Synthesis of Neutral Dimethylaluminum Complexes Bearing Imino-Phenoxide Ligands

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Synthesis of neutral dimethylaluminum complexes ligated by bidentate N,O salicylaldimine ligands is reported. Treatment of the imino-phenoxide ligands 3-R-2-(OH)C_6H_3CH=N(2,6-i$Pr_2C_6H_3$) [R = 9-anthracenyl (**1a**) and 1-naphthyl (**1b**)] with Al(CH_3)$_3$ in toluene affords the corresponding yellow dimethylaluminum compounds {3-R-2-(OH)C_6H_3CH=N(2,6-i$Pr_2C_6H_3$)}Al(CH_3)$_2$ [R = 9-anthracenyl (**2a**) and 1-naphthyl (**2b**)] in high yields. Reactions cleanly proceed by protodealumination of the Al-CH_3 bond with concomitant elimination of methane. Toluene solutions of **2a-b**, when activated with 1 equivalent of B(C_6F_5)$_3$, polymerized ethylene to solid polyethylene with low activity.

Key Words: Organometallic, Salicylaldimine, Phenoxy-imine, Aluminum, Complex, Ligand.

INTRODUCTION

Transition metal mediated olefin polymerization catalysts have grown dramatically over the past half a century and they have been the main cause behind the development of the polyolefin industry. Well-defined distinct molecular catalysts equipped with appropriately designed organic ligands have allowed researchers to understand and even control the reactivity and the selectivity of olefin polymerizations in a rational manner, which was unattainable with the traditional ill-defined Ziegler-Natta catalysts[1]. Because of this the discovery of metallocene catalysts is such a big breakthrough within the development of olefin polymerization catalysis.

Post-metallocene catalysts[2] have sterically and electronically offered a much higher degree of freedom for catalyst design than metallocene catalysts. Hence these catalysts have offered further diversity and opportunities for the development of olefin polymerization catalysis. Among the post-metallocene catalysts developed, salicylaldimine (sal) ligands[3] (Fig. 1) possess a particularly large diversity of structures because of their straightforward synthesis and modular properties. Such variability has led to remarkable progress in phenoxy-imine based catalyst development.
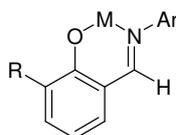

Fig. 1. Sal (phenoxy-imine) framework

Additionally, upon complexation within the sal framework, the substituents (particularly R and Ar, Fig. 1) are properly situated around the metal center for strategically controlling the polymerization reactions. Furthermore, these ligands are structurally flexible due to the labile imine donors and, therefore, can be electronically flexible, too, allowing phenoxy-imine ligands to show both electron-receptive and electron-donating properties, depending on the state of the metal center[4]. These inherent features pertaining to phenoxy-imine ligands have resulted in their great ability to be olefin polymerization catalysts independent of the early to late transition metal centers.

In recent years there has been great interest in the chemistry of transition metal complexes of Schiff bases[5], since these ligands offer opportunities for inducing substrate chirality, tuning the metal-centered electronic factor and enhancing the solubility and stability of either homogeneous or heterogeneous catalysts[6]. Moreover, the Schiff base complexes have become increasingly important as biochemical, analytical and antimicrobial reagents[7]. Salicylaldimine ligands have also been employed to afford olefin polymerization catalysts for aluminum[8], group IV[9], group VI[10] and group X[11] metal systems.

Salicylaldimine ligand is usually reacted with B(C_6F_5)$_3$ in hydrocarbon or THF solvent to generate stable cationic aluminum alkyls[8]. These cationic species are highly electrophilic and therefore more active as olefin polymerization catalysts.

As part of our research investigation into the coordination chemistry of these novel ligand platforms, we describe herein the synthesis of neutral dimethylaluminum complexes

carrying bidentate sal ligands and their activity in ethylene polymerization.

Synthesis of {3-(9-anthracenyl)-2-(O)C$_6$H$_3$CH=N(2,6-iPr$_2$C$_6$H$_3$)}Al(CH$_3$)$_2$ (2a): Trimethylaluminium solution (169 μL, 0.337 mmol, 2.0 M in toluene) was slowly added to a solution of 3-(9-anthracenyl)-2-(OH)C$_6$H$_3$CH=N(2,6-iPr$_2$C$_6$H$_3$) (147 mg, 0.321 mmol) in toluene (5 mL) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 12 h. The volatiles were then removed under reduced pressure, to afford **2a** as a yellow solid in 88 % yield (145 mg). The ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 8.33 (s, Anth-C10-H, 1H), 8.15 (s, CH=N, 1H), 8.13 (d, J = 7.6 Hz, Anth-C4,5-H, 2H), 7.95 (d, J = 7.1 Hz, Anth-C1,8-H, 2H), 7.48 (d, J = 7.3 Hz, OAr-H, 1H), 7.43-7.28 (m, Anth-C2,3,6,7-H and OAr-H, 5H), 7.19-7.06 (m, NAr-H, 3H), 6.84 (t, J = 7.5 Hz, OAr-H, 1H), 3.31 [(sept, J = 6.7 Hz, CH(CH$_3$)$_2$, 2H)], 1.29 [(d, J = 6.8 Hz, CH(CH$_3$)$_2$, 6H)], 1.06 [(d, J = 6.8 Hz, CH(CH$_3$)$_2$, 6H)], -0.49 [(s, Al(CH$_3$)$_2$, 6H)]; ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 174.1 (CH=N), 164.8 (C-O), 142.7 (C-N), 135.9 (NArC-iPr), 134.2, 132.8 (both OArC-4,6), 131.6, 129.5, 129.0, 128.9, 128.44, 128.3, 127.4, 126.7, 126.5 (all Anth-C and OArC-3), 126.0, 125.1 (both NArC-3,4), 120.2 (OArC-5), 118.6 (OArC-1), 29.1 [CH(CH$_3$)$_2$], 26.6 [CH(CH$_3$)$_2$], 23.2 [CH(CH$_3$)$_2$], -8.6 [Al(CH$_3$)$_2$]; Anal. Calcd. for C$_{35}$H$_{36}$NOAl: C, 81.84; H, 7.06; N, 2.73. Found: C, 81.55; H, 6.86; N, 2.74.

Synthesis of {3-(1-naphthyl)-2-(O)C$_6$H$_3$CH=N(2,6-iPr$_2$C$_6$H$_3$)}Al(CH$_3$)$_2$ (2b): Trimethylaluminium solution (169 μL, 0.337 mmol, 2.0 M in toluene) was slowly added to a solution of 3-(1-naphthyl)-2-(OH)C$_6$H$_3$CH=N(2,6-iPr$_2$C$_6$H$_3$) (131 mg, 0.321 mmol) in toluene (5 mL) at 0 ºC. The reaction was allowed to warm to room temperature and stirred for 12 h. The volatiles were then removed under reduced pressure, to afford **2b** as a yellow solid in 92 % yield (137 mg). The ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.98 (d, J = 8.3 Hz, Naph-C4-H, 1H), 7.90 (s, CH=N, 1H), 7.61 (2 × d, J = 8.1 Hz, 7.8 Hz, Naph-C5,8-H, 2H), 7.49 (d, J = 7.1 Hz, OAr-H, 1H), 7.47-7.20 (m, OAr-H, Naph-C3,6,7-H, 4H), 7.12-6.94 (m, NAr-H, 3H), 6.84 (d, J = 7.9 Hz, Naph-C2-H, 1H), 6.63 (t, J = 7.5 Hz, OAr-H, 1H), 3.22 [(sept, J = 6.7 Hz, CH(CH$_3$)$_2$, 1H)], 3.03 [(sept, J = 6.7 Hz, CH(CH$_3$)$_2$, 1H)], 1.19 [(d, J = 6.8 Hz, CH(CH$_3$)$_2$, 3H)], 1.09 [(d, J = 6.8 Hz, CH(CH$_3$)$_2$, 3H)], 0.95 [(d, J = 6.8 Hz, CH(CH$_3$)$_2$, 3H)], 0.79 [(d, J = 6.7 Hz, CH(CH$_3$)$_2$, 3H)], -0.45 [(s, Al(CH$_3$)$_2$, 3H)], -0.64 [(s, Al(CH$_3$)$_2$, 3H)]; ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 174.2 (CH=N), 164.2 (C-O), 143.3 (C-N), 143.0 (NArC-iPr), 141.0 (NaphC-1), 135.7 (OArC-6), 133.9 (OArC-4), 132.5, 132.3, 129.9, 129.4, 129.1, 128.7, 128.5, 128.3, 127.8, 126.6 (all Naph-C and OArC-3), 126.2, 125.1 (both NArC-3,4), 119.9 (OArC-5), 118.5 (OArC-1), 29.1 [CH(CH$_3$)$_2$], 26.5 [CH(CH$_3$)$_2$], 23.0 [CH(CH$_3$)$_2$], -8.6 [Al(CH$_3$)$_2$]; Anal. Calcd. (%) for C$_{31}$H$_{34}$NOAl: C, 80.31; H, 7.39; N, 3.02. Found (%): C, 79.98; H, 7.26; N, 2.98.

A typical polymerization experiment was performed in a 30 mL glass reactor charged under nitrogen with a stir bar and 5 mL of toluene. The inert gas was replaced by ethylene at 20 psi, then 11.25 mg (22 μmol) of **2a** and 11.26 mg (22 μmol) of B(C$_6$F$_5$)$_3$ were injected. The reactor was fed with constant monomer pressure (100 psi) and maintained for 1 h at 40 °C. The reaction was then stopped by the addition of methanol. The solution was poured into 100 mL of 5 vol % HCl in methanol and stirred overnight. The polymer was recovered by filtration, washed with fresh methanol and dried under vacuum.

The particular interest in bulky sal ligands stems from neutral nickel ethylene polymerization catalysts, (sal)Ni(Ph)PPh$_3$, developed by Grubbs[11a,b]. Salicylaldimine ligands 3-R-2-(OH)C$_6$H$_3$CH=N(2,6-iPr$_2$C$_6$H$_3$) [R = 9-anthracenyl (**1a**) and 1-naphthyl (**1b**)][11a,12] were prepared by condensation of the corresponding salicylaldehyde and 2,6-diisopropylaniline. Treatment of ligands **1a-b** with 1.0 equivalent of Al(CH$_3$)$_3$ in toluene at room temperature readily affords the corresponding aluminum complexes {3-R-2-(O)C$_6$H$_3$CH=N(2,6-iPr$_2$C$_6$H$_3$)}Al(CH$_3$)$_2$ [R = 9-anthracenyl (**2a**) and 1-naphthyl (**2b**)], respectively (yields **2a** = 88 %, **2b** = 92 %) (**Scheme-I**). The Al complexes (**2a-b**) proved to be yellow solids, which is typical of the bidentate N,O salicylaldimine complexes of Al[8].
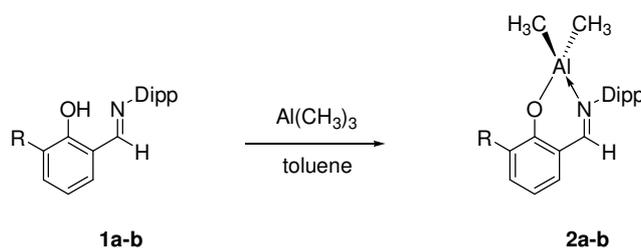
Dipp = 2,6-diisopropylphenyl
R = 9-anthracenyl, **a**
R = 1-naphthyl, **b**

Scheme-I: Synthesis of Al salicylaldimine complexes

The disappearance of the O-H signal of the ligands at δ = 13.3 in the ^{1}H NMR spectra of **2a-b** (room temperature, C$_6$D$_6$) and the appearance of a high-field signals (δ = 0.49, 6H, **2a**) and (δ = 0.64, 0.45, 6H, **2b**) compatible with Al(CH$_3$)$_2$ protons, reveal that the reaction proceeds by protodealumination of the Al-CH$_3$ bond with concomitant elimination of methane. The methyl groups bound to the aluminum atom show characteristic resonances at δ = -8.60 (**2a**) and -8.63 (**2b**) in the ^{13}C NMR spectra. Diagnostic signals for the imine function appear at δ = 8.15 (**2a**) and 7.90 (**2b**) in the ^{1}H NMR spectra and at δ ≈ H 174 in the ^{13}C NMR spectra. The elemental analysis is consistent with the expected products **2a-b**.

Preliminary polymerization tests were conducted for the synthesized Al complexes. Complexes **2a-b** were combined with 1.0 equivalent of B(C$_6$F$_5$)$_3$ in toluene and polymerized ethylene to solid polyethylene with low activity [**2a**: 78 g PE (mmol cat)$^{-1}$(h)$^{-1}$; **2b**: 105 g PE (mmol cat)$^{-1}$(h)$^{-1}$]. It is possible that the bulk at the site ortho to the phenoxide moieties retards ethylene binding and catalytic activity, by rendering the metal less electrophilic. It is also possible that the extreme bulk of the two Dipp substituents flanking the complex active site provides too much steric hindrance, thus averting ethylene association at that position.

It has been demonstrated the synthesis of neutral aluminum alkyls **2a-b** bearing bidentate N,O sal ligands cleanly and in high yields. These complexes, when treated with 1 equivalent of B(C$_6$F$_5$)$_3$, did not undergo methyl abstraction to afford alkylaluminum cations. Thus ethylene does not polymerize

appreciably under these conditions. We are currently trying to develop more reliable ethylene polymerization systems using less bulky and less electron rich salicylaldimine ligands.

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