

coordinate the Ru-atom during the crystallization of the product.

[1] (a) J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus, A.H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791. (b) S.B. Garber, J.S. Kingsbury, B.L. Gray, A.H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168. (c) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 9973. [2] IUPAC Gold Book <http://goldbook.iupac.org/M03878.html> [PAC, 1994, *66*, 1077 (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*) on page 1139] (25.05.2009). [3] A. Szadkowska, A. Makal, K. Woźniak, R. Kadyrov, K. Greła, *Organometallics* **2009**, *28*, 2693. [4] A. Szadkowska, K. Zukowska, A. Pazio, K. Woźniak, R. Kadyrov, K. Greła, *Organometallics* **2011**, *30*, 1130–1138.

**Keywords:** crystal structure analysis, metalloorganic catalysts, metathesis

## MS31.P16

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### Aluminium hydroxide molecular derivatives. Stabilization and structural characterization

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Group 13 elements attracts wide attention not only because of its rich chemistry, but also due to the important applications that those elements exhibit in areas as diverse as organic synthesis, electronic materials, structural materials and catalysis.<sup>1</sup> In particular, aluminium derivatives play an essential role in a vast array of catalytic reactions. As an example, aluminoxanes acting as co-catalysts constitute a key part in the Ziegler-Natta olefin polymerization processes being one of the more important activators in industrial processes.<sup>2</sup> As well, aluminium alkoxide complexes have shown to be very active catalysts in ring opening polymerization reactions.<sup>3</sup>

Aluminoxanes are derivatives of general formula  $[AlRO]_n$  or  $[R_2AlOAlR_2]_n$ , and can be considered as intermediates in the hydrolysis of organometallic aluminium compounds to aluminium oxide. It is possible to prepare them by the controlled reaction of aluminium alkyl derivatives with water or O-donor reactive species. [4]. Many controlled hydrolysis studies have been done and during these investigations some aluminoxane species could be isolated, by using bulkier groups than methyl [5]. However, none of these prepared species are co-catalysts as efficient as methylaluminoxane (MAO) for olefin polymerization. As such, design and synthesis of new aluminium derivatives able to behave as co-catalyst is still an open challenge.

In this context, we have prepared a series of alkyl and hydride derivatives of aluminium with functionalized aryloxy groups. We have carried out controlled hydrolysis on these species. These studies have allowed us to isolate new species such as the molecular hydroxide compound shown in figure 1.

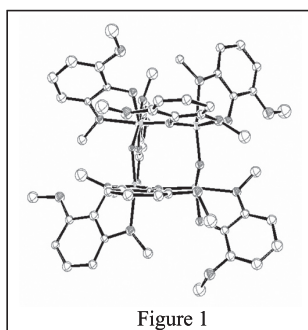


Figure 1

[1] A.J. Downs, ed., *Chemistry of Aluminium, Gallium, Indium and Thallium*, Blackie Academic, Glasgow, **1993**; J. Ni, H. Yan, A.C. Wang, Y. Yang, C.L. Stern, A. Metz, S. Jin, L. Wang, T.J. Marks, J.R. Ireland, C.R. Kannewurf, *J. Am. Chem. Soc.* **2005**, *127*, 5613; P.P. Power, *Chem. Rev.* **1999**, *99*, 3463; C.N.R. Rao, F.L. Deepak, G. Gundiah, A. Govindaraj, *Progress in Solid State Chemistry* **2003**, *31*, 5. [2] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99; E.Y.-X. Chen, T.J. Marks, *Chem. Rev.* **2000**, *100*, 1391. [3] T.

Kitayama, H. Yamaguchi, T. Kanzawa, T. Hirano, *Polym. Bull.* **2000**, *45*, 97; M. H. Chisholm, J. Gallucci, D. Navarro-Llobet, H. S. Zhen, *Polyhedron* **2003**, *22*, 557; T. A. Zevaco, J. Sypien, A. Janssen, O. Walter, E. Dinjus, *Catal. Today* **2006**, *115*, 151. [4] M.R. Mason, J.M. Smith, S.G. Bott, A.R. Barron, *J. Am. Chem. Soc.* **1993**, *115*, 4971; R.J. Wehmschulte, P.P. Power, *J. Am. Chem. Soc.* **1997**, *119*, 8387; H.W. Roesky, M.G. Walawalkar, R. Murugavel, *Acc. Chem. Res.* **2001**, *34*, 201. [5] M. Watanabi, C.N. McMahon, C.J. Harlan, A.R. Barron, *Organometallics* **2001**, *20*, 460; G. Bai, S. Singh, H.W. Roesky, M. Noltmeyer, H.-G. Schimidt, *J. Am. Chem. Soc.* **2005**, *127*, 3449.

**Keywords:** aluminum, catalysis, polymerization

## MS31.P17

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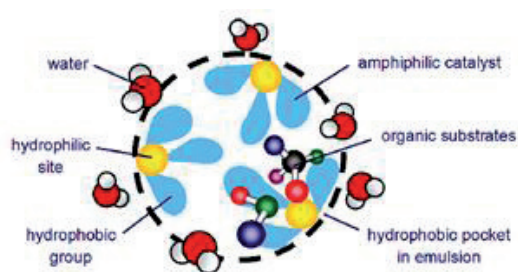
### Structural effects of amphiphilic dendritic organocatalysts in aldol reactions

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Three series of surfactant-like chiral amphiphilic dendritic organocatalysts containing an optically active polar proline-derived core and one or two nonpolar hydrocarbon dendrons were prepared. These dendritic organocatalysts were employed in the asymmetric aldol additions in oil-in-water emulsions to reveal the effects of dendron size and branching on the catalytic properties. [1] The incorporation of larger hydrophobic dendrons [2] has the advantages of promoting emulsion formation in water, improving the reaction enantioselectivity, decreasing catalyst loading (to 1 mol %), and facilitating catalyst recovery after the reactions.

Inside the hydrophobic pocket, the reaction proceeds in a concentrated organic phase generated by the organic substrates and the surfactant-like organocatalyst inside the emulsion droplets. The structural effects of the size and shape of the surfactant appendages were found to have different results on the micelle formation efficiency and the catalytic properties in the asymmetric aldol reactions. In general, the larger dendrons tended to lower catalyst reactivity due to their increasing steric blocking effect. However, some astonishing observations were found in some of the G1 and G2 dendritic organocatalysts, wherein an increase in the steric bulkiness and branching of the dendron resulted in better catalyst reactivity. It was also found that higher product yields and enantioselectivities were obtained in the aldol reactions when the aromatic aldehyde contains an electron-withdrawing substituent.

The catalysts could be recycled and reused five times in the asymmetric aldol reactions without significant drop in product yields and enantioselectivities. In addition, cross product contamination was not found when the recovered G3 catalyst was subsequently used in another reaction involving different substrates.



[1] C.-M. Lo, H.-F. Chow *J. Org. Chem.* **2009**, *74*, 5181-5191. [2] H.-F. Chow, K.-F. Ng, Z.-Y. Wang, C.-H. Wong, T. Luk, C.-M. Lo, Y.-Y. Yang, *Org. Lett.* **2006**, *8*, 471-474.

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## MS31.P18

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### Potential Pt-complexes for catalytic water splitting

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To meet the ever-growing demand for green and carbon neutral energy, water splitting for the generation of hydrogen fuel represents an appealing strategy. Platinum is currently being investigated to mediate mono-nuclear water splitting reactions in an effort to understand the fundamental steps of O-H and O-O bond activation. This research is directed at synthesizing and studying plausible organometallic intermediates (Pt-OH and Pt-H species) in order to determine what role they play in the water activation process. The crystal structures of the following complexes will be presented:

(I)  $C_{79}H_{88}N_2$ ; MW = 1065.51; T = 100 K;  $\lambda = 1.54178 \text{ \AA}$ ; triclinic; P 1; a = 10.4847(2), b = 10.8571(3), c = 14.8431(3)  $\text{\AA}$ ,  $\alpha = 77.447(1)$ ,  $\beta = 82.283(1)$ ,  $\gamma = 85.908(1)^\circ$ , V = 1632.76(6)  $\text{\AA}^3$ ; Z = 1;  $D_c = 1.084 \text{ Mg/m}^3$ ; u = 0.460  $\text{mm}^{-1}$ ; F(000) = 576; R [ $I > 2\sigma(I)$ ] = 0.0589; twin fraction = 0.46(10).

(II)  $C_{92}H_{102}ClN_3O_3Pt$ ; MW = 1528.31; T = 173 K;  $\lambda = 0.71073 \text{ \AA}$ ; triclinic; P -1; a = 11.9160(4), b = 17.2432(4), c = 21.2196(7)  $\text{\AA}$ ,  $\alpha = 77.787(2)$ ,  $\beta = 87.935(1)$ ,  $\gamma = 74.098(2)^\circ$ ; V = 4097.1(2)  $\text{\AA}^3$ ; Z = 2;  $D_c = 1.239 \text{ Mg/m}^3$ ; u = 1.794  $\text{mm}^{-1}$ ; F(000) = 1588; R [ $I > 2\sigma(I)$ ] = 0.0761.

(III)  $C_{85}H_{101}ClN_2O_4Pt$ ; MW = 1445.22; T = 173 K;  $\lambda = 0.71073 \text{ \AA}$ ; triclinic; P -1; a = 10.8290(1), b = 19.6712(4), c = 20.7832(4)  $\text{\AA}$ ,  $\alpha = 63.472(1)$ ,  $\beta = 77.109(1)$ ,  $\gamma = 74.190(1)^\circ$ ; V = 3784.73(11)  $\text{\AA}^3$ ; Z = 2;  $D_c = 1.268 \text{ Mg/m}^3$ ; u = 1.939  $\text{mm}^{-1}$ ; F(000) = 1504; R [ $I > 2\sigma(I)$ ] = 0.0382.

(IV)  $C_{83}H_{96}N_4O_8Pt$ ; MW = 1472.73; T = 173 K;  $\lambda = 0.71073 \text{ \AA}$ ; triclinic; P -1; a = 11.0942(6), b = 11.0872(5), c = 16.7892(7)  $\text{\AA}$ ,  $\alpha = 98.593(3)$ ,  $\beta = 99.870(3)$ ,  $\gamma = 110.025(2)^\circ$ ; V = 1862.6(2)  $\text{\AA}^3$ ; Z = 1;  $D_c = 1.313 \text{ Mg/m}^3$ ; u = 1.941  $\text{mm}^{-1}$ ; F(000) = 764; R [ $I > 2\sigma(I)$ ] = 0.0670; Flack parameter = 0.100(11).

The ligand was made to be "super" bulky to prevent dimerization (in an attempt to study mono-nuclear water splitting). The nitro and chloro complexes were made as precursors to making the hydroxide compound.

**Keywords:** organometallic, intermediates, catalysts

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### XRD, SAXS and XANES studies of mesoporous zirconia-based materials

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The synthesis of ordered mesoporous zirconia based structures

for catalytic applications is a research area under development. These systems are also potential candidates as anodes in intermediate temperature solid oxide fuel cells [1-3]. Ordered mesoporous zirconia can be formed with a polymeric template, but during the calcination process the amorphous walls crystallize, causing the collapse of the ordered network [3]. Nevertheless, many synthesis strategies can be explored in order to attain high surface areas (50-100  $\text{m}^2/\text{g}$ ), even in disordered porous networks. In this work the zirconia based materials were prepared with ZrCl<sub>4</sub>, Pluronic P123, ethanol and water, varying some synthesis parameters. SAXS, XRD, and XANES at Zr L<sub>2</sub> and L<sub>3</sub> edges were performed to characterize the samples.

For samples heated in water vapor, the SAXS results showed that the ordered mesoporous structure vanished after calcination. The XRD data revealed a single tetragonal zirconia crystalline wall, free of chloride species after a 400°C calcination process. On the other hand, the SAXS data related to the sample that remained in an autoclave for 48 hours, showed a partially ordered structure after calcination. The XRD results showed a mixture of tetragonal and monoclinic phases, besides chloride species that did not decompose at 540°C. The use of a less acidic precursor solution overcame this problem.

In order to study probable changes on the Zr first shell in pure ZrO<sub>2</sub> samples prepared by different synthesis processes, XANES data were collected by TEY at Zr L<sub>2,3</sub> edges at the D04A/SXS beamline of LNLS (Brazil). ZrO<sub>2</sub> monoclinic standard (coordination number, CN=7), BaZrO<sub>3</sub> and ZrSiO<sub>4</sub> standards (CN equal to 6 and 8, respectively) were measured. A calibration curve was built, fitting each spectrum of the Zr L<sub>3</sub> edge and taking the energy split of the molecular orbitals. The sample synthesized with hydrothermal treatment in water vapor and calcinated at 400°C should present a CN close to 8, since its XRD data revealed a tetragonal structure, but the XANES analysis showed a CN close to 7. Previous XAS results of nanocrystalline tetragonal zirconia at Zr K edge showed a lower coordination number, related to the high disorder of the O atoms in Zr first shell [4,5], in agreement with the present work. For the samples calcinated at 540°C the mixture of crystalline phases detected by XRD are in agreement with the obtained CN close to 7.

[1] D.Y. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science* **1998**, *279*, 548-552. [2] C. Yu, Y. Yu, D. Zhao, *Chem. Comm.* **2000**, 575-576. [3] M. Mamak, N. Coobs, G. Ozin, *J. Am. Chem. Soc.* **2000**, *122*, 8932-8939. [4] I.O. Fábregas, R.O. Fuentes, D.G. Lamas, M.E.F. De Rapp, N.E. Walsöe de Reça, M.C.A. Fantini, A.F. Craievich, R.J. Prado, R.P. Millen, M. Temperini, *J. Phys. Condens. Mater.* **2006**, *18*, 7863-7881. [5] L.M. Acuña, D.G. Lamas, R.O. Fuentes, I.O. Fábregas, M.C.A. Fantini, A.F. Craievich, R. J. Prado, *J. Appl. Cryst.* **2010**, *43*, 227-236.

**Keywords:** zirconia, porous, XANES.

## MS31.P20

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### Structure/activity relationships: pre-catalysts for alkene methoxycarbonylation

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Catalytic reactions in which the elements of carbon monoxide (CO) and water / alcohols are added to the double bond of alkenes are referred to as hydrocarbonylations / alkoxy carbonylations [1]. Palladium / phosphine systems are generally the preferred catalysts in these reactions since they work under relatively mild conditions [1]. The regioselectivity (linear to branched ratio) of these Pd-catalyzed reactions has been extensively investigated for styrene and related vinylarenes aimed at the synthesis of non-steroidal anti-inflammatory