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Synthesis and characterization of trichlorotitanium 2-(2-pyridinyliminomethyl) phenolates and their ethylene (co-)polymerization behavior

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The series of trichlorotitanium 2-(2-pyridinyliminomethyl)phenolates, $[4,6\text{-}tBu_2C_6H_2O\text{-}2\text{-}CH{=}NC_5R^{1-4}N]TiCl_3$ ($R^{1-4} = H$ (**1**); $R^{1,3,4} = H$, $R^2 = Me$ (**2**); $R^{1,2,4} = H$, $R^3 = Me$ (**3**); $R^{2,4} = H$, $R^{1,3} = Me$ (**4**); $R^{1,3} = H$, $R^2 = CF_3$, $R^4 = Cl$ (**5**)), were synthesized and characterized by elemental analysis and $^1H/^{13}C$ NMR spectroscopy. The molecular structures of the representative complexes **2** and **4** were confirmed by single-crystal X-ray diffraction, and revealed distorted octahedral geometry at titanium. In the presence of MAO, all titanium pro-catalysts showed good activities for ethylene polymerization with good thermal stability at the optimum temperature of 50 °C. In comparison with the ethylene polymerization results, the activity observed for the co-polymerization of ethylene/1-hexene was far lower, but the polymers produced were of high molecular weight. For the co-polymerization of ethylene/1-octene, enhanced catalytic activity was observed, with 1-octene incorporation of up to 3.83 mol%.

1. Introduction

Bis(phenoxyimino)titanium dichlorides (titanium FI catalysts) [1–3] and bis(pyrrolide-imino)titanium dichlorides (titanium PI catalysts) [4] are easily synthesized pro-catalysts with high activities in α-olefin polymerization. The FI catalysts sometime perform olefin polymerization in a living manner and are capable of producing functional polymers [1,5,6]. The activity of such FI catalysts decreases sharply at elevated temperature [7,8], meanwhile with limited co-polymerization behavior. As a consequence, the PI catalysts are developed with better stability and good co-polymerization behavior due to the more open space at the metal in the active species [9]. Subsequently, various modifications to the FI catalysts have been carried out in order to achieve better co-polymerization behavior [10–12]. More attractively, a novel polymerization process has been developed by using dual catalytic systems including one FI catalyst with the assistance of Zn-shuttle reagents [13]. We have also explored the use of titanium complexes [14,15] and half-titanocenes [16,17] as pro-catalysts for ethylene (co-)polymerization. Their ease of synthesis and better catalytic performance suggests that such systems have high potential in both academic and industrial studies. Interestingly, hybridized (salicylaldiminato)(pyrrolylaldiminato)titanium dichlorides have shown high productivities in ethylene polymerization, but were synthesized via multi-step syntheses [18]. Beyond the modification of FI catalysts [19–21], the (side-chain phenoxylimino)titanium trichlorides were also explored and screening studies indicated enhanced stability and higher activity (see **I** [22] and **II** [23] Scheme 1). Recently, it was reported that increased pyridine content in latex-supported FI catalyst systems resulted in higher activity [24]. With this in mind, a series of 2-(pyridin-2-ylimino)methylphenols were synthesized in order to have one pyridine in the ligand backbone, and subsequently the trichlorotitanium 2-(pyridin-2-ylimino)methyl phenolates (see **III**, Scheme 1) were prepared.

The new titanium complexes possess a 4-membered metallocyclic ring, in contrast to the more commonly encountered 5 and 6-membered metallocyclic rings in such species [22,23]. The title titanium complexes, when activated with methylaluminoxane (MAO), showed good catalytic activities and thermal stability in ethylene (co)polymerization. Herein, the synthesis and characterization of these trichlorotitanium 2-(pyridin-2-ylimino)methylphenolates are reported, and their catalytic performance toward ethylene has been investigated.

2. Experimental

2.1. General procedure

All manipulations of air and/or moisture-sensitive compounds were carried out under nitrogen atmosphere in a glove-box or

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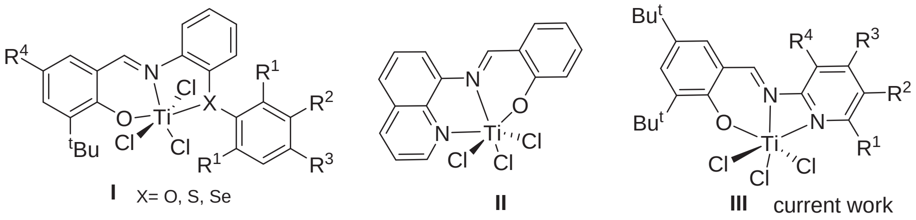


Scheme 1. Model pro-catalysts of tridentate trichlorotitanium complexes.

using standard Schlenk techniques. Methylaluminoxane (MAO, 1.46 M in toluene) was purchased from Albemarle. Potassium hydride (KH) was washed with *n*-hexane before use to remove contained mineral oil. Toluene, *n*-hexane and *n*-heptane were refluxed in the presence of sodium and benzophenone, then freshly distilled under nitrogen atmosphere before to use, respectively. Dichloromethane, 1-hexene and 1-octene were dried over calcium hydride. Elemental analysis was performed on a Flash EA 1112 microanalyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard at 25 °C ^{13}C NMR spectra of the polymers were recorded on a Bruker DMX-300 MHz instrument at 110 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard. DSC trace and melting points of polyethylene were obtained from the second scanning run on a Perkin–Elmer DSC-7 at a heating rate of 10 °C/min. Molecular weights and polydispersity indices (PDI) of (co-)polyethylenes were determined using a PL-GPC 220 instrument at 135 °C in 1, 2, 4-trichlorobenzene with polystyrene as the standard.

2.2. Synthesis of ligands *L1*–*L5*

Synthesis of 2-(2-pyridinyliminomethyl)phenols (**L1**–**L5**)

As for our previous method [25], 10 mmol equivalent amounts of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and the corresponding arylamine were mixed in an open flask and placed in the microwave for 2 min on the “M-High” setting (616W). The products were extracted with ethanol and recrystallized as yellow microcrystals.

2.2.1. 4,6-Di-tert-butyl-2-(pyridin-2-ylimino)methylphenol (*L1*)

Obtained as a yellow solid in 81.2% yield (2.52 g). Mp: 116 °C, IR (KBr, cm^{-1}): 3000 (O–H) (w), 2960 (s), 2906 (m), 2867 (m), 1610 (CH═N) (m), 1579 (s), 1461 (s), 1432 (s), 1360 (m), 1198 (m), 1169 (s), 881 (m), 791 (m), 769 (m), 736 (m). ^{1}H NMR: (CDCl$_3$, 400 MHz, ppm): δ 13.90 (s, 1H, O*H*), 9.47 (s, 1H, C*H*═N), 8,50 (d, 1H, *J* = 3.60 Hz, Py-*H*), 7.76 (t, 1H, *J* = 7.56 Hz, Py-*H*), 7.49 (s, 1H, Ar–*H*), 7.35 (d, 1H, *J* = 6.24 Hz, Py-*H*), 7.26 (s, 1H, Ar–*H*), 7.19 (t, 1H, *J* = 5.68 Hz, Py-*H*), 1.50 (s, 9H, t-Bu-*H*), 1.34 (s, 9H, t-Bu-*H*). ^{13}C NMR: (CDCl$_3$, 100 MHz, ppm): δ 165.8, 159.2, 157.9, 149.0, 140.8, 138.5, 137.0, 128.9, 128.2, 122.3, 120.4, 118.2, 35.2, 34.3, 31.5, 29.5. Anal. Calcd. For $C_{20}H_{26}N_2O$: C, 77.38; H, 8.44; N, 9.02%. Found: C, 77.26; H, 8.50; N, 9.09%.

2.2.2. 4,6-Di-tert-butyl-2-(5-methylpyridin-2-ylimino) methylphenol (*L2*)

Obtained as yellow crystals in 73.8% yield (2.39 g). Mp: 146 °C. IR (KBr, cm^{-1}): 2997 (w), 2958 (s), 2906 (m), 2868 (m), 1612 (CH═N) (m), 1570 (s), 1462 (s), 1386 (m), 1358 (m), 1251 (m), 1169 (s), 1022 (m), 881 (m), 828 (m), 769 (w), 680 (w). ^{1}H NMR: (CDCl$_3$, 400 MHz, ppm): δ 13.93 (s, 1H, O*H*), 9.42 (s, 1H, C*H*═N), 8.31 (s, 1H, Py-*H*), 7.56 (d, 1H, *J* = 7.88 Hz, Py-*H*), 7.46 (s, 1H, Ar–*H*), 7.34 (s, 1H, Ar–*H*), 7.23 (d, 2H, *J* = 8.64 Hz, Py-*H*), 2.37 (s, 3H, C*H*$_3$), 1.48 (s, 9H, t-Bu-*H*), 1.32 (s, 9H, t-Bu-*H*). ^{13}C NMR: (CDCl$_3$, 100 MHz, ppm): δ 164.8, 159.1, 155.7, 149.2, 140.7, 139.0, 136.9, 132.0, 128.6, 128.0, 119.8, 118.3, 35.2, 34.2, 31.5, 29.5, 18.1. Anal. Calcd. For $C_{21}H_{28}N_2O$: C, 77.74; H, 8.70; N, 8.63%. Found: C, 77.87; H, 8.64; N, 8.54%.

2.2.3. 4,6-Di-tert-butyl-2-(4-methylpyridin-2-ylimino) methylphenol (*L3*)

Obtained as yellow crystals in 74.5% yield (2.42 g). Mp: 125 °C, IR (KBr, cm^{-1}): 3049 (w), 2960 (s), 2908 (m), 2868 (m), 1607 (CH═N) (s), 1584 (s), 1549 (s), 1456 (s), 1362 (m), 1251 (m), 1206 (m), 1157 (m), 1028 (w), 947 (w), 886 (w), 716 (w). ^{1}H NMR: (CDCl$_3$, 400 MHz, ppm): δ 13.95 (s, 1H, O*H*), 9.44 (s, 1H, C*H*═N), 8.35 (d, 1H, *J* = 4.48 Hz, Py-*H*), 7.47 (t, 1H, Py-*H*), 7.34 (s, 1H, Ar–*H*), 7.17 (s, 1H, Ar–*H*), 7.01 (d, 1H, *J* = 4.73 Hz, Py-*H*), 2.39 (s, 3H, C*H*$_3$), 1.48 (s, 9H, t-Bu-*H*), 1.32 (s, 9H, t-Bu-*H*). ^{13}C NMR: (CDCl$_3$, 100 MHz, ppm): δ165.6, 159.3, 157.9, 149.9, 148.7, 140.7, 137.0, 128.8, 128.1, 123.4, 121.1, 118.3, 35.2, 34.3, 31.5, 29.5, 21.1. Anal. Calcd. For $C_{21}H_{28}N_2O$: C, 77.74; H, 8.70; N, 8.63%. Found: C, 77.62; H, 8.76; N, 8.60%.

2.2.4. 4,6-Di-tert-butyl-2-(4,6-dimethylpyridin-2-ylimino) methylphenol (*L4*)

Obtained as yellow crystals in 59.2% yield (2.01 g). Mp: 122 °C, IR (KBr, cm^{-1}): 3005 (w), 2960 (s), 2869 (m), 1609 (CH═N) (s), 1589 (s), 1549 (s), 1456 (s), 1362 (m), 1251 (m), 1207 (m), 1174 (m), 1153 (m), 1028 (w), 985 (w), 716 (w). ^{1}H NMR: (CDCl$_3$, 400 MHz, ppm): δ 14.07 (s, 1H, O*H*), 9.42 (s, 1H, C*H*═N), 7.45 (s, 1H, Py-*H*), 7.34 (s, 1H, Py-*H*), 6.96 (s, 1H, Ar–*H*), 6.89 (s, 1H, Ar–*H*), 2.53 (s, 3H, C*H*$_3$), 2.34 (s, 3H, C*H*$_3$), 1.47 (s, 9H, t-Bu-*H*), 1.33 (s, 9H, t-Bu-*H*). ^{13}C NMR: (CDCl$_3$, 100 MHz, ppm): δ 165.2, 159.3, 157.7, 157.3, 149.7, 140.5, 136.9, 128.5, 128.0, 122.9, 118.3, 118.0, 35.2, 34.3, 31.6, 29.5, 24.3, 20.9. Anal. Calcd. For $C_{22}H_{30}N_2O$: C, 78.06; H, 8.93; N, 8.28%. Found: C, 78.11; H, 8.99; N, 8.20%.

2.2.5. 4,6-Di-tert-butyl-2-(3-chloro-5-(trifluoromethyl)pyridin-2-ylimino)methylphenol (*L5*)

Obtained as yellow crystals in 30.3% yield (1.25 g). Mp: 130 °C, IR (KBr, cm^{-1}): 3001 (w), 2961 (s), 2916 (m), 2363 (s), 2343 (m), 1625 (CH═N) (m), 1564 (s), 1455 (s), 1319 (s), 1275 (m), 1253 (m), 1163 (s), 1122 (s), 1089 (m), 978 (w), 738 (w). ^{1}H NMR: (CDCl$_3$, 400 MHz, ppm): δ 13.68 (s, 1H, O*H*), 9.51 (s, 1H, C*H*═N), 8.64 (s, 1H, Py-*H*), 8.05 (s, 1H, Py-*H*), 7.57 (s, 1H, Ar–*H*), 7.37 (s, 1H, Ar–*H*), 1.50 (s, 9H, t-Bu-*H*), 1.34 (s, 9H, t-Bu-*H*). ^{13}C NMR: (CDCl$_3$, 100 MHz, ppm): δ 168.5, 160.3, 157.2, 143.9, 141.3, 137.7, 135.9, 130.8, 128.7, 127.4, 125.7, 124.3, 118.1, 35.3, 34.3, 31.5, 29.5. Anal. Calcd. For $C_{21}H_{24}ClF_3N_2O$: C, 61.09; H, 5.86; N, 6.78%. Found: C, 61.15; H, 5.89; N, 6.73%.

2.3. Synthesis of trichlorotitanium 2-(2-pyridinyliminomethyl) phenolates *1*–*5*

To a stirred solution of 2-(pyridin-2-ylimino)methyl-phenol (**L1**) (0.324 g, 1.00 mmol) in dried THF (30 mL), KH (0.040 g, 1.00 mmol) was added at −25 °C. The mixture was stirred for an additional 3 h, then $TiCl_4(THF)_2$ (0.334 g, 1.00 mmol) was added to the solution at −78 °C, and the resultant mixture was allowed to warm to room temperature and stirred for an additional 24 h. The residue, obtained by removing the solvent under vacuum, was extracted with CH_2Cl_2 (3 × 20 mL) and the combined filtrates were concentrated in vacuum to 20 mL. The complex **1** was recrystallized from its dichloromethane solution at −20 °C as brown powder. Yield: 0.25 g (49%). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.96 (s, 1H, C*H*=N), 8.93 (s, 1H, Py-*H*), 8.12 (s, 1H, Py-*H*), 7.85 (s, 1H, Py-*H*), 7.69 (d, 1H, *J* = 7.8 Hz, Py-*H*), 7.53 (s, 1H, Ar–*H*), 7.24 (s, 1H, Ar–*H*), 1.58 (s, 9H, t-Bu-*H*), 1.37 (s, 9H, t-Bu-*H*) ^{13}C NMR: ($CDCl_3$, 100 MHz, ppm): δ 162.2, 157.8, 154.9, 147.9, 146,7, 141.8, 134.5, 130.4, 127.2, 124.5, 111.8, 35.9, 31.3, 30.1, 29.8. Anal. Calcd. For $C_{20}H_{25}Cl_3N_2OTi$: C, 51.81; H, 5.43; N, 6.04%. Found: C, 51.87; H, 5.41; N, 6.09%.

Using the same procedure as for **1,2** (0.25 g) was formed as a red solid in 52.3% yield. ^{1}H NMR: ($CDCl_3$, 400 MHz, ppm): δ 8.85 (s, 1H, C*H*=N), 8.81 (s, 1H, Py-*H*), 7.93 (d, 1H, *J* = 6.42, Py-*H*), 7.82 (s, 1H, Ar–*H*), 7.54 (d, 1H, *J* = 7.31 Hz, Py-*H*), 7.18 (s, 1H, Ar–*H*), 2.54 (s, 3H, C*H*$_3$), 1.58 (s, 9H, t-Bu-*H*), 1.37 (s, 9H, t-Bu-*H*). ^{13}C NMR: ($CDCl_3$, 100 MHz, ppm): δ 145.3, 145.2, 143.8, 141.5, 137.8, 132.6, 132.2, 129.6, 122.8, 122.1, 114.1, 111.1, 31.9, 31.3, 29.6, 22.8, 14.2. Anal. Calcd. For $C_{21}H_{27}Cl_3N_2OTi$: C, 52.80; H, 5.70; N, 5.86%. Found: C, 52.84; H, 5.75; N, 5.80%.

Using the same procedure as for **1**, **3** (0.41 g) was prepared by using **L3** instead of **L1** and isolated as red crystals in 86.5% yield. ^{1}H NMR: ($CDCl_3$, 400 MHz, ppm): δ 8.86 (s, 1H, C*H*=N), 8.81 (d, 1H, *J* = 5.08 Hz, Py-*H*), 7.85 (s, 1H, Py-*H*), 7.52 (s, 1H, Ar–*H*), 7.47 (s, 1H, Ar–*H*), 7.38 (d, 1H, *J* = 5.02 Hz, Py-*H*), 2.51 (s, 3H, C*H*$_3$), 1.58 (s, 9H, t-Bu-*H*), 1.37 (s, 9H, t-Bu-*H*). ^{13}C NMR: ($CDCl_3$, 100 MHz, ppm): δ162.8, 158.6, 157.7, 154.4, 154.2, 147.8, 145.9, 137.9, 134.4, 126.9, 112.0, 100.1, 35.9, 31.3, 30.1, 22.3, 14.2. Anal. Calcd. For $C_{21}H_{27}Cl_3N_2OTi$: C, 52.80; H, 5.70; N, 5.86%. Found: C, 52.82; H, 5.75; N, 5.82%.

Using the same procedure as for **1**, **4** (0.403 g) was formed as a red solid in 82.2% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.82 (s, 1H, C*H*=N), 7.82 (s, 1H, Py-*H*), 7.50 (s, 1H, Py-*H*), 7.24 (s, 1H, Ar–*H*), 7.17 (s, 1H, Py-*H*), 2.99 (s, 3H, C*H*$_3$), 2.55 (s, 3H, C*H*$_3$), 1.59 (s, 9H, t-Bu), 1.37 (s, 9H, t-Bu). ^{13}C NMR: ($CDCl_3$, 100 MHz, ppm): δ 161.9, 157.2, 156.2, 154.4, 154.3, 147.7, 134.0, 130.0, 127.1, 125.4, 109.1, 35.9, 34.9, 31.3, 30.0, 22.7, 22.0. Anal. Calcd. For $C_{22}H_{29}Cl_3N_2OTi$: C, 53.74; H, 5.94; N, 5.70%. Found: C, 53.71; H, 5.97; N, 5.73%.

Using the same procedure as for **1**, **5** (0.11g, 0.529 mmol) was formed as a red solid in 52.9% yield. ^{1}H NMR: ($CDCl_3$, 400 MHz, ppm): δ 9.74 (s, 1H, C*H*=N), 9.18 (s, 1H, Py-*H*), 8.31 (s, 1H, Py-*H*), 7.93 (s, 1H, Ar–*H*), 7.58 (s, 1H, Ar–*H*), 1.58 (s, 9H, t-Bu-*H*), 1.39 (s, 9H, t-Bu-*H*). ^{13}C NMR: ($CDCl_3$, 100 MHz, ppm): δ 162.4, 160.5, 155.8, 154.8, 148.5, 142.2, 140.4, 136.4, 132.1, 127.8, 127.3, 127.0, 123.7, 35.8, 34.9, 31.1, 29.9. Anal. Calcd. For $C_{21}H_{23}Cl_4F_3N_2OTi$: C, 44.56; H, 4.10; N, 4.95%. Found: C, 44.59; H, 4.13; N, 4.98%.

2.4. Procedures for ethylene polymerization and co-polymerization

A stainless steel autoclave (250 mL) equipped with a mechanical stirrer and a temperature controller was heated in vacuum at 80 °C and recharged with ethylene three times, then cooled to room temperature under ethylene atmosphere. A toluene solution of the titanium pro-catalyst (with co-monomer) was transferred into the reactor. After the desired reaction temperature was reached and the required amount of co-catalyst (with total 100 mL volume maintained through adding toluene) was added, the autoclave was immediately pressurized to 10 atm. The ethylene pressure was kept constant during the reaction through feeding ethylene. After the required time, the ethylene feed was stopped, and the autoclave was placed in a water-ice bath for 1 h. The resultant mixture was poured into 10% HCl–ethanol solution, and the solid polymer was collected and washed with water and ethanol several times and dried under vacuum to constant weight.

2.5. X-ray structure determination

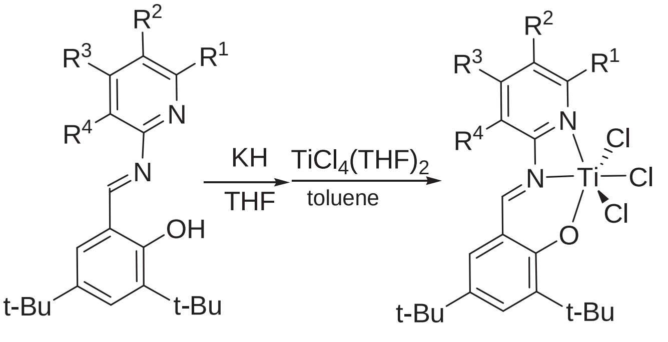
Crystals of **2** and **4** suitable for single-crystal X-ray diffraction were obtained by laying *n*-heptane onto dichloromethane solutions of **2** and **4**, respectively. Single-crystal X-ray diffraction for **2** and **4** was performed on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173(2) K. Cell parameters are obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures are solved by direct methods and refined by full-matrix least-squares on *F*2. All non-hydrogen atoms are refined anisotropically. Structure solution and refinement are performed by using the SHELXL-97 package [26]. Details of crystal data collection and refinements are given in (Table 1).

3. Results and discussion

3.1. Synthesis and characterization

The 2-(pyridin-2-ylimino)methylphenols (**L1**–**L5**) were synthesized according to the literature method [25]. To the solution of the corresponding 2-(pyridin-2-ylimino)methylphenol with one equivalent of KH in THF, one equivalent of $TiCl_4(THF)_2$ was added to form the titanium complexes **1**–**5** in good yields (Scheme 2). The titanium complexes thereby obtained were characterized and confirmed as the formulas [4,6-tBu$_2$C$_6$H$_2$O-2–CH=NC$_5$R$^{1-4}$N]TiCl$_3$ (R^{1-4} = H (**1**); $R^{1,3,4}$ = H, R^2 = Me (**2**); $R^{1,2,4}$ = H, R^3 = Me (**3**); $R^{2,4}$ = H, $R^{1,3}$ = Me (**4**); $R^{1,3}$ = H, R^2 = CF_3, R^4 = Cl (**5**)) by ^{1}H/^{13}C NMR spectroscopy and elemental analysis. In the case of using 2 or 3 equivalents of potassium salts of **L2** on reaction with $TiCl_4(THF)_2$, a mixture of **L**TiCl$_3$ and **L**$_2$TiCl$_2$ was detected by ^{1}H NMR spectroscopy, however the two titanium complexes could not be separated and pure **L**$_2$TiCl$_2$ could not be obtained.

The absorptions associated with the Ar–O*H* (14.1–13.6 ppm) of the 2-(2-pyridinylimino)methylphenols disappeared in the ^{1}H NMR spectra of the titanium complexes, confirming the formation of the Ti–O bond. The peak for C*H*=N (9.5–9.4 ppm) in the ligands **L1**–**L4** was shifted to higher field (8.82–8.96 ppm) in the titanium complexes **1**–**4**, but that of **L5** (9.51 ppm) moved to lower field in **5** (9.74 ppm), due to the substituents bearing halogens; these NMR



L1-L5 **1-5**

Ln	Complex	R^1	R^2	R^3	R^4
L1	**1**	H	H	H	H
L2	**2**	H	Me	H	H
L3	**3**	H	H	Me	H
L4	**4**	Me	H	Me	H
L5	**5**	H	CF$_3$	H	Cl

Scheme 2. Synthesis of titanium complexes (**1**–**5**).

spectral changes indicated the effective coordination of the N_{imine} to the Ti center.

The structures of the representative complexes **2** and **4** were further confirmed by single-crystal X-ray diffraction, and the molecular structures are shown in Figs. 1 and 2, respectively. As shown in Fig. 1, the titanium is coordinated by N_{py}, N_{imine}, O and three chlorides to give a distorted octahedral geometry, for which the titanium is coplanar with the coordinated atoms of O1, N1, N2 and Cl1; the other two chlorines (Cl2 and Cl3) are located in *trans*-positions with an angle Cl3–Ti1–Cl2 of 164.36(4)°. The phenyl and pyridyl rings are almost coplanar. Moreover, a 4-membered metallocyclic ring comprising of Ti1, N1, C8 and N2 (the additional N_{py}) is formed; a few titanium complexes containing such 4-membered rings have been reported in the literature [27–30]. The Ti–Cl bond lengths are consistent with those previously reported [22,23].

According to Fig. 2, the distorted octahedral geometry around the Ti center in **2** is repeated in complex **4**, though slight differences are observed within the bond lengths Ti–O, Ti-N_{imine} [1.804(2), 2.130(3) Å] in **4** and in **2** [1.791(2), 2.128(2) Å], and shorter bond length of Ti-N_{py} [2.202(3) Å] in **4** than that of **2** [2.255(3) Å], which was caused by the stronger electron donation due to methyl substituents in **4**.

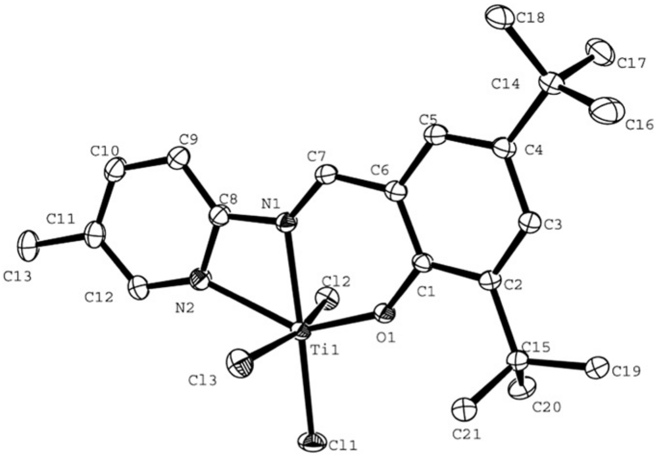


Fig. 1. ORTEP drawing of **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (°) and selected bond angles (Å): Ti1–O1 1.791(2), Ti1–N1 2.128(2), Ti1–N2 2.255(3), Ti1–Cl1 2.2803(10), Ti1–Cl3 2.2979(10), Ti1–Cl2 2.3282(11), N1–C7 1.286(4), N1–C8 1.390(4), O1–C1 1.347(3), N2–C12 1.337(4), N2–C8 1.342(4), O1–Ti1–N1 81.28(9), O1–Ti1–N2 140.67(9), N1–Ti1–N2 59.55(9), O1–Ti1–Cl1 102.23(7), N1–Ti1–Cl1 174.93(7), N2–Ti1–Cl1 117.08(7), O1–Ti1–Cl3 96.21(8), N1–Ti1–Cl3 91.13(7), N2–Ti1–Cl3 82.22(8), Cl1–Ti1–Cl3 92.10(4), O1–Ti1–Cl2 98.77(8), N1–Ti1–Cl2 86.75(7), N2–Ti1–Cl2 83.36(7), Cl1–Ti1–Cl2 89.09(4), Cl3–Ti1–Cl2 164.36(4), C8–N2–Ti1 95.14(18).

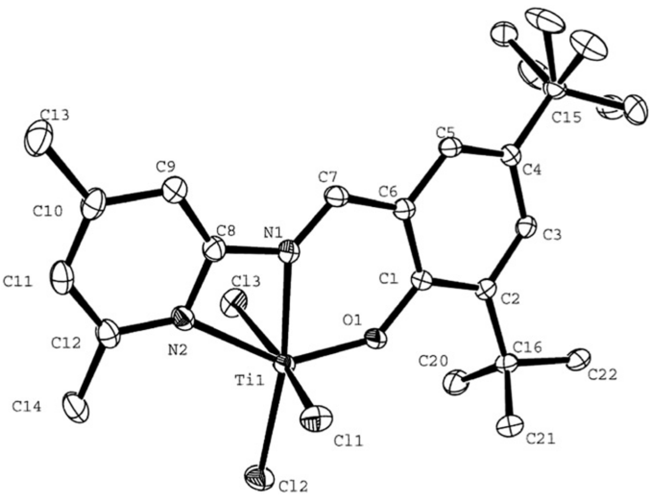


Fig. 2. ORTEP drawing of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (°) and selected bond angles (Å): Ti1–O1 1.804(2), Ti1–N1 2.130(3), Ti1–N2 2.202(3), Ti1–Cl2 2.2647(11), Ti1–Cl1 2.3234(12), Ti1–Cl3 2.3342(12), O1–C1 1.347(3), N2–C12 1.346(4), N2–C8 1.347(4), N1–C7 1.287(4), N1–C8 1.402(4). O1–Ti1–N1 81.68(10), O1–Ti1–N2 141.85(10), N1–Ti1–N2 60.18(10), O1–Ti1–Cl2 108.09(8), N1–Ti1–Cl2 170.23(8), N2–Ti1–Cl2 110.05(8), O1–Ti1–Cl1 95.17(8), N1–Ti1–Cl1 86.78(8), N2–Ti1–Cl1 84.24(7), Cl2–Ti1–Cl1 92.56(4), O1–Ti1–Cl3 94.44(8), N1–Ti1–Cl3 86.11(8), N2–Ti1–Cl3 82.89(7), Cl2–Ti1–Cl3 92.63(5), Cl1–Ti1–Cl3 167.09(4), O1–Ti1–C8 112.38(10), N1–Ti1–C8 30.70(9), N2–Ti1–C8 29.50(9), Cl2–Ti1–C8 139.54(7), Cl1–Ti1–C8 83.88(7), Cl3–Ti1–C8 84.51(7), C1–O1–Ti1 141.7(2).

3.2. Catalytic behavior in polymerization

3.2.1. Ethylene polymerization

Various alkylaluminium reagents as co-catalysts were investigated with pro-catalyst **4**. The trialkylaluminium reagents $AlEt_3$ or $AlMe_3$ afforded little or no activity, however, methylaluminoxane (MAO) and modified methylaluminoxane (MMAO) showed considerable catalytic activity for ethylene polymerization under 10 atm ethylene with 1000:1 M ratio of Al/Ti at 20 °C over 30 min, and the system with MAO performed with an activity of 2.3×10^4 g mol^{-1}(Ti)·h^{-1}, which is several times higher that that found with MMAO 0.60×10^4 g mol^{-1}(Ti)·h^{-1}. As a consequence, MAO was chosen as the co-catalyst for further investigation. The reaction parameters of Al/Ti molar ratio (runs 1–6, Table 2) and temperature (runs 3, 7–10, Table 2) were varied, and the optimum conditions were found as a Al/Ti molar ratio 5000:1 at 50 °C. Checking the properties of the polyethylenes obtained, it was not difficult to conclude that melting points decreased along with elevating either the reaction temperature or the molar ratio of Al/Ti. These results are consistent with enhanced termination at high temperature or higher ratio of Al/Ti, which resulted in more chain transfer from titanium to aluminum for the termination [31]. The values of the melting points were also consistent with the molecular weights and distributions of the polyethylenes, and decreased with either higher temperatures or with higher Al concentration. The optimum condition for ethylene polymerization was with a Al/Ti molar ratio of 5000:1 at 50 °C under 10 atm ethylene, indicating the active species requiring the association with alkylaluminium was efficiently activated at the elevated temperature. In most cases, high Al concentration increased the chain transfer from the Ti-species, and resulted in lower molecular weights and broader molecular weight distributions, which agree with recent restults by trichlorotitanium and half-titanocene pro-catalysts [32,33]. Given this, ethylene polymerization using **1**–**5**/MAO systems were carried out with the Al/Ti ratio of 5000:1 at 50 °C under 10 atm ethylene, and the results are tabulated in Table 2.

The catalytic performances by the titanium pro-catalysts varied due to the different ligand environments present (runs 8, 11–14, Table 2). The **5/MAO** ($R^2 = CF_3$, $R^4 = Cl$) system exhibited the highest activity (run 14, Table 2), whilst the **2/MAO** ($R^2 = Me$) system showed a higher activity (run 12, Table 2) than did the other three pro-catalysts for which $R^2 = H$. These results indicated the positive influence on activity caused by the *meta*-substituents of the pyridyl framework. The catalytic system **1** showed better activity than the pro-catalysts **3** and **4** (runs 8, 11, and 13, Table 2), indicating a negative response from the *para*-methyl groups on the pyridyl framework. For **4** with $R^1 = Me$, a slightly better activity than that for **3** was observed.

Table 1
Crystal refinement of **2** and **4**.

	2	**4**
CCDC No.	807956	807957
Empirical formula	$C_{21}H_{27}Cl_3N_2OTi$	$C_{22}H_{29}Cl_3N_2OTi$
Formula weight	477.70	491.72
Crystal color	Brown	red
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
space group	P2(1)/n	P2(1)/n
a (Å)	10.178(2)	10.106(2)
b (Å)	14.711(3)	15.088(3)
c (Å)	15.268(3)	17.570(4)
á (°)	90.00	90.00
β (°)	93.95(3)	94.77(3)
ã (°)	90.00	90.00
Volume ($Å^3$)	2280.7(8)	2669.7(9)
Z	4	4
*D*calc (Mg m^{-3})	1.391	1.223
μ (mm^{-1})	0.741	0.635
F (000)	992	1024
Crystal size (mm)	0.17 × 0.16 × 0.10	0.240 × 0.226 × 0.208
θ range (°)	1.34–27.49	1.78–27.47
Limiting indices	$-13 \le h \le 11$	$-13 \le h \le 12$
No. of rflns collected	20069	23629
No. of unique rflns	5161	6029
Rint	0.0518	0.0542
Completeness to θ (%)	98.8%	98.6%
Goodness-of-fit on F^2	1.162	1.174
Final R indices [I > 2σ (I)]	R1 = 0.0608, wR2 = 0.1362	R1 = 0.0650, wR2 = 0.1654
R indices (all data)	*R*1 = 0.0668, wR2 = 0.1400	*R*1 = 0.0770, wR2 = 0.1759
Largest diff peak, hole (e $Å^{-3}$)	0.704, −0.341	0.565,−0.459

3.2.2. Co-polymerization of ethylene with α-olefin

The trichlorotitanium complexes provide more space for the co-monomer to coordinate. As the highest activity in ethylene polymerization was observed using pro-catalyst **5**, this system was employed in selecting the monomer concentration by using the same optimum reaction conditions as for the ethylene polymerization runs. Surprisingly, lower activities were observed by the title titanium pro-catalysts for the co-polymerization of ethylene with 1-hexene, and the results are collected in Table 3. The T_m values for the resultant polymers (runs 1–3, Table 3) decreased along with higher 1-hexene concentration. A 3.28% molar incorporation of 1-hexene was achieved in the system with 1.0 mol/L 1-hexene [34]. The best performance was achieved with 0.3 mol/L 1-hexene, and thus such conditions were employed in the further investigations of the other pro-catalysts. Compared with the activity data for ethylene polymerization, although lower, the activities for the co-polymerization of ethylene and 1-hexene showed the same trends due to the environmental influences exerted by the ligands, thus the activities decreased in the order: **5** (CF_3, Cl) > **2** (4-Me) > **1** (H) > **3** (3-Me) > **4** (2,4–diMe) (runs 2, 4–7, Table 3).

Table 2
Ethylene polymerization results by **1**–**5**/MAO.[a]

Run	Cat.	Al/Ti	T/(°C)	PE (g)	Act[b]	M_w[c,d]	M_w/M_n[c]	T_m[e](°C)
1	**4**	3000	20	0.122	4.86	91.4	4.1	134.3
2	**4**	4000	20	0.293	11.7	80.5	4.1	133.8
3	**4**	5000	20	0.355	14.2	73.9	3.4	132.7
4	**4**	6000	20	0.263	10.5	40.2	4.5	131.1
5	**4**	7000	20	0.172	6.89	28.3	9.5	130.8
6	**4**	8000	20	0.128	5.10	25.1	13.3	128.2
7	**4**	5000	40	0.376	15.1	77.3	5.4	132.8
8	**4**	5000	50	0.513	20.5	46.0	5.6	132.5
9	**4**	5000	70	0.490	19.6	32.4	6.8	132.1
10	**4**	5000	80	0.469	18.8	20.3	8.1	131.8
11	**1**	5000	50	0.630	25.2	18.7	8.1	131.8
12	**2**	5000	50	0.795	31.8	37.7	6.1	132.6
13	**3**	5000	50	0.498	19.9	62.1	7.0	133.0
14	**5**	5000	50	1.328	53.1	11.9	3.3	133.1

[a] Condition: 5 μmol Ti, 10 atm ethylene, toluene (total volume 100 mL), 30 min.
[b] Activity: 10^4 g mol^{-1}(Ti) h^{-1}.
[c] Determined by GPC.
[d] 10^4 g mol^{-1}.
[e] Determined by DSC.

Table 3
Co-polymerization of Ethylene with 1-Hexene by **1**–**5**/MAO.[a]

Run	Cat.	$1-C_6H_{12}$ (mol/L)	Poly (g)	Act[b]	M_w[c,d]	M_w/M_n[c]	T_m[e] (°C)
1	**5**	0.1	0.144	0.58	32.0	6.4	129.6
2	**5**	0.3	0.642	2.59	48.3	9.0	124.8
3	**5**	1.0	0.222	0.89	–[f]	–	118.9
4	**1**	0.3	0.334	1.34	36.7	10.8	127.6
5	**2**	0.3	0.717	2.87	22.5	9.1	128.1
6	**3**	0.3	0.275	1.10	27.0	9.3	125.6
7	**4**	0.3	0.186	0.75	53.8	6.7	125.8

[a] Conditions: 5 μmol Ti, MAO, Al/Ti = 5000, 10 atm, toluene (total volume 100 mL), 1-hexene (mol/L), 30 min. 50 °C.
[b] Activity: 10^5 g mol^{-1} h^{-1}.
[c] Determined by GPC.
[d] 10^4 g mol^{-1}.
[e] Determined by DSC.
[f] Polymer partly unsolvable.

All the co-polymers obtained had higher molecular weights ($27.0–53.8 \times 10^4$ g mol^{-1}) with broader distributions, which was probably caused by the presence of several active species generated during the catalytic process. On checking structural information in the literature, it appears that four-membered metallocycles of titanium with pyridyl and imino groups are not configurationally stable in solution, and can thus generate different active sites [35,36]. The polyethylenes obtained in the ethylene polymerization were also found to possess broader molecular weight distributions. Another plausible reason is the instability associated with the imino (C=N) group [1,37–41]. The lower T_m values of co-polymers (124–127 °C) compared with those of the polyethylene (131–133 °C) suggested that some branched polymers resulted.

The co-polymerization of ethylene with 1-octene by the **1**–**5**/MAO systems was also conducted, and the results are collected in Table 4. Interestingly, higher activities were achieved in the co-polymerization of ethylene with 1-octene, suggesting here a positive "co-monomer effect", which was significantly different to the co-polymerization of ethylene with 1-hexene (Table 3). The environmental influences of the ligands were similar to the above copolymerzation of ethylene with 1-hexene.

Resultant co-polymers had lower molecular weights ($16.8–28.5 \times 10^4$ g mol^{-1}) and broader distributions than the co-polymers obtained by the co-polymerization of ethylene with 1-hexene. ^{13}C NMR spectra of the poly(ethylene-*co*-1-octene) (shown in Fig. 3) revealed a 3.83% molar incorporation of 1-octene.

Table 4
Co-polymerization of Ethylene with 1-octene by **1**–**5**/MAO.[a]

Run	Cat	Poly(g)	Act[b]	M_w[c,d]	M_w/M_n[c]	T_m[e] (°C)
1	**1**	0.699	2.79	26.1	19.2	124.8
2	**2**	0.600	2.39	23.6	19.5	125.1
3	**3**	0.583	2.33	16.8	16.6	124.7
4	**4**	0.564	2.26	28.5	25.1	126.1
5	**5**	1.78	7.12	24.7	14.6	123.8

[a] Conditions: 5 μmol of cat, MAO, Al/Ti = 5000, 10 atm, toluene, total volume 100 mL, 0.3 mol/L 1-octene, 30 min. 50 °C.
[b] Activity:10^5 g mol^{-1} h^{-1}.
[c] Determined by GPC.
[d] 10^4 g mol^{-1}
[e] Determined by DSC.

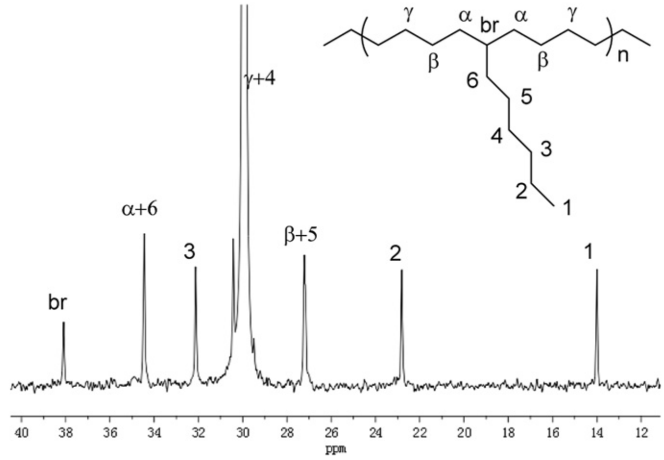


Fig. 3. ^{13}C NMR spectrum of the co-polymer of ethylene with 1-octene by **5**/MAO (run 5, Table 4).

4. Conclusion

The trichlorotitanium 2-(2-pyridinyliminomethyl)phenolates **1**–**5** were found to possess distorted octahedral geometry at Ti, and included a 4-membered titanocyclic ring involving the imino and pyridyl groups. In the presence of MAO, such titanium pro-catalysts performed with high activities in ethylene (co) polymerization with an optimum reaction temperature of 50 °C. Good incorporation of α-olefins in co-polymerizations was achieved with more than 3 mol% for both 1-hexene and 1-octene; a negative "co-monomer effect" was observed for 1-hexene, but a positive effect was seen for 1-octene. Regarding the environmental influence of ligands, pro-catalysts with *meta*-substituents at the pyridyl group generally showed higher activity, but negative influences were commonly encountered by pro-catalysts bearing *para*-substituents at the pyridyl group.

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