

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

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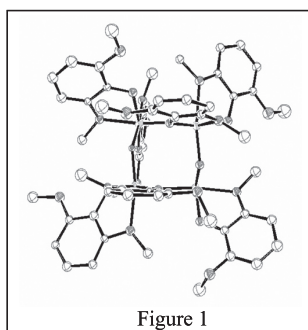
Aluminium hydroxide molecular derivatives. Stabilization and structural characterization

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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.¹ 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.² As well, aluminium alkoxide complexes have shown to be very active catalysts in ring opening polymerization reactions.³

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.



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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.

