ionization of surface oxidized metal pieces or metal oxide pellets, and the reagents were admitted to the instrument through a leak valve; argon, introduced through pulsed valves, was used for collisional cooling of the reagent ions and also for CID studies.

2-butene was used as a model substrate for the reactivity studies with unsaturated hydrocarbons, involving oxide cluster ions of all the lanthanide series metals with different compositions. In all cases, no reactions with 2-butene were observed. For some cluster ions containing representative lanthanide series metals, the reaction with 1,4-cyclohexadiene, for which the formation of benzene plus hydrogen is by itself exothermic, was also tried, but again no reactions were observed.

The only process that could be detected in these studies was the sequential coordination to the cluster ions of water molecules, present in the background of the mass spectrometer; this observation prompted us to study the reactivity of several lanthanide ($\text{Ln} = \text{La}, \text{Pr}, \text{Eu}, \text{Tb}, \text{Ho}, \text{Tm}, \text{Lu}$) oxide cluster cations with O_2 , N_2O and H_2O . Oxidation reactions with O_2 and N_2O were observed for some cluster ions, while the reactivity with water corresponded only to adduct formation. Several effects of the formal metal valency in the cluster ions as well as of the cluster size on the reactivity and the kinetics could be observed.

These reactivity studies indicate that the lanthanide oxide cluster ions are closed-shell species with very stable structures, a fact that is corroborated by CID studies in which fragmentation of the cluster ions could only be observed for high excitation energies of the ions.

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Gas Phase Synthesis and Reactivity of MFe^+ Ions ($M = \text{Lanthanide, Actinide}$)

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Abstract

The formation of intermetallic ions involving metals of the f and d blocks was studied using FTICR/MS. In particular, the series of ions $LnFe^+$ ($Ln = \text{La} - \text{Lu}$), as well as $ThFe^+$ and UFe^+ , were synthesized by gas phase reaction of the metal ions, produced by laser ionization of pure metal pieces, with the volatile carbonyl complex $Fe(CO)_5$, followed by excitation and collision with argon of the $MFe(CO)_x^+$ ($x = 2-4$) product ions formed, a technique previously described by Freiser and co-workers [1-2].

Differences in the reactivity along the lanthanide series and between these elements and the actinides, previously observed in reactivity studies with hydrocarbon substrates [3-6], are also present in the reactions with $Fe(CO)_5$, with a larger reactivity corresponding to the formation of $MFe(CO)_x^+$ ions with a lower number of carbonyls.

The reactivity of the MFe^+ ions with small hydrocarbons was studied and comparisons are made with the reactivity of the "bare" metal ions.

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Gas Phase Reactivity of Rare Earth Cations with Phenols: Competitive Activation of C–O, O–H and C–H bonds

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Abstract

Recent work on the gas phase reactivity of rare earth cations, Sc^+ , Y^+ and Ln^+ ($Ln = \text{La} - \text{Lu}$), with substrates such as arenes [1-4] and alcohols [5-8] has shown that factors like the electron configurations of the metal ions and their oxophilicity play important roles in the observed chemistry. This prompted us to study the gas phase reactions of the rare earth cations with substrates where both the alcohol functionality and an aromatic ring are present. Therefore, the gas phase reactions of Sc^+ , Y^+ and Ln^+ ($Ln = \text{La} - \text{Lu}$) ions with phenol and 2,4,6-

trimethylphenol were studied by FTICR/MS. The metallic ions were produced by laser ionisation of the corresponding metals and were thermalised by collisions with argon; the reagents were introduced through leak valves.

All the ions reacted exothermically with both phenols, activating O-H, C-O or C-H bonds, with formation as primary products of MO^+ , MOH^+ and ions that resulted from the elimination of H_2 , MOC_6H_4^+ in the case of phenol and $\text{MOC}_9\text{H}_{10}^+$ in the case of 2,4,6-trimethylphenol. The primary product ions participate in subsequent reactions that lead to $\text{M}(\text{OR})_x(\text{HOR})_y^+$ species, where $x = 1-2$ and $y = 0-2$. The detailed study of the reaction sequences and of the kinetics of the various steps, showed important differences in the relative reactivity of the metallic ions.

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Reactivity in the Gas Phase of Transition Metal Oxide Cluster Anions

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Abstract

The gas phase transition metal ion chemistry has attracted considerable interest in recent years due to the important role play by these compounds in a variety of chemical and biochemical transformations (1,2). In this work, gas phase reactions of transition metal oxide anions ($[\text{M}_x\text{O}_y]^-$; $\text{M} = \text{Mn, Fe, Co, Ni, Cu}$; $x = 1-4$; $y = 2-4$) with methanol. were investigated by Fourier-transform ion cyclotron resonance mass spectrometry using a Extrel FTMS 2001-DT. The cluster anions were generated by laser desorption/ionization from the appropriate metal oxides and thermalised with argon or methane in order to remove possible excess internal/translational energy prior to the ion/molecule reactions. Rate constants were determined from the analysis of the pseudo-first-order kinetics. Reagent gases were introduced to the FTICR cell via pulsed or leak valves.

The MO_2^- , M_2O_3^- and M_2O_4^- cluster anions react exothermically with methanol leading to the MO_2H_2^- , $\text{M}_2\text{O}_3\text{H}_2^-$ and $\text{M}_2\text{O}_4\text{H}_2^-$ primary products, respectively. Secondary products for water elimination were observed at long reaction times. The dehydrogenation of methanol by the

MO_3^- and M_4O_4^- anions was not observed. The rate constants determined for the various reactions suggest that the M_2O_4^- ions react much more efficiently with methanol than the MO_2^- ion and that higher efficiencies were observed when the metal was iron. These results are in accordance with the conclusion that the reactivity of the bimolecular chemistry of metal-containing anions may be determined by the number of valence electrons (3). In order to discuss possible reaction mechanisms and the occurrence of isotope effects labelling studies were performed with D_4 -methanol or methanol labelled with deuterium in the hydroxyl group.

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Gas Phase Reactions of Lanthanide and Actinide Ions with Methanol and Ethanol

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Abstract

The gas phase reactions of the lanthanide series ions $\text{La}^+ - \text{Lu}^+$ (except Pm^+) and of the actinide series ions Th^+ and U^+ with methanol and ethanol were studied by FTICR/MS. The metallic ions were produced by laser ionisation of the corresponding metals and thermalised by collisions with argon, which was introduced in the instrument through pulsed valves; the reagents were introduced through a leak valve.

All the ions react exothermically with the alcohols, with formation of MO^+ and MOH^+ ions as main primary products, which participate in subsequent reactions that lead to other species involving oxo, hydroxo and alkoxo ligands, ending in ions of the type $\text{M}(\text{OR})_x(\text{HOR})_y^+$, where $x = 1-2$ and $y = 0-3$ in the case of the lanthanides, and $x = 3$ and $y = 0-2$ in the case of the actinides. In the case of uranium, the formation of the MO_2^+ ion was also observed, introducing differences in the reaction sequences relatively to thorium.

The results obtained for some of the lanthanide series ions show close similarities with those obtained by Geribaldi and co-workers with group 3 metal ions [1-2]. The detailed study of the reaction sequences and of the corresponding kinetics showed the existence of important differences in the relative reactivity of the metallic ions, in agreement with the known data on the reactivity of the lanthanide and actinide series ions with other organic molecules [3-8].

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Communication to: *3º Encontro Nacional de Espectrometria de Massa*, Lisboa (1997).

Reactivity in the Gas Phase of Transition Metal Oxide Cluster Ions

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Abstract

The chemistry of metal oxide clusters has attracted considerable attention due to the important role that these compounds play in a number of fields ranging from catalysis to microelectronics.^{1,2} Moreover, the knowledge of the intrinsic properties and the reactivity of metal oxide clusters in the gas phase are an important contribute to a better understanding of the condensed phase behaviour of these compounds.

In this work, the reactivity of transition metal oxide cluster ions ($[M_xO_y]^\pm$; M = Mn, Fe, Co, Ni, Cu; x = 1-4; y = 2-4) towards various organic compounds were investigated by Fourier-transform ion cyclotron resonance mass spectrometry using a Finnigan FTMS 2001-DT. The cluster ions were generated by laser desorption/ionization from appropriate metal oxides pellets and thermalised with argon or methane in order to remove possible excess of internal/translational energy prior to the ion/molecule reactions. Rate constants were determined from the analysis of the pseudo-first-order kinetics. Reagent gas was introduced to the FTICR cell via leak valves and the pressure maintained at 6×10^{-8} torr.

The $[MO_2]^-$, $[M_2O_3]^-$ and $[M_2O_4]^-$ cluster anions react exothermically with methanol leading to the $[MO_2H_2]^-$, $[M_2O_3H_2]^-$ and $[M_2O_4H_2]^-$ anions as primary products, respectively. The dehydrogenation of methanol by the $[MO_3]^-$ and $[M_4O_4]^-$ cluster anions was not observed. The rate constants determined for the various reactions suggest that the $[M_2O_3]^-$ and $[M_2O_4]^-$ cluster anions react much more efficiently with methanol than the $[MO_2]^-$ anion and on the other hand that reaction efficiencies decrease when the metal vary from iron to copper. These results are in accordance with previous reports in that the reactivity of the bimolecular processes involving metal-containing anions may be determined by the electronic configuration of the metals.³

The experimental studies of the reactions of $[M_xO_y]^+$ cluster cations with different substrates are yet in progress.

In order to discuss reaction mechanisms and the occurrence of intramolecular isotope effects studies were performed using labelled compounds and molecular orbital calculations using the density functional theory (DFT)⁴ approach were carried out to establish the structures and stability of the clusters under study.

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Communication to: *3º Encontro Nacional de Espectrometria de Massa*, Lisboa (1997).

Gas Phase Synthesis and Reactivity of MFe^+ Ions (M = Lanthanide, Actinide)

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Abstract

The formation of intermetallic ions involving metals of the f and d blocks was studied using FTICR/MS. In particular, the series of ions $LnFe^+$ ($Ln = La - Lu$), as well as $ThFe^+$ and UFe^+ , were synthesized by gas phase reaction of the metal ions, produced by laser ionization of pure metal pieces, with the volatile carbonyl complex $Fe(CO)_5$, followed by excitation and collision with argon of the $MFe(CO)_x^+$ ($x = 2-4$) product ions formed, a technique previously described by Freiser and co-workers [1-2].

Differences in the reactivity along the lanthanide series and between these elements and the actinides, previously observed in reactivity studies with hydrocarbon substrates [3-6], are also present in the reactions with $Fe(CO)_5$, with a larger reactivity corresponding to the formation of $MFe(CO)_x^+$ ions with a lower number of carbonyls, as can be seen in Table 1.

Table 1. Primary Product Distributions in the Reactions $M^+ + Fe(CO)_5$ (%)

M^+	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
$MFe(CO)_2^+$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	80	43
$MFe(CO)_3^+$	100	100	100	100	24	0	100	100	8	13	24	0	0	67	20	57
$MFe(CO)_4^+$	0	0	0	0	76	100	0	0	92	87	76	100	100	33	0	0

The reactivity of selected MFe^+ ions with small hydrocarbons was studied and comparisons are made with the reactivity of the "bare" metal ions.

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Gas Phase Reactions of Thorium and Uranium Ions with Alcohols

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Abstract

As part of a research programme to study the reactivity of lanthanide [1] and actinide metal ions [2] towards organic substrates, the gas phase reactions of the actinide ions Th⁺ and U⁺ with methanol, ethanol and phenol were studied by FTICR/MS. The metallic ions were produced by laser ionization of the corresponding metals and thermalised by collisions with argon, which was introduced in the instrument through pulsed valves; the reagents were introduced through a "leak valve".

Both ions react exothermically with the alcohols and O-H, C-O and C-H bond activations were observed. The MO⁺ and MOH⁺ ions were the main primary products and other species, involving oxo, hydroxo and alkoxo ligands were formed on subsequent reactions, ending in ions of the type M(OR)₃(HOR)_x⁺. Species with 4 alkoxo ligands were obtained for uranium, with a formal oxidation state 5, however further experiments are needed to confirm if the parent ions were thermalised. In the case of uranium the formation of the MO₂⁺ ion was observed but the analogous species was not obtained for thorium and therefore the reaction sequences were different.

¹ Yin, W. W.; Marshall, A. G.; Marçalo, J.; Pires de Matos, A. *J. Am. Chem. Soc.* **1994**, *116*, 8666.

² Marçalo, J.; Leal, J. P.; Pires de Matos, A. *Int J. Mass Spectrom. Ion Processes* **1996**, *157/158*, 265.

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Gas-Phase Reactivity of Rare Earth Cations with Phenol: Competitive Activation of C–O, O–H, and C–H bonds

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Abstract

The gas-phase reactions of Sc⁺, Y⁺, and Ln⁺ (Ln = La - Lu, except Pm) ions with phenol were studied by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS). All the ions except Yb⁺ were observed to react with the organic substrate, activating O–H, C–O, and/or C–H bonds, with formation of MO⁺, MOH⁺, and/or MOC₆H₄⁺ ions as primary products. The product distributions and the reaction efficiencies obtained showed the existence of important differences in the relative reactivity of the rare earth metal cations, which are discussed in terms of factors like the electron configurations of the metal ions, their oxophilicity, and the second ionization energies of the metals. The primary product ions

participated in subsequent reactions, yielding species such as $M(OH)(OC_6H_5)^+$, which lead mainly to $M(OC_6H_5)_2(HOC_6H_5)_n^+$ ions, where $n = 0-2$. Formation of $M(OC_6H_5)(HOC_6H_5)_n^+$ species was also observed in the case of the metals which have high stabilities of the formal oxidation state 2+, Sm and Eu.

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Current Work

Gas Phase Studies of Lanthanide Chloride Ions

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The formation and reactivity in the gas phase of lanthanide (Ln = Pr, Sm, Dy, Yb) chloride cations was studied by FT-ICR/MS. The ions were produced by direct laser desorption/ionization of anhydrous metal trichloride pellets and had the composition Ln_xCl_y^+ , with $x = 1, y = 1, 2$, and $x = 2, y = 3-5$. For the reactivity studies, the reagents were admitted to the mass spectrometer through a leak valve and argon was used for collisional cooling of the reagent ions. The overall reactivity of these lanthanide chloride cations towards hydrocarbons was probed employing 1,4-cyclohexadiene ($c\text{-C}_6\text{H}_8$) and 1-butene (C_4H_8); with $c\text{-C}_6\text{H}_8$ both H_2 -elimination and adduct formation reactions were observed, while C_4H_8 was unreactive. Side reactions with residual water were also observed.

Reactivity of Transition Metal Oxide Cluster Cations in the Gas Phase

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Laser desorption/ionization FT-ICR/MS was used to produce and characterize first-row transition metal oxide cations of the type M_xO_y^+ , with $\text{M} = \text{Mn, Fe, Co, Ni}$ and Cu . Metal oxide pellets were used as targets and argon was used for collisional cooling of the reagent ions. Methanol was used to probe the reactivity of these species, namely the effects of the nature of the metal and of cluster size in the reaction products formed and in the kinetic efficiencies.

THERMOCHEMISTRY

Chemical Ionization Mass Spectrometry Study of Some Monoterpenes

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Abstract

Monoterpenes are emitted into the atmosphere from vegetation in a large scale. Their tropospheric chemistry therefore has been investigated, in particular the interaction with ozone [1,2]. Their impact in nitrogen cycle has been also under study [3]. On the other hand these important natural products are extensively employed in industry.

Their relevance led to mass spectrometry studies in order to characterize them and clarify their chemistry in the gas phase. Nevertheless some difficulties were found, in electron impact ionization studies, resulting from isomerization, to a common structure, of long lived molecular ions [4,5].

In this work chemical ionization mass spectra of some monoterpenes were performed in a Fourier Transform Ion Cyclotron Resonance mass spectrometer after the optimization of the experimental conditions being established. Furthermore some irradiation and collision induced decomposition experiments were carried out to examine the main fragmentation and ion formation routes under those ionization conditions.

The outcome of this study pointed out the possibility of characterization of some monoterpenes under chemical ionization conditions as well as the preferential paths of ion formation.

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Communication to: *3º Encontro de Espectrometria de Massa da SPQ*, Lisboa (1997).

Energetics of Compounds of Alkaline and Alkaline-Earth Metals

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Abstract

Using a somehow large amount of enthalpies of formation for alkaline salts of alcohols, thiols, amines and cyclopentadienyls determined in our laboratory an effort was made to have an integrated idea of them, the chances to develop a estimation method for new alkaline, alkaline-earth and lanthanide species and, when possible, their relationship to the structural aspects of the compounds.

Communication to: *3º Encontro Nacional de Química-Física da Sociedade Portuguesa de Química*, Monte de Caparica, Portugal (1997).

Standard Enthalpy of Formation of Lithium, Sodium and Potassium Cyclopentadienyls

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Abstract

Cp ligand can be viewed as the most significant one on the organometallic chemistry of the past decades. In reactional schemes it is used as an alkaline metal or thallium salt. In this communication the enthalpies of formation of lithium, sodium and potassium cyclopentadienyls are measured using a reaction-solution calorimeter. The lattice energies were also calculated in order to test an estimation method for the unknown enthalpies of formation of other compounds.

Communication to: *3º Encontro Nacional de Química-Física da Sociedade Portuguesa de Química*, Monte de Caparica, Portugal (1997).

Current Work

Enthalpy of Formation of Alkaline Metal Thiolates

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Some sodium and potassium thiolates have been synthesized and the appropriate reactions for calorimetric study were defined. The first results of formation enthalpies are obtained:

Compound	ΔH_f° (kJ/mol)
NaSEt	-198±10
KSEt	-235±10
CsSEt	-245±10

Equilibrium Studies of Phenols in Gas Phase

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Gas phase acidity of p-t-BuPhOH was determined as well as the electroacidity of PhOH, p-t-BuPhOH and Vitamin E (α -Tocopherol).

Enthalpy of Formation of Lanthanide or Actinide-Transition Metal Binary Intermetallic Compounds

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The first compounds were synthesized and the measurement reaction defined (reaction of the intermetallic compound with 5M hydrochloric acid). The first results of formation enthalpies are obtained for a known compound (UFe_2) and are in a good agreement with the literature values:

Source	ΔH_f° (kJ/mol)
Our results	-22±9
1	-44±15
2	-32±8

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SURFACE STUDIES

Adsorption of Azides on Ag (111)

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Abstract

Azide compounds are used in biology [1], as seismic explosives [2], in superconductors [3], etc. Due to their instability, the mechanisms of their decompositions are largely unknown. The control of the decompositions, either in the gas phase or in gas-surface interface, is difficult to achieve. There is a need to characterise the decompositions in much more detail. The analysis of the decomposition occurring after adsorption on surface is of scientific, and technological interest. Preliminary results of azides adsorption on Ag (111) will be presented. Experiments (XPS, AES, SIMS) have been carried out at room temperature. Comparison with gas phase results (UPS) [4] will be discussed.

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XPS Analysis of Krytox Liquid Film

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Abstract

A liquid sample of PFPE, with the commercial designation of Krytox 16256, was characterized by XPS (X-ray Photoelectron Spectroscopy) in a multitechnique system conceived for surface studies (SIMS/AES/XPS/ESS/ESD) [1]. As the liquid PFPE ($\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_{63}\text{CF}_2\text{CF}_3$) has a vapour pressure of 10^{-15} mbar, at room temperature, it can be studied in this system with a working pressure of 10^{-9} mbar. XPS spectra were run with an angle of 20 degrees measured in function of the normal that is formed between the surface and the analyser. The analysis of the spectra shows the character of the bonds in the molecule. The spectra concerning the O 1s and F 1s orbitals present only one peak. However, concerning the

C 1s orbital, the spectrum obtained presents three peaks which reflects the existence of three different neighbourhood of the carbon atoms at the molecule.

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Ultra High Vacuum Sample Holder

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Abstract

A project of a sample holder which allows quick cycles of cooling and heating, in the temperature range 77-1300 K, in UHV, will be presented. The properties of the system will allow to perform surface studies with different techniques, e.g., XPS- X-Ray Photoelectron Spectroscopy; AES- Auger Electron Spectroscopy, ESD- Electron Stimulated Desorption, TDS- Thermal Desorption Spectroscopy [1]. The sample holder will allow to do the annealing of crystals, such as silicium, *in situ*. The heating is done by electronic bombardment. The cooling system is of the "cold finger" type, using nitrogen as cooling liquid. In the conditions mentioned above the cycles will take about 10 minutes to be achieved. Results concerning the preliminary tests of the system in a UHV camera will be presented.

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