The Design of Non-Metallocene Analogues as Polymerization Catalysts

By

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ABSTRACT

The main aim of this project was to prepare novel "non-metallocene" complexes and to test their ability to act as catalysts for the polymerisation of ethylene.

To do this, firstly, two new polyamine ligands, 1,4-bis(2-aminophenyl)piperazine **L2** and 1,7-bis(2-aminophenyl)-1,4,7,10-tetraazacyclododecane **L5** have been prepared and fully characterised. A preliminary investigation into the co-ordination chemistry of these potentially tetra- and hexa-dentate ligands with first row transition metals, such as Ti, Zr and Nb have been studied.

L2 has been silylated at the aniline nitrogens by treatment with n-BuLi and Me_3SiCl to give 1,4-bis(2-trimethylsilylaminophenyl)piperazine **L3** in good yield. The co-ordination of L3, as it's dianion, with $TiCl_4$, $ZrCl_4$.2thf and $NbCl_4$.2thf has been investigated. However, no tractable metal complex was formed with Ti(IV), while the Zr and Nb systems resulted in the elimination of Me_3SiCl in solution and deposition of **L2**, as shown by ^{1}H-NMR.

Secondly, with the aim of testing suitable oxalic amidine 'non-metallocene' type catalyst system to use with co-catalysts of methylaluminoxane (MAO) and selected Lewis acids, in polymerization of ethylene has been studied.

The oxalic amidine ligand $C_6H_5N{=}C(\ NH^tBu)\text{-}C(\ NH^tBu\ ){=}NC_6H_5$ **L6** and $C_6H_5N{=}C[N(^tBu)(SiMe_3)]\text{-}C[N(^tBu)(SiMe_3)]{=}NC_6H_5$ **L7** are described. Treatment of **L6** with $Ti(NMe_2)_4$ gives bimetallic complex of $[Ti(NMe_2)_3.C_6H_5N.C.(N^tBu)\text{-}]_2$ **C8**. The activity towards ethylene polymerization has been investigated for ligand **C8**.

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