Branched Polyethylene



Biaryl Group 4 Metal Complexes as Non-Metallocene Catalysts for Polyethylene with Long Chain Branching

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Abstract: A series of biaryl Group 4 complexes with a bidentate and a tridentate pincer ligand have been synthesized and characterized. The complexes have been applied as metallocene analogues for the controlled polymerization of ethylene

Introduction

Polyethylene (PE) is currently the most widely used and least expensive synthetic polymer on the market, accounting for ca. 32 % of global plastics demand in 2015, which translates to approximately 86 million tonnes. Metal catalysed polyethylene production has revolutionised the PE film industry and Group 4 metallocene complexes of type I have been at the forefront of these catalyst developments (Figure 1).^[1] The success of metallocenes in olefin polymerisation is in part due to the catalyst stability offered by the cyclopentadienyl (Cp) ligand scaffold and the tuneability in terms of polymer properties such as molecular weight and chain branching. Chain branching is classified as either short chain branching (SCB) or long chain branching (LCB). By convention, SCB implies branches of 6 or less carbon atoms, while LCB implies branches of approximately 140 or more carbons.^[2] Even a small degree of LCB (e.g. a few branches per 10⁶ carbon atoms) can result in large improvements in the rheological behaviour compared to purely linear PE, which dramatically impacts processing and handling properties.^[2,3] The origin of LCB formation is not well understood and several mechanisms based on macromers, C-H-activation or chain walking have been proposed.[2-4]

In search of alternative non-metallocene catalysts that enable control over branching levels, we have investigated whether bi-aryl complexes of type **II** and pincer-type complexes

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ticular focus on the control of the degree of long chain branching in these polymers.

and the copolymerization of ethylene and 1-hexene, with a par-



Figure 1. Group 4 metallocene (I), bidentate (II) and tridentate (III) biaryl complexes.

of type **III** could serve as metallocene alternatives with improved branching control. The orthogonal planar steric requirements of η^1 -phenyl donors compared to η^5 -Cp ligands allow easier access to the metal centre, a feature that could potentially affect SCB or LCB formation.

Group IV complexes with σ -bound aryl ligand(s) have been previously used as catalysts for ethylene polymerization. An early example by van Koten used the 2,6-bis[(dimethylamino)methyl]phenyl pincer ligand in combination with TiCl₄,^[5] which were active in both ethylene homo-polymerisation and co-polymerisation with 1-hexene.^[6] Another important class of aryl Group IV catalysts for olefin polymerization, identified by high throughput screening methods, are the tridentate aryl pyridine amide pincer complexes reported in 2003.^[7,8] These complexes received considerable attention and have shown activity in both ethylene homo-polymerisation and co-polymerisation with alkenes, as well as 1-hexene polymerisation.[9-12] Around the same time, tridentate aryl pyridine aryloxide ligands were reported by Chan and co-workers following the reaction of 2-(2'-phenol)-6-arylpyridine substrates with tetrabenzyltitanium and -zirconium precursors.^[13] Synthetic variations on tridentate pyridine-2-phenolate-6-(σ -aryl) templates have been subsequently investigated with titanium, zirconium and hafnium.^[14–16] More recent examples of mono-aryl complexes are Phebox-based complexes^[17] and the aryl bis(aryloxide) complexes reported by Veige and Bercaw.^[18,19] Only a few biaryl Group 4 metal complexes of type II have been reported,^[20] in-

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variably either with X being cyclopentadienyl,^[21,22] or as *bis*- or *tris*(biaryl) complexes.^[23,24]

We report here the first *mono*(biaryl) complexes of type **II** and tridentate pincer complexes of type **III** with ancillary X ligands that can be activated with co-catalysts for ethylene polymerisation catalysis. M–C(aryl) bonds are generally stronger than aliphatic M–C bonds which should ensure that ethylene insertion occurs preferentially in M–C(alkyl) bonds, rather than the M–C (phenyl) bonds.^[25,26] However, it has been shown that alkene insertion into the M–C(aryl) bond can be an essential catalyst activation process.^[9,12]

Results and Discussion

Synthesis of the ligand precursor 3,3',5,5'-tetra(*tert*-butyl)-biphenyl (1) was achieved via Suzuki-coupling of 3,5-di(*tert*-butyl)phenyl bromide and 3,5-di(*tert*-butyl)phenyl boronic acid,^[27] followed by bromination to give $1-Br_2$ in 86 % yield.^[28] Lithiation of $1-Br_2$ in pentane resulted in a suspension of $1-Li_2$ (see Figure 2). Initial attempts to prepare Group 4 metal complexes were carried out using the tin precursor $1-SnMe_2$, which was prepared from $1-Li_2$ and Me₂SnCl₂, but none of the transmetalation attempts using $1-SnMe_2$ were successful. Addition of $1-Li_2$ to $[Ti(NMe_2)_2Cl_2]$ did give the yellow complex $1-Ti(NMe_2)_2$ in moderate yield. Purification was achieved by washing with tetramethylsilane (TMS) to remove any residual biphenyl (1). Attempts to convert $1-Ti(NMe_2)_2$ to $1-TiCl_2$ with Me₃SiCl were unsuccessful.

Other Group 4 complexes **1-Zr(NMe₂)₂**, **1-ZrCl₂** and **1-HfCl₂** were prepared in a similar manner, using [Zr(NMe₂)₂Cl₂] or freshly sublimed ZrCl₄ and HfCl₄ respectively (see Supporting Information). Crystals suitable for X-ray analysis of **1-Ti(NMe₂)₂** were obtained from a concentrated solution in hexane at -30 °C



Figure 3. Molecular structure of $1-Ti(NMe_2)_2$. Selected bond lengths (Å) and angles (°): Ti(1)–N(20) 1.852(2), Ti(1)–C(1) 2.1061(13), N(20)–Ti(1)–N(20A) 111.25(18), C(1A)–Ti(1)–C(1) 88.39(7), N(20)–Ti(1)–C(1) 111.81(10).

and the molecular structure is shown in Figure 3. All complexes are highly air-sensitive and traces of moisture result in the formation of biphenyl **1**.

In order to improve catalyst stability, a tridentate dianionic diphenylpyridine ligand **2** with an additional donor was investigated. This C–N–C pincer type ligand has been extensively used for late transition metal complexes,^[29–38] but there are no reports of early transition metal complexes with such ligands. 2,6-*Bis*(2-bromophenyl)pyridine **2-Br**₂ was prepared as reported previously,^[39] with improved yields obtained using the 2,6-diiodopyridine precursor instead of 2,6-dibromopyridine. Lithiation of 2,6-*bis*(2-bromophenyl)pyridine **2-Br**₂ in diethyl ether at –30 °C^[40] resulted in the dilithium salt **2-Li**₂-OEt₂, which was treated with [Ti(NMe₂)₂Cl₂] to give **2-Ti(NMe**₂)₂ as a yellow-brown complex in 44 % yield (see Figure 4). Attempts to convert **2-Ti(NMe**₂)₂ into the dichloro complex by reaction with Me₃SiCl were unsuccessful.



Figure 2. Synthesis of Group 4 complexes with bidentate biaryl ligand 1.

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Figure 4. Synthesis of a titanium complex with tridentate biaryl ligand 2.

Crystals were obtained from a concentrated solution of complex **2-Ti(NMe₂)**₂ in diethyl ether at -30 °C. (see Supporting Information). XRD analysis shows a distorted trigonal bipyramidal geometry with the N-atoms in the equatorial plane and C-atoms in axial position (Figure 5). The C–Ti–C angle of 145.4 °C and the Ti–N and Ti–C bond lengths are within the typical range.^[40,41]



Figure 5. Molecular structure of complex **2-Ti(NMe₂)**₂. Selected bond lengths (Å) and angles (°): Ti(1A)–N(19A) 1.8760(16), Ti(1A)–C(8A) 2.176(2), Ti(1A)–N(1A) 2.2290(15), N(19A)–Ti(1A)–N(22A) 109.68(7), N(19A)–Ti(1A)–C(8A) 98.19(7), C(8A)–Ti(1A)–C(14A) 145.38(8), N(19A)–Ti(1A)–N(1A) 121.97(7).

Ethylene Polymerisation Results

Ethylene polymerisation reactions were carried out in toluene at 4 bar pressure, using MAO as the co-catalyst, either with or without H_2 as chain transfer agent (Table 1). The best activities were

Table 1. Ethylene polymerisation with Ti and Zr catalyst of 1.

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#	Complex ^[a] [µmol]	T [℃]	PE [g]	A ^[b]	<i>M</i> n [kDa]	<i>M_w</i> [kDa]	PDI	$E_a^{[d]}$
1	1-Ti(NMe ₂) ₂ (25) ^[c]	25	2.8	22	46	664	14	46±2
2	1-Ti(NMe ₂) ₂ (24)	80	11.0	92	24	301	13	52±7
3	1-Ti(NMe ₂) ₂ (25) ^[c]	80	11.7	94	30	282	10	44±2
4	1-Zr(NMe ₂) ₂ (14)	25	3.1	44	8.9	418	47	43±2
5	1-Zr(NMe ₂) ₂ (14) ^[c]	25	2.7	39	10.7	480	45	51±1
6	1-Zr(NMe ₂) ₂ (21)	50	11	104	5.3	226	43	38±1
7	1-Zr(NMe ₂) ₂ (14) ^[c]	80	6.1	87	2.0	110	53	23±5

[a] Conditions: 300 mL of toluene, 500 equiv. MAO, 4 bar, 75 min. [b] A: activity in g mmol⁻¹ h⁻¹ bar⁻¹. [c] 1 mol-% H₂ added. [d] Flow activation energy in kJ mol⁻¹, determined by rheology.

obtained with the titanium complex **1-Ti(NMe₂)**₂ at 80 °C and at 50 °C for the zirconium analogue **1-Zr(NMe₂)**₂. Polymer molecular weights decrease at higher polymerization temperatures. In the case of **1-Zr(NMe₂)**₂, rather broad molecular weight distributions are observed, the origins of which are unclear at this stage but could indicate the formation of multiple active sites upon activation of these pre-catalysts. Complexes **2-Ti(NMe₂)** and **1-HfCl**₂ gave low activities (< 5 g mmol⁻¹ h⁻¹ bar⁻¹) and the polymer products were not analysed in this case.

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The best performing catalyst **1-Ti(NMe₂)**₂ was also evaluated for ethylene/1-hexene co-polymerisation under industrially more relevant conditions. From Table 2 it can be seen that activities have significantly improved under these conditions and excellent incorporation levels of 1-hexene up to 18 wt.-% was achieved at 70 °C. The polymer melting points for these copolymers are relatively high for this level of 1-hexene incorporation, but they are considerably lower than for the PE homopolymer obtained under similar reaction conditions (run 10), whose molecular weight was too high to be determined by GPC. The reason for the higher melting points are not fully understood at this stage, but could be due to the very high molecular weights ($M_w \approx 1,000$ kDa) obtained for these co-polymers.

Table 2. Ethylene/1-hexene polymerisation with 1-Ti(NMe2)2.

#	<i>Т</i> [°]С	PE g	A ^[c]	M _n kDa	<i>M_w</i> kDa	PDI	C ₆ ^[d] wt%	SCB /1000C	Mp. ^[e] [°]C
8 ^[a]	70	22	182	57	985	17	18	30	129
9 ^(a)	90	31	256	34	925	28	11	19	127
10 ^[b]	70	7	350	_[f]	-	-	-	-	136

[a] Conditions: **1-Ti(NMe₂)**₂ (12.1 µmol), 1.8 L isobutane. Activating support (MAO on silica): 200 mg, 10 bar, 60 min, 1-hexene: 30 g, $H_2/C_2H_4 = 0.15$ mol-%. [b] Conditions: **1-Ti(NMe₂)**₂ (2 µmol), 1.8 L isobutane, MMAO (20 mmol), 10 bar, 60 min, $H_2/C_2H_4 = 0.15$ mol-%. [c] A: activity in g mmol⁻¹ h⁻¹ bar⁻¹. [d] Determined by IR. [e] Determined by DSC. [f] Polymer was too viscous for GPC analysis.

Polymer Analysis

Polymer analysis was carried out using GPC, IR and melt rheology measurements. In general, all polymers in Table 1 and Table 2 show high molecular weight and broad polydispersity. The response of M_n and M_w values to the addition of H₂ (1 mol-%) was investigated, but the addition of H₂ offered little control over the molecular weight with these catalysts.

The presence of long chain branching in the polyethylene materials was investigated using flow activation energies (E_a), which are listed in Table 1. E_a values are a measure of the flow activation energy required for polymer chains to overcome internal resistance. They are determined from rheology measurements by measuring the storage modulus G', the loss modulus G'' and the complex viscosity η^* vs. the oscillating frequency ω . Polyethylene samples are measured at four different temperatures between 160 and 190 °C, using Time Temperature Superposition (TTS), whereby the data at 190 °C are taken as the reference curve.^[42,43] Figure 6 shows a typical analysis obtained from frequency sweep measurements at various temperatures. Shifting the graphs to the 190 °C-reference curve and plotting the displacement a_T against 1/T allows the flow activation en-



ergy E_a to be determined from the slope (see Supporting Information for details).^[44]



Figure 6. Rheological determination of storage (G') and loss modulus (G''), as well as complex viscosity η^* vs. oscillating frequency ω from 160–200 °C for PE samples from run 3 in Table 1.

Flow activation energies of up to 28 kJ mol⁻¹ are typically reported for linear high density polyethylene, while higher values indicate the presence of long chain branches by virtue of entanglement effects.^[44] Benchmarking studies using a bis(2,6diisopropylphenylimine)pyridine iron catalyst that produces highly linear polyethylene,^[45] and a bis(diisopropylphenyl)diimine nickel catalyst that produces highly branched polyethylene (including LCB),^[46] resulted in E_a values of 29 and 65 kJ/ mol, respectively. The E_a values of \approx 40–60 kJ/mol for the polymers obtained with 1-Ti(NMe₂)₂ and 1-Zr(NMe₂)₂ indicate the formation of long chain branches in these materials. The excellent 1-hexene incorporation with 1-Ti(NMe₂)₂ would favour LCB formation via the insertion of macromers mechanism.^[2] For 1-Ti(NMe₂)₂, LCB formation appears to be largely independent of the polymerisation temperature or the addition of hydrogen. For both systems, 1-Ti(NMe₂)₂ and 1-Zr(NMe₂)₂, at higher temperature the polymer molecular weight decreases, probably due to much faster rates of termination vs. propagation. Interestingly, in the case of 1-Zr(NMe₂)₂, this results in a decrease in the activation energy E_a . This could be as a result of a decrease in long chain branch formation, although, the lower molecular weight polymer obtained at higher temperatures would increase the macromer concentration, which should lead to increased LCB levels. However, the precise mechanism for LCB formation in these systems is as yet unknown. An alternative explanation could be the presence of a very low molecular weight fraction (below the entanglement molecular weight $T_{\rm e}$ = 1160 Da) which affects the rheology measurements and decreases the flow activation energy. Further studies are underway to control and understand branch formation in this new class of non-metallocene polymerisation catalysts.

Conclusions

Group 4 complexes containing biaryl-type ligands **1** and **2** have been synthesised and characterised. Activation of these non-

metallocene catalysts with the co-catalyst MAO results in active ethylene polymerisation catalysts that show good incorporation of 1-hexene. Analyses of the polyethylene homopolymers by rheological measurements have established the presence of long chain branches, presumably formed via macromer insertion.

Deposition Numbers 1552482–1552483 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Conflict of Interest

There are no conflicts to declare.

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Keywords: Ethylene · Polymerisation · Titanium · Pincer · Branching

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 Biaryl Group 4 Metal Complexes as
Non-Metallocene Catalysts for Polyethylene with Long Chain Branching



A series of non-metallocene Group 4 metal complexes containing bidentate and tridentate pincer ligands with η^1 -aryl donors has been investigated as catalysts for polyethylene formation, with a particular focus on long chain branching as determined by rheology measurements.

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