Titanium isopropoxide complexes of a series of sterically demanding aryloxo based $[N_2O_2]^{2-}$ ligands as precatalysts for ethylene polymerization†

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Several titanium isopropoxide complexes [*N*,*N*′-*bis*(2-oxo-3-R_1-5-R_2-phenylmethyl)-*N*,*N*′-*bis*(methylene-*p*-R_3-C_6H_4)-ethylenediamine]Ti(O^iPr)$_2$ [R_1 = *t*-Bu, R_2 = Me, R_3 = H (**1b**); R_1 = R_2 = *t*-Bu, R_3 = H, (**2b**); R_1 = R_2 = Cl, R_3 = H, (**3b**), R_1 = *t*-Bu, R_2 = Me, R_3 = Cl (**4b**); R_1 = R_2 = *t*-Bu, R_3 = Cl, (**5b**); R_1 = R_2 = R_3 = Cl, (**6b**)] supported over sterically demanding aryloxy based $[N_2O_2]H_2$ ligands have been designed as precatalysts for the ethylene polymerization. Specifically, the **1b–6b** complexes, when treated with methylaluminoxane (MAO) under 88 ± 0.5 psi of ethylene at 30 °C for 3 h, produced polyethylene polymers of high molecular weight (M_w = *ca.* 7.2–8.3 × 10^5 g mol^{-1}) having broad molecular weight distribution (PDI = *ca.* 13.1–14.6). The **1b–6b** complexes were conveniently synthesized from the direct reaction of the $[N_2O_2]H_2$ ligands, **1a–6a**, with Ti(O^iPr)$_4$ in 69–86% yield.

Introduction

The area of early transition metal mediated Ziegler–Natta polymerization is inundated with diverse initiators varying from the metallocenes[1] to half sandwich[2] "constrained geometry"[3] catalysts to a variety of non-metallocene ones[4] like the diamides,[5] phenoxy imines[6] and the amidinates[7] *etc.* Over the years the rational catalyst design approach was effectively employed in synthesizing improved initiators and thus has enormously contributed to the developments in the field. Notable among the post-metallocene catalysts are the aryloxy ones,[8] which are particularly known for their special ability to stabilize the early transition metal complexes by forming strong metal–O (aryloxy) bonds owing to the good π-donor ability of the aryloxy-O atom, and have been shown to be active in the ethylene homo-polymerization[9] and in co-polymerizations.[10] Surprisingly enough, despite the more familiar use of the aryloxy based precatalysts in ethylene polymerization, the same use of the alkoxy counterparts is conspicuously less. The alkoxy moiety, by virtue of being extremely basic, exhibits intriguing chemistry and is often found bridging between metal centres resulting in agglomerated multinuclear frameworks and thus the alkoxy ligands as such do not provide conducive platforms for the design of discrete well-defined olefin polymerization initiators. As the synthesis of mononuclear alkoxy initiators of early transition metals poses a formidable challenge, with well-defined examples of such initiators being rare, we became interested in designing simple monomeric titanium alkoxy initiators, like its isopropoxide derivative, for ethylene polymerization and intended to do so by employing sterically demanding chelating aryloxo based $[N_2O_2]$ ligand scaffolds. We rationalized the hard N and O donors of the aryloxo based $[N_2O_2]$ and the alkoxy ligands on titanium together would bring about additional stabilization of the diamagnetic d^0 Ti(IV) center against any reduction to a paramagnet d^1 Ti(III) state particularly during the course of olefin polymerization in the presence of the large excess of electron rich methylaluminoxane (MAO) activator.

Furthermore, keeping the extreme reactivity of the simple alkoxy moieties in mind, we chose to target the O^iPr derivatives, as opposed to the less bulkier OMe or OEt derivatives for designing titanium initiators for ethylene polymerization, with the sole intent of isolating well-defined discrete monomeric precatalysts. In this regard it is worth noting that the use of simple alkoxy complexes of group 4 metals is rare in ethylene polymerization with only a handful of examples of the use of initiators like Ti(OBu)$_4$,[11] and CpTi(OBz)$_3$,[12] existing, which when activated with coinitiators like Et_3Al or $Et_2Al_2Cl_3$, exhibited ethylene polymerization as well as copolymerization activities.

With our interest being in exploring the utility of transition metal complexes in biomimetic chemistry[13] and in chemical catalysis namely, the C–C[14] and C–N[15] bond forming reactions, the ring-opening polymerization (ROP) of L-lactide[16] and the sulfoxidation reaction,[17] we set out to examine the potential of titanium isopropoxy complexes in another important application like the ethylene polymerization.

In this contribution, we report a series of titanium isopropoxy complexes [*N*,*N*′-*bis*(2-oxo-3-R_1-5-R_2-phenylmethyl)-*N*,*N*′-*bis*(methylene-*p*-R_3-C_6H_4)-ethylenediamine]Ti(O^iPr)$_2$ [R_1 = *t*-Bu, R_2 = Me, R_3 = H (**1b**); R_1 = R_2 = *t*-Bu, R_3 = H, (**2b**); R_1 = R_2 = Cl, R_3 = H, (**3b**); R_1 = *t*-Bu, R_2 = Me, R_3 = Cl (**4b**); R_1 = R_2 = *t*-Bu, R_3 = Cl, (**5b**); R_1 = R_2 = R_3 = Cl, (**6b**)] supported over sterically demanding aryloxy based $[N_2O_2]H_2$ ligands as

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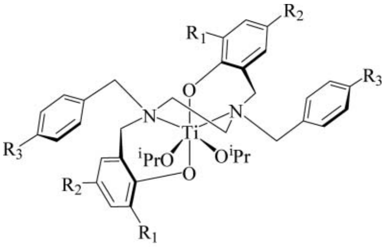
precatalysts for ethylene polymerization (Fig. 1). Specifically, when activated with methylaluminoxane (MAO) the complexes **1b–6b** exhibited appreciable ethylene polymerization activities yielding high molecular weight polyethylene polymers in presence of ethylene gas at 30 °C.



R$_1$ = *t*-Bu, R$_2$ =Me, R$_3$ = H (**1b**)
R$_1$ = R$_2$ = *t*-Bu, R$_3$ = H (**2b**)
R$_1$ = R$_2$ = Cl, R$_3$ = H (**3b**)
R$_1$ = *t*-Bu, R$_2$ =Me, R$_3$ = Cl (**4b**)
R$_1$ = R$_2$ = *t*-Bu, R$_3$ = Cl (**5b**)
R$_1$ = R$_2$ = R$_3$ = Cl (**6b**)

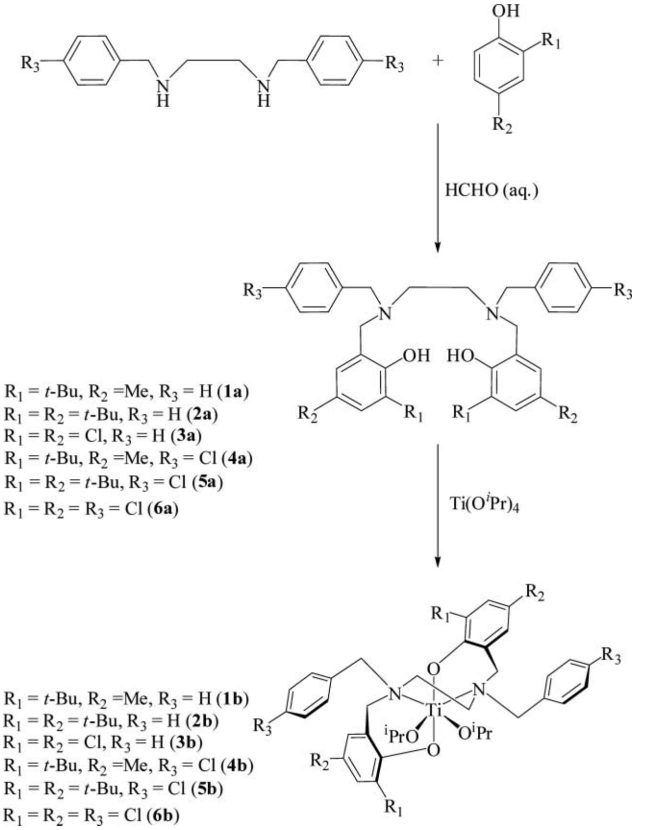
Fig. 1 Titanium isopropoxide **1b–6b** complexes supported over $[N_2O_2]^{2-}$ ligands.

Results and Discussion

A set of sterically demanding aryloxy based $[N_2O_2]H_2$ ligands namely *N*,*N′*-*bis*(2-hydroxo-3-R$_1$-5-R$_2$-phenylmethyl)-*N*,*N′*-*bis*(methylene-*p*-R$_3$-C$_6$H$_4$)-ethylenediamine [R$_1$ = *t*-Bu, R$_2$ = Me, R$_3$ = H (**1a**); R$_1$ = R$_2$ = *t*-Bu, R$_3$ = H, (**2a**); R$_1$ = R$_2$ = Cl, R$_3$ = H, (**3a**), R$_1$ = *t*-Bu, R$_2$ = Me, R$_3$ = Cl (**4a**); R$_1$ = R$_2$ = *t*-Bu, R$_3$ = Cl, (**5a**); R$_1$ = R$_2$ = R$_3$ = Cl, (**6a**)] were employed in stabilizing the titanium isopropoxide **1b–6b** complexes for their utility in ethylene polymerization (Fig. 1). The **1a–6a** ligands were obtained by the Mannich condensation reaction of the *N*,*N′*-*bis*(methylene-*p*-R$_3$-C$_6$H$_4$)-ethylenediamine (R$_3$ = Cl, H), formaldehyde and the respective 2,4-disubstituted phenols in 36–57% yield (Scheme 1).

The titanium isopropoxide complexes, **1b–6b**, were synthesized by the direct reaction of the **1a–6a** ligands with Ti(O^{i}Pr)$_4$ in 69–86% yield (Scheme 1). Of particular interest are the titanium bound two O^{i}Pr moieties that appeared as a septet at 4.86–5.18 ppm ($^3J_{HH}$ = 6 Hz) and as two doublets at 1.14–1.33 ppm ($^3J_{HH}$ = 6 Hz) and 0.86–1.30 ppm ($^3J_{HH}$ = 6 Hz) in the ^{1}H NMR spectrum and at 25.9–27.1 ppm and 25.7–26.7 ppm respectively in the corresponding ^{13}C{^{1}H} NMR spectrum of the **1b–6b** complexes (ESI Fig. S4–S19†). More interestingly so, the hydrogen resonances of the two of the three methylene (C*H*$_2$) groups in the **1b–6b** complexes were found to be diastereotopic in nature with each appearing as two sets of doublets at 4.22–4.29 ppm ($^2J_{HH}$ = 13 Hz) and 3.23–3.41 ppm ($^2J_{HH}$ = 13 Hz) and at 2.62–2.90 ppm ($^2J_{HH}$ = 10 Hz) and 2.29–2.44 ppm ($^2J_{HH}$ = 10 Hz) consistent with the C_2 symmetric octahedral geometry of the complexes in solution. The hydrogens of the third methylene (C*H*$_2$) group were however not diastereotopic and appeared as a singlet at 4.15–4.22 ppm.

As intended with the incorporation of the O^{i}Pr moieties on titanium, and also having further stabilization from the sterically demanding aryloxy based $[N_2O_2]^{2-}$ ligand, the molecular structures as determined by X-ray diffraction studies, indeed, revealed the **1b–6b** complexes[18] to be discrete monomers with the metal centers residing in distorted octahedral environments. The two metal bound O^{i}Pr moieties occupied adjacent *cis* positions while the $[N_2O_2]^{2-}$ ligand occupied the remaining four sites in a C_2 symmetric fashion. (Tables 1–2, Fig. 2–3 and ESI Fig. S1–S2†).



Scheme 1 General synthetic procedure of the **1b–6b** complexes.

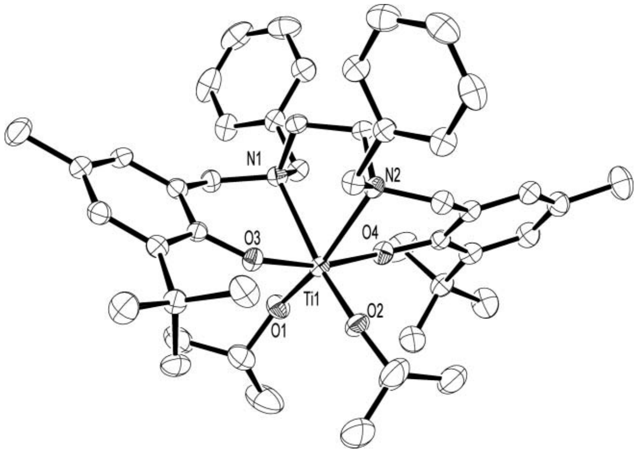


Fig. 2 ORTEP view of the solid state structure of **1b**. The thermal ellipsoids are shown in 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are given: Ti1–O1 1.812(2), Ti1–O2 1.792(2), Ti1–O3 1.902(2), Ti1–O4 1.900(2), Ti1–N1 2.373(3), Ti1–N2 2.378(2), O2–Ti1–O1 104.86(10), O2–Ti1–O4 97.23(10), O1–Ti1–O4 91.59(9), O2–Ti1–O3 92.28(10), O1–Ti1–O3 95.76(9), O4–Ti1–O3 166.09(9), O2–Ti1–N1 164.48(9), O1–Ti1–N1 89.78(9).

Table 1 X-Ray crystallographic data for **1b**, **4b–6b**

Compound	**1b**, toluene	**4b**, benzene	**5b**, toluene	**6b**
Lattice	Triclinic	Triclinic	Monoclinic	Trigonal
Formula	$C_{53}H_{72}N_2O_4Ti$	$C_{55}H_{71}Cl_2N_2O_4Ti$	$C_{65.17}H_{84.35}Cl_2N_2O_4$ Ti	$C_{36}H_{38}Cl_6N_2O_4Ti$
Formula weight	849.03	942.94	1078.56	823.28
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$R\bar{3}c$
a/Å	12.660(3)	12.046(4)	21.794(5)	25.591(4)
b/Å	14.159(10)	13.411(5)	20.558(3)	25.591(4)
c/Å	15.4004(16)	17.802(6)	15.600(3)	29.747(6)
α (°)	83.58(2)	95.17(3)	90.00	90.00
β (°)	74.622(14)	102.22(3)	117.09(3)	90.00
γ (°)	64.80(5)	110.10(3)	90.00	120.00
V/Å^3	2408.4(19)	2597.8(15)	6223(2)	16871(5)
Z	2	2	4	18
T/K	120(2)	150(2)	150(2)	150(2)
Radiation (λ/Å)	0.71073	0.71073	0.71073	0.71073
ρ(calcd.),g cm^{-3}	1.171	1.205	1.151	1.459
μ(Mo-Kα)/mm^{-1}	0.223	0.313	0.269	0.697
θ max,deg.	25.00	25.00	32.64	25.18
Reflection collected/unique	20221/8412	18346/9114	30359/10357	36190/3371
R(int)	0.0951	0.1056	0.0677	0.2525
Data/restraints/parameters	8412/0/554	9114/0/589	10357/0/378	3371/0/224
R indices (all data)	$R_1 = 0.0866$, w$R_2 = 0.1717$	$R_1 = 0.2158$, w$R_2 = 0.1803$	$R_1 = 0.1501$, w$R_2 = 0.1456$	$R_1 = 0.1305$, w$R_2 = 0.2108$
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0617$, w$R_2 = 0.1506$	$R_1 = 0.0918$, w$R_2 = 0.1424$	$R_1 = 0.0577$, w$R_2 = 0.1265$	$R_1 = 0.0741$, w$R_2 = 0.1939$
GOF	1.036	0.988	0.840	0.959

Table 2 Comparison of bond lengths (Å) and bond angles (°) in the **1b–6b** complexes

Complex	Ti–O(^{i}Pr) bond	Ti–O (aryloxy) bond	Ti–N bond	∠Ti–O(^{i}Pr)–C(^{i}Pr)	∠O (^{i}Pr)–Ti–O (^{i}Pr)	∠O (aryloxy)–Ti–O (aryloxy)	Reference
1b	1.812(2), 1.792(2)	1.902(2), 1.900(2)	2.373(3), 2.378(2)	133.3(2), 165.2(3)	104.86(10)	166.09(9)	this work
2b	1.800(5), 1.818(4)	1.895(4), 1.890(4)	2.415(4), 2.419(5)	138.3(4), 148.9 (5)	105.07(9)	166.20(8)	[a]
3b	1.798(3), 1.782(3)	1.919(3), 1.916(3)	2.376(3), 2.331(3)	138.9(3), 142.8(3)	105.25(14)	164.16(12)	[b]
4b	1.811(4), 1.796(4)	1.903(4), 1.884(4)	2.372(5), 2.395(5)	136.1(4), 157.7(4)	106.09 (18)	165.01(16)	this work
5b	1.823(2)	1.887(2)	Ti1–N1 2.401(3)	136.0(2)	108.72(15)	168.70 (15)	this work
6b	1.767(4)	1.909(4)	Ti1–N1 2.354(4)	158.9(7)	106.9(3)	162.9 (2)	this work

[a] S. H. Kim, J. Lee, D. J. Kim, J. H. Moon, S. Yoon, H. J. Oh, Y. Do, Y. S. Ko, J. H. Yim and Y. Kim, *J. Organomet. Chem*, 2009, **694**, 3409–3417.
[b] M. K. Panda, M. M. Shaikh and P. Ghosh, *Dalton Trans.* 2010, **39**, 2428–2440.

Of particular interest are the Ti–O bond lengths in the **1b–6b** complexes that exhibited two different distances consisting of a shorter Ti–O(isopropoxy) bond [1.767(4)–1.823(2) Å] and a longer Ti–O(phenoxy) bond [1.884(4)–1.919(3) Å] (Tables 1–2, Fig. 2–3 and ESI Fig. S1–S2†). The shorter Ti–O(isopropoxy) bond lengths in **1b–6b** can be ascribed to an additional π-type interaction of an oxygen lone pair of the O^{i}Pr moiety with an empty metal d orbital of titanium, common in many related titanium isopropoxide complexes observed earlier by us[17] as well as by others.[19] Additionally, the wide bond angles of the titanium bound isopropoxy oxygens [∠ Ti–O–C 133.3(2)°–165.2(3)°] in the **1b–6b** complexes further testified toward the presence of π-type interaction between the isopropoxy group and the metal. The Ti–O(phenoxy) distances of 1.884(4)–1.919(3) Å were relatively longer suggesting lesser degree of the π-type interaction prevalent between the aryloxy group and titanium and so the Ti–O(phenoxy) distances were slightly shorter than the sum of the individual covalent radii of Ti and O (1.984 Å).[20] The Ti–N distances [2.331(3)–2.413(2) Å] on the other hand resembled elongated single bond distances as these appeared even longer than the sum of the individual covalent radii of Ti and N (2.024 Å).[20]

Table 3 The MAO: catalyst variation study for precatalyst **1b**

S. No	Al(MAO)/Ti	activity/g of PEmol^{-1}Tih^{-1}
1.	500	4010
2.	1000	24300
3.	1500	20000
4.	2000	20500

Polymerization conditions: polymerization pressure: 88 ± 2 Psi, temperature: 30 ± 1 °C, time: 3 h.

Significantly enough, all of the isopropoxy **1b–6b** complexes were found to be active for ethylene polymerization upon activation with MAO. In particular, the **1b–6b** complexes exhibited ethylene polymerization activity when treated with methylaluminoxane (MAO) in the presence of ethylene at 30 °C. The optimal polymerization conditions were obtained for a representative precatalyst **1b** by varying the precatalyst to MAO mole ratio from 1 : 500 to 1 : 2000 and which showed that the precatalyst activity increased from 4.0 Kg of PE mol^{-1} h^{-1} to 20.5 Kg of PE mol^{-1} h^{-1} respectively with the maximum activity of 24.3 Kg of PE mol^{-1} h^{-1} observed for the 1 : 1000 ratio (Table 3). Furthermore, the time dependence study performed with the same representative precatalyst **1b** showed similar increase of activity with time with the maximum increase seen at 3 h after which it plateaued off

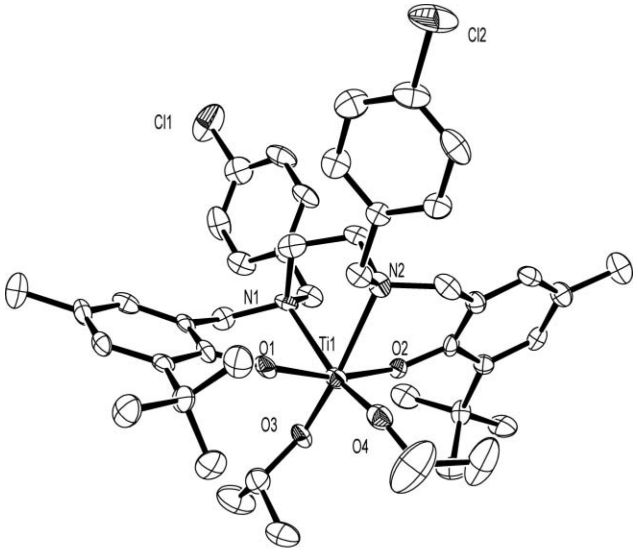


Fig. 3 ORTEP view of the solid state structure of 4b. The thermal ellipsoids are shown in 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are given: Ti1–O1 1.903(4), Ti1–O2 1.884(4), Ti1–O3 1.811(4), Ti1–O4 1.796(4), Ti1–N1 2.372(5), Ti1–N2 2.395(5), O4–Ti1–O3 106.09(18), O4–Ti1–O2 97.30(16), O3–Ti1–O2 92.86(17), O4–Ti1–O1 93.79(17), O4–Ti1–N1 160.92(18), O3–Ti1–N1 92.29(16), O2–Ti1–N1 86.62(15), O1–Ti1–N1 79.68(16).

(Table 4). Based on the above observations, the **1b–6b** complexes, thus, when activated with 1000 equivalents of methylaluminoxane (MAO) and subjected to 88 psi of ethylene for 3 h, yielded high molecular weight polyethylene polymers with broad molecular weight distributions (Table 5). The most of the polyethylene polymers were found to be insoluble in the 1,2,4-trichlorobenzene at 150 °C thereby suggesting the formation of very high molecular weight polymers. The polyethylene polymers that could be analyzed by high temperature gel permeation chromatography (GPC) showed high molecular weight (M_w = *ca.* 7.2–8.3 × 10^5 g mol^{-1}) with broad molecular weight distribution (PDI = *ca.* 13.1–14.6) with long tailing in the low and high molecular weight regions. Similar observation has been made for zirconium(IV) complexes $[(CF_3)_2C(O)CH_2C(R^1) = NPh]_2ZrCl_2$ (R^1 = Me, Ph, Ar^F),[21] a titanium(IV) complex, $Tp^{Ms*}TiCl_3$ and a titanium(III) complex $K[Tp^{Ms*}TiCl_3]$ {(Tp^{Ms*} = HB(3-mesitylpyrazolyl) 2(5-mesityl-pyrazolyl)}[22] that also produced insoluble polyethylene polymers when activated with MAO but for different metal and ligand systems exhibiting different mechanisms and deactivation pathways. In this regard, it should be noted that the direct comparisons of **1b–6b** with other systems, however, is difficult since the polymerization conditions as well as the metal and ligand systems vary drastically from each other. The observed broad PDI values of the polymers may arise due to the long activation period leading to low initiation efficiency in the alkylation step of the **1b–6b** complexes by MAO. However, other factors like the change in $R_{growth}/R_{transfer}$ ratio during polymerization as a result of chain-transfer to MAO,[23] or the presence of multiple active species or even the heterogeneity of the reaction medium arising out of the precipitation of the polyethylene polymer may also contribute to the observed broadening of the PDI values.

Table 4 Time dependent study of ethylene polymerization by **1b**

S. No	Time/h	Activity/g of PEmol^{-1}Tih^{-1}
1	0.5	0
2	3	4010
3	4	4600
4	5	5000

Polymerization conditions: polymerization pressure: 88 ± 2 Psi, temperature: 30 ± 1 °C, Al(MAO)/Ti: 500.

An assessment about the degree of crystallinity in the polyethylene polymer was obtained using differential scanning calorimetry (DSC) studies that showed the polymer melting temperature (T_m) of 137–139 °C and the crystallization temperature (T_c) of 112–114 °C (Table 4) indicating the presence of linear polymer chains with little branching contents. The $^{13}C\{^1H\}$ NMR analysis of the polymer showed no minor peak except for only one strong peak assignable to the backbone methylene (CH_2) resonance suggesting the formation of linear polymer chains.[6h,i]

More interestingly so, the methylaluminoxane (MAO) activated ethylene polymerization of the titanium isopropoxide **1b–6b** precatalysts proceeded *via* a coordination-insertion pathway by the elimination of two *cis* labile isopropoxide groups while the other possibility of a radical pathway was ruled out based on EPR studies. Specifically, the EPR analysis of a solution of a representative precatalyst **2b** containing a large excess (226 equivalents) of methylaluminoxane (MAO) in toluene showed no presence of any radical species, thereby ruling out the radical pathway (see ESI Fig. S3†). The lack of any reduction of the diamagnetic d^0 Ti(IV) **2b** precatalyst to a paramagnetic d^1 Ti(III) radical species in presence of the large excess of the electron rich methylaluminoxane (MAO) coinitiator can be attributed to the stabilization of the Ti(IV) **2b** precatalyst by the hard N and O donors of the aryloxy based $[N_2O_2]^{2-}$ ligand.[24]

Table 5 Ethylene polymerization by precatalysts **1b–6b** activated by methylaluminoxane (MAO)

S. No.	precatalyst	Activity/g of PEmol^{-1}Tih^{-1}	$M_w \times 10^{-5}$/g mol^{-1}	M_w/M_n	T_m/°C	T_c/°C
1	**1b**	24300	7.2	13.1	138	113
2	**2b**	13400	insoluble[a]		139	112
3	**3b**	3400	insoluble[a]		137	112
4	**4b**	3660	8.3	14.6	139	114
5	**5b**	14600	insoluble[a]		137	112
6	**6b**	15100	insoluble[a]		138	114

Polymerization conditions: polymerization pressure: 88 ± 2 Psi, temperature: 30 ± 1 °C, Al(MAO)/Ti: 1000, time 3 h.[a] GPC could not be carried out due to insolubility of polymer in 1,2,4-trichlorobenzene at 150 °C.

The comparison of the **1b–6b** precatalysts with other reported titanium isopropoxy complexes for olefin polymerization is important. Although titanium halide complexes have long been studied for olefin polymerization,[25] the reports of titanium isopropoxy based ones are relatively rare. In this regard we are aware of only a handful of reports of the titanium isopropoxide based initiators for the styrene[26] and ethylene polymerizations[21,27] and the ethylene-styrene copolymerization.[10g] Of particular interest are the $[(CF_3)_2C(O)CH_2C(R^1)=NPh]_2Ti(O^iPr)_2$ (R^1 = Me, Ph) complexes, which when activated with MAO (MAO/Ti = 1100–1500), produced polyethylene polymers of high molecular weight ($M_w = 3.7–4.3 \times 10^5$ g mol^{-1}) having a narrow polydispersity index (PDI) range of 2.7–4.7,[21] and which is only similar to the molecular weight ($M_w = 7.2–8.3 \times 10^5$ g mol^{-1}) but different from the broad molecular weight distribution (PDI = 13.1–14.6) observed for the **1b–6b** precatalysts. Also, another isopropoxy complex, [1-*di*-R-amino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-olate]$_2$Ti(O^{i}Pr)$_2$, (R = ^{i}Pr, CH$_2$Ph, ^{t}Bu),[28] polymerized ethylene in presence of MAO (MAO/Ti = 500–1000) giving extremely high molecular weight ($M_w = 1.11–1.50 \times 10^6$ g mol^{-1}) polyethylene polymer exhibiting a modestly broad polydispersity index (PDI = 2.1–6.3).

Conclusion

In summary, relatively rare titanium isopropoxide based precatalysts, **1b–6b**, supported over sterically demanding $[N_2O_2]H_2$ ligands have been designed for the ethylene polymerization. The **1b–6b** complexes when activated with methylaluminoxane (MAO) produced high molecular weight (M_w) polyethylene polymers with broad molecular weight distributions. The EPR studies indicated that the ethylene polymerization by the **1b–6b** complexes proceeded *via* a coordination-insertion pathway.

Experimental Section

General Procedures

All manipulations were carried out using standard Schlenk techniques and glove box. Solvents were purified and degassed by standard procedures. The 2,4-di-*t*-butylphenol, 2-*t*-butyl-4-methylphenol and Ti(O^{i}Pr)$_4$ were purchased from Sigma Aldrich, Germany and used without any further purification. The 2,4-*di*-chlorophenol was purchased from Spectrochem, India. The *N*,*N′*-di-benzylethylenediamine and *N*,*N′*-di-*p*-chlorobenzylethylenediamine were prepared according to literature procedure.[29] The **2a**,[30] **2b**,[30] **3a**[17] and **3b**[17] were prepared by following a modified literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. ^{1}H NMR peaks are labelled as singlet (s), doublet (d), triplet (t) and septet (sept). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer. X-Ray diffraction data were collected on a Bruker P4 difractometer equipped with a SMART CCD detector. The crystal data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 6.10).[31] CCDC 643954, CCDC 709171, CCDC 722297 and CCDC 715915 contain the supplementary crystallographic data for the palladium **1b**, **4b–6b** complexes respectively. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or in the ESI.† Elemental analysis was carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer.

Synthesis of *N*,*N′*-*Bis*(2-hydroxo-3-*t*-butyl-5-methylphenylmethyl)-*N*,*N′*-dibenzylethylenediamine (1a)

A solution of *N*,*N′*-dibenzylethane-1,2-diamine (1.50 g, 6.25 mmol), 2-*t*-butyl-4-methylphenol (2.05 g, 12.5 mmol) and aqueous formaldehyde (37% w/v, 2.06 g, 25.0 mmol) in methanol (*ca.* 20 mL) was refluxed for 24 h. A white precipitate was formed which was filtered and washed with methanol (*ca.* 4 × 20 mL) and then vacuum dried to obtain product **1a** as white solid (1.50 g, 41%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C), δ 10.5 (s, 2H, O*H*), 7.26-7.24 (m, 6H, C$_6$*H*$_5$), 7.14 (d, 4H, $^3J_{HH}$ = 8 Hz, C$_6$*H*$_5$), 6.97 (s, 2H, C$_6$*H*$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 6.59 (s, 2H, C$_6$*H*$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 3.59 (s, 4H, C*H*$_2$), 3.47 (s, 4H, C*H*$_2$), 2.63 (s, 4H, C*H*$_2$), 2.22 (s, 6H, C*H*$_3$), 1.40 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C), δ 154.1 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 136.8 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 136.5 (*C*$_6$H$_5$), 129.7 (*C*$_6$H$_5$), 128.7 (*C*$_6$H$_5$), 127.7 (*C*$_6$H$_5$), 127.6 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 127.4 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 126.9 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 121.9 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 58.9 (*C*H$_2$), 58.3 (*C*H$_2$), 50.0 (*C*H$_2$), 34.7 (*C*(CH$_3$)$_3$), 29.7 (C(*C*H$_3$)$_3$), 20.8 (*C*H$_3$). IR Data (KBr pellet cm^{-1}): 3428 (w), 3066 (w), 3030 (w), 2951 (s), 2905 (s), 2866 (s), 2807 (m), 1885 (w), 1760 (w), 1605 (m), 1481 (s), 1457 (s),1445 (s), 1361 (s), 1304 (m), 1239 (s), 1203 (m), 1165 (m), 1076 (m), 1029 (w), 968(w), 880 (m), 824 (m), 742 (s), 701 (s), 679 (w), 466 (w). HRMS (ES): *m*/*z* 593.4097 [(ligand+H)]$^+$, Calcd. 593.4107. Anal. Calcd. for $C_{40}H_{52}N_2O_2$: C, 81.04; H, 8.84; N, 4.73. Found: C, 81.41; H, 9.20; N, 5.13.

Synthesis of [*N*,*N′*-*Bis*(2-oxo-3-*t*-butyl-5-methylphenylmethyl)-*N*,*N′*-dibenzylethylenediamine]Ti(O^{i}Pr)$_2$ (1b)

To a solution of ligand *N*,*N′*-*bis*(2-hydroxo-3-*t*-butyl-5-methylphenylmethyl)-*N*,*N′*-dibenzylethylenediamine **1a** (0.153 g, 0.258 mmol) in toluene (*ca.* 5 mL), a solution of Ti(O^{i}Pr)$_4$ (0.147 g, 0.516 mmol) in toluene (*ca.* 1 mL) was added. The resulting solution was stirred at 50 °C for 4 h after which the volatiles were removed under reduced pressure. The residue was washed with hexane (*ca.* 2 ml) and dried under vacuum to obtain product **1b** as a yellow solid (0.168 g, 86%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C), δ 7.23 (br, 8H, C$_6$*H*$_5$), 7.16 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_6$*H*$_5$), 6.91 (s, 2H, C$_6$*H*$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 6.43 (s, 2H, C$_6$*H*$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$), 4.86 (sept, 2H, $^3J_{HH}$ = 6 Hz, OC*H*(CH$_3$)$_2$), 4.24 (d, 2H, $^2J_{HH}$ = 13 Hz, C*H*$_2$), 4.15 (s, 4H, C*H*$_2$), 3.23 (d, 2H, $^2J_{HH}$ = 13 Hz, C*H*$_2$), 2.86 (d, 2H, $^2J_{HH}$ = 10 Hz, C*H*$_2$), 2.29 (d, 2H, $^2J_{HH}$ = 10 Hz, C*H*$_2$), 2.11 (s, 6H, C*H*$_3$), 1.42 (s, 18H, C(C*H*$_3$)$_3$), 1.21 (d, 6H, $^3J_{HH}$ = 6 Hz, OCH(C*H*$_3$)$_2$), 1.08 (d, 6H, $^3J_{HH}$ = 6 Hz, OCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C), δ 159.7 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 136.8 (*C*$_6$H$_5$), 132.7 (*C*$_6$H$_5$), 129.2 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 128.5 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 128.3 (*C*$_6$H$_5$), 128.2 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 127.4 (*C*$_6$H$_5$), 125.5 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 124.0 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 77.8 (O*C*H(CH$_3$)$_2$), 59.6 (*C*H$_2$), 59.1 (C*H*$_2$), 44.9 (C*H*$_2$), 35.0 (*C*(CH$_3$)$_3$), 30.5 (C(*C*H$_3$)$_3$), 26.9 (OCH(*C*H$_3$)$_2$), 26.6 (OCH(*C*H$_3$)$_2$), 21.0 (*C*H$_3$). IR Data (KBr pellet cm^{-1}): 3432 (m), 3027 (w), 2963 (s), 2922 (m), 2860 (s), 2548 (s), 1776 (w), 1603 (w), 1541 (m), 1467 (s),1439 (s), 1376 (w), 1358 (w), 1293 (m), 1263 (s), 1202 (w), 1157 (s), 1124 (s), 1076 (w), 1056 (w), 1002 (s), 989 (s), 915 (w), 861 (m), 842 (s), 797 (w), 783 (w), 731 (w), 705 (m), 630 (w), 609 (m), 582 (w), 564 (s). Anal. Calcd. for $C_{46}H_{64}N_2O_4Ti\cdot C_6H_5CH_3$: C, 74.98; H, 8.55; N, 3.30. Found: C, 74.94; H, 8.97; N, 3.18.

Synthesis of *N*,*N′*-*bis*(2-hydroxo-3-*t*-butyl-5-methylphenylmethyl)-*N*,*N′*-*bis*(*p*-chlorobenzyl)ethylenediamine (4a)

A solution of *N*,*N′*-di-*p*-chlorobenzylethylenediamine (0.403 g, 1.31 mmol), 2-*t*-butyl-4-methylphenol (0.425 g, 2.62 mmol) and aqueous formaldehyde (37% w/v, 0.432 g, 5.25 mmol) in methanol (*ca.* 30 mL) was refluxed for 24 h. A white precipitate was formed which was filtered and washed with methanol (*ca.* 4 × 20 mL) and then vacuum dried to obtain product **4a** as a white solid (0.358 g, 41%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C), δ 10.2 (s, 2H, O*H*), 7.23 (d, 4H, $^3J_{HH}$ = 8 Hz, C$_6$*H*$_4$Cl), 7.06 (d, 4H, $^3J_{HH}$ = 8 Hz, C$_6$*H*$_4$Cl), 6.95 (s, 2H, C$_6$*H*$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 6.57 (s, 2H, C$_6$*H*$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 3.58 (s, 4H, C*H*$_2$), 3.42 (s, 4H, C*H*$_2$), 2.59 (s, 4H, C*H*$_2$), 2.22 (s, 6H, C*H*$_3$), 1.38 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C), δ 153.9 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 136.6 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 135.4 (*C*$_6$H$_4$Cl), 133.6 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 130.9 (*C*$_6$H$_4$Cl), 128.9 (*C*$_6$H$_4$Cl), 127.6 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 127.1 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 127.0 (*C*$_6$H$_2${2-OH,3-C(CH$_3$)$_3$,5-CH$_3$}), 121.7 (*C*$_6$H$_4$Cl), 59.0 (*C*H$_2$), 57.8 (*C*H$_2$), 50.4 (*C*H$_2$), 34.7 (*C*(CH$_3$)$_3$), 29.7 (C(*C*H$_3$)$_3$), 20.9 (*C*H$_3$). IR Data (KBr pellet cm^{-1}): 3378 (s), 3049 (w), 3000 (w), 2949 (s), 2913 (w), 2863 (w), 2823 (m), 1755 (s), 1599 (w), 1544 (w), 1493 (s), 1446 (s), 1408 (w), 1390 (w), 1357 (m), 1302 (w), 1240 (s), 1206 (w), 1144 (m), 1091 (m), 1016 (m), 927 (m), 865 (m), 849 (w), 801 (m), 759 (w), 716 (m), 666 (w), 592 (w), 563 (w), 516 (w), 469 (w). HRMS (ES): *m*/*z* 661.3355 [ligand+H]$^+$, Calcd. 661.3328. Anal. Calcd. for $C_{40}H_{50}Cl_2N_2O_2$: C, 72.60; H, 7.62; N, 4.23. Found: C, 72.38; H, 7.75; N, 4.20.

Synthesis of [*N*,*N′*-*bis*(2-oxo-3-*t*-butyl-5-methylphenylmethyl)-*N*,*N′*-*bis*(*p*-chlorobenzyl)ethylenediamine]Ti(O^{i}Pr)$_2$ (4b)

To a solution of *N*,*N*'-*bis*(2-hydroxo-3-*t*-butyl-5-methylphenylmethyl)-*N*,*N′*-*bis*(*p*-chlorobenzyl)ethylenediamine **4a** (0.203 g, 0.307 mmol) in toluene (*ca.* 5 mL), a solution of Ti(O^{i}Pr)$_4$ (0.174 g, 0.614 mmol) in toluene (*ca.* 2 mL) was added. The resulting solution was stirred at 50 °C for 4 h after which the volatiles were removed under reduced pressure. The residue was washed with hexane (*ca.* 2 mL) and dried under vacuum to obtain product **4b** as a yellow solid (0.181 g, 72%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C), δ 7.29 (d, 4H, $^3J_{HH}$ = 8 Hz, C$_6$*H*$_4$Cl), 6.99 (d, 4H, $^3J_{HH}$ = 7 Hz, C$_6$*H*$_4$Cl), 6.96 (s, 2H, C$_6$*H*$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 6.51 (s, 2H, C$_6$*H*$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 4.92 (sept, 2H, $^3J_{HH}$ = 6 Hz, OC*H*(CH$_3$)$_2$), 4.28 (d, 2H, $^2J_{HH}$ = 13 Hz, C*H*$_2$), 4.18 (s, 4H, C*H*$_2$), 3.25 (d, 2H, $^2J_{HH}$ = 13 Hz, C*H*$_2$), 2.90 (d, 2H, $^3J_{HH}$ = 10 Hz, C*H*$_2$), 2.30 (d, 2H, $^3J_{HH}$ = 10 Hz, C*H*$_2$), 2.19 (s, 6H, C*H*$_3$), 1.48 (s, 18H, C(C*H*$_3$)$_3$), 1.26 (d, 3H, $^3J_{HH}$ = 6 Hz, CH(C*H*$_3$)$_2$), 1.21 (d, 3H, $^3J_{HH}$ = 6 Hz, CH(C*H*$_3$)$_2$. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C), δ 159.6 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 136.8 (*C*$_6$H$_4$Cl), 134.4 (*C*$_6$H$_4$Cl), 133.8 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 131.0 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 128.5 (*C*$_6$H$_4$Cl), 128.4 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 127.5 (*C*$_6$H$_4$Cl), 125.6 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 123.7 (*C*$_6$H$_2$O{3-C(CH$_3$)$_3$,5-CH$_3$}), 77.9 (O*C*H(CH$_3$)$_2$), 59.6 (*C*H$_2$), 58.3 (*C*H$_2$), 44.9 (*C*H$_2$), 35.0 (*C*(CH$_3$)$_3$), 30.5 (C(*C*H$_3$)$_3$), 26.9 (CH(*C*H$_3$)$_2$), 26.6 (CH(*C*H$_3$)$_2$), 21.0 (*C*H$_3$). IR Data (KBr pellet cm^{-1}): 2963 (s), 1467 (s), 1262 (s), 1124 (m), 986 (m), 840 (s), 607 (m), 565 (s). Anal. Calcd. for $C_{55}H_{71}Cl_2N_2O_4Ti$: C, 66.91; H, 7.57; N, 3.39. Found: C, 66.84; H, 7.35; N, 3.09.

Synthesis of *N*,*N′*-*bis*(2-hydroxo-3,5-*di*-*t*-butylphenylmethyl)-*N*,*N′*-*bis*(*p*-chlorobenzyl)ethylenediamine (5a)

A solution of *N*,*N′*-di-*p*-chlorobenzylethylenediamine (0.603 g, 1.95 mmol), 2,4-di-*t*-butylphenol (0.804 g, 3.92 mmol) and aqueous formaldehyde (37% w/v, 0.652 g, 7.92 mmol) in methanol (*ca.* 50 mL) were refluxed for 24 h. A white precipitate formed which was filtered and washed with methanol (*ca.* 4 × 20 mL) and then vacuum dried to obtain product **5a** as a white solid (0.503 g, 36%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C), δ 10.2 (s, 2H, O*H*), 7.23 (d, 4H, $^3J_{HH}$ = 8 Hz, C$_6$*H*$_4$Cl), 7.16 (s, 2H, C$_6$*H*$_2${2-OH,3,5-C(CH$_3$)$_3$}), 7.07 (d, 4H, $^3J_{HH}$ = 8 Hz, C$_6$*H*$_4$Cl), 6.73 (s, 2H, C$_6$*H*$_2${2-OH,3,5-C(CH$_3$)$_3$}), 3.61 (s, 4H, C*H*$_2$), 3.45 (s, 4H, C*H*$_2$), 2.63 (s, 4H, C*H*$_2$), 1.39 (s, 18H, C(C*H*$_3$)$_3$), 1.25 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C), δ 153.8 (*C*$_6$H$_2${2-OH,3,5-C(CH$_3$)$_3$}), 141.1 (*C*$_6$H$_2${2-OH,3,5-C(CH$_3$)$_3$}), 136.0 (*C*$_6$H$_4$Cl), 135.4 (*C*$_6$H$_2$(OH){3,5-C(CH$_3$)$_3$}), 133.6 (*C*$_6$H$_2${2-OH,3,5-C(CH$_3$)$_3$}), 130.9 (*C*$_6$H$_4$Cl), 128.9 (*C*$_6$H$_4$Cl), 123.8 (*C*$_6$H$_2${2-OH,3,5-C(CH$_3$)$_3$}), 123.4 (*C*$_6$H$_2${2-OH,3,5-C(CH$_3$)$_3$}), 121.0 (*C*$_6$H$_4$Cl), 59.4 (*C*H$_2$), 57.7 (*C*H$_2$), 50.5 (*C*H$_2$), 35.0 (*C*(CH$_3$)$_3$), 34.3 (*C*(CH$_3$)$_3$), 31.9 (C(*C*H$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$). IR Data (KBr pellet cm^{-1}): 2951 (s), 2862 (m), 1599 (w), 1480 (s), 1462 (s), 1404 (m), 1364 (m), 1304 (w), 1241 (s), 1205 (w), 1165 (w), 1089 (m), 986 (w), 825 (w). HRMS (ES): *m*/*z* 745.4283 [ligand+H]$^+$, Calcd. 745.4267. Anal. Calcd. for $C_{46}H_{62}Cl_2N_2O_2$: C, 74.07; H, 8.38; N, 3.76. Found: C, 73.97; H, 8.57; N, 4.08.

Synthesis of [*N*,*N′*-*bis*(2-oxo-3,5-*di*-*t*-butylphenylmethyl)-*N*,*N′*-*bis*(*p*-chlorobenzyl)ethylenediamine]Ti(O^{i}Pr)$_2$ (5b)

To a solution of *N*,*N′*-*bis*(2-hydroxo-3,5-*di*-*t*-butylphenylmethyl)-*N*,*N′*-*bis*(*p*-chlorobenzyl)ethylenediamine **5a** (0.515 g, 0.690 mmol) in dichloromethane (*ca.* 10 mL), Ti(O^{i}Pr)$_4$ (0.353 g, 1.38 mmol) in dichloromethane (*ca.* 2 mL) was added. The resulting solution was stirred for 3 h after which the volatiles were removed under reduced pressure. The residue was washed with hexane (*ca.* 2 mL) and dried under vacuum to obtain product **5b** as yellow solid (0.539 g, 86%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C), δ 7.29 (d, 4H, $^3J_{HH}$ = 8 Hz, C$_6$*H*$_4$Cl), 7.21 (s, 2H, C$_6$*H*$_2$O{3,5-C(CH$_3$)$_3$}), 6.94 (d, 4H, $^3J_{HH}$ = 8 Hz, C$_6$*H*$_4$Cl), 6.65 (s, 2H, C$_6$*H*$_2$O{3,5-C(CH$_3$)$_3$}), 4.94 (sept, 2H, $^3J_{HH}$ = 6 Hz, OC*H*(CH$_3$)$_2$), 4.22 (d, 2H, $^2J_{HH}$ = 13 Hz, C*H*$_2$), 4.19 (s, 4H, C*H*$_2$), 3.26 (d, 2H, $^2J_{HH}$ = 13 Hz, C*H*$_2$), 2.72 (d, 2H, $^3J_{HH}$ = 10 Hz, C*H*$_2$), 2.35 (d, 2H, $^3J_{HH}$ = 10 Hz, C*H*$_2$), 1.49 (s, 18H, C(C*H*$_3$)$_3$), 1.25 (s, 18H, C(C*H*$_3$)$_3$), 1.21 (d, 6H, $^3J_{HH}$ = 6 Hz, CH(C*H*$_3$)$_2$), 1.13 (d, 6H, $^3J_{HH}$ = 6 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100 MHz, 25 °C), δ 160.0 (*C*$_6$H$_2$O{3,5-C(CH$_3$)$_3$}), 139.9 (*C*$_6$H$_4$Cl), 136.7 (*C*$_6$H$_2$O{3,5-C(CH$_3$)$_3$}), 134.7 (*C*$_6$H$_2$O{3, 5-C(CH_3)$_3$}), 134.0 (C_6H_4Cl), 131.1 (C_6H_4Cl), 128.9 (C_6H_4Cl), 124.9 (C_6H_2O{3,5-C(CH_3)$_3$}), 124.4 (C_6H_2O{3,5-C(CH_3)$_3$}), 123.8 (C_6H_2O{3,5-C(CH_3)$_3$}), 78.2 (O*C*H(CH_3)$_2$), 60.8 (CH_2), 59.0 (CH_2), 45.6 (CH_2), 35.8 (*C*(CH_3)$_3$), 34.5 (*C*(CH_3)$_3$), 32.1 (C(CH_3)$_3$), 31.0 (C(CH_3)$_3$), 27.2 (CH(CH_3)$_2$), 26.9 (CH(CH_3)$_2$). IR Data (KBr pellet cm^{-1}): 2962 (s), 1597 (w), 1471 (s), 1360 (w), 1276 (m), 1203 (w), 1125 (s), 988 (m), 846 (s), 811 (m), 749 (w), 609 (m), 553 (s), 472 (m). Anal. Calcd. for $C_{52}H_{74}Cl_2N_2O_4Ti\cdot CH_2Cl_2$: C, 63.99; H, 7.70; N, 2.82. Found : C, 63.22; H, 7.89; N, 2.23.

Synthesis of *N*,*N*′-*bis*(2-hydroxo-3,5-*di*-chlorophenylmethyl)-*N*,*N*′-*bis*(*p*-chlorobenzyl)ethylenediamine (6a)

A solution of *N*,*N*′-di-*p*-chlorobenzylethylenediamine (0.503 g, 1.62 mmol), 2,4-di-chlorophenol (0.530 g, 3.25 mmol) and aqueous formaldehyde (37% w/v, 0.535 g, 6.50 mmol) in methanol (*ca.* 30 mL) was refluxed for 24 h. A white precipitate formed which was filtered and washed with methanol (*ca.* 6 × 20 mL) and then vacuum dried to obtain product **6a** as a white solid (0.613 g, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 11.0 (s, 2H, O*H*), 7.34 (d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4Cl), 7.26 (d, 2H, $^4J_{HH}$ = 2 Hz, C_6H_2{2-OH,3,5-Cl_2}), 7.07 (d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4Cl), 6.79 (d, 2H, $^4J_{HH}$ = 2 Hz, C_6H_2{2-OH,3,5-Cl_2}), 3.62 (s, 4H, CH_2), 3.49 (s, 4H, CH_2), 2.60 (s, 4H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C), δ 152.1 (C_6H_2{2-OH,3,5-Cl_2}), 134.4 (C_6H_4Cl), 133.8 (C_6H_2{2-OH,3,5-Cl_2}), 130.8 (C_6H_4Cl), 129.3 (C_6H_4Cl), 127.1 (C_6H_2{2-OH,3,5-Cl_2}), 127.0 (C_6H_2{2-OH,3,5-Cl_2}), 124.3 (C_6H_2{2-OH,3,5-Cl_2}), 123.5 (C_6H_2{2-OH,3,5-Cl_2}), 121.9 (C_6H_4Cl), 58.5 (CH_2), 58.1 (CH_2), 50.4 (CH_2). IR Data (KBr pellet cm^{-1}): 2955 (w), 2842 (w), 1598 (w), 1455 (s), 1387 (m), 1237 (w), 1171 (m), 1089 (m), 1015 (w), 970 (w), 863 (m), 803 (m), 731 (m). HRMS (ES): *m*/*z* 657.0208 [ligand+H]$^+$, Calcd. 657.0204. Anal. Calcd. for $C_{30}H_{26}Cl_6N_2O_2$: C, 54.66; H, 3.98; N, 4.25. Found: C, 54.12; H, 3.62; N, 4.43.

Synthesis of [*N*,*N*′-*bis*(2-oxo-3,5-*di*-chlorophenylmethyl)-*N*,*N*′-*bis*(*p*-chlorobenzyl)ethylenediamine]Ti(O^{i}Pr)$_2$ (6b)

To a solution of *N*,*N*′-*bis*(2-hydroxo-3,5-*di*-chlorophenylmethyl)-*N*,*N*′-*bis*(*p*-chlorobenzyl)ethylenediamine **6a** (0.256 g, 0.388 mmol) in dichloromethane (*ca.* 10 mL), Ti(O^{i}Pr)$_4$ (0.220 g, 0.775 mmol) in dichloromethane (*ca.* 2 mL) was added. The resulting solution was stirred for 3 h after which the volatiles were removed under reduced pressure. The residue was washed with hexane (*ca.* 2 mL) and dried under vacuum to obtain product **6b** as yellow solid (0.248 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 7.34 (d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4Cl), 7.26 (s, 2H, C_6H_2O{3,5-Cl_2}), 7.06 (d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4Cl), 6.84 (s, 2H, C_6H_2O{3,5-Cl_2}), 5.15 (sept, 2H, $^3J_{HH}$ = 6 Hz, OC*H*(CH_3)$_2$), 4.26 (d, 2H, $^2J_{HH}$ = 14 Hz, CH_2), 4.23 (s, 4H, CH_2), 3.39 (d, 2H, $^2J_{HH}$ = 14 Hz, CH_2), 2.64 (d, 2H, $^3J_{HH}$ = 10 Hz, CH_2), 2.36 (d, 2H, $^3J_{HH}$ = 10 Hz, CH_2), 1.31 (d, 6H, $^3J_{HH}$ = 6 Hz, CH(CH_3)$_2$), 1.28 (d, 6H, $^3J_{HH}$ = 6 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C), δ 158.1 (C_6H_2O{3,5-Cl_2}), 134.8 (C_6H_2O{3,5-Cl_2}), 133.6 (C_6H_4Cl), 130.7 (C_6H_4Cl), 129.5 (C_6H_4Cl), 128.8 (C_6H_4Cl), 128.2 (C_6H_2O{3,5-Cl_2}), 126.4 (C_6H_2O{3,5-Cl_2}), 122.6 (C_6H_2O{3,5-Cl_2}), 121.5 (C_6H_2O{3,5-Cl_2}), 80.1 (O*C*H(CH_3)$_2$), 58.8 (CH_2), 57.1 (CH_2), 48.6 (CH_2), 26.1 (CH(CH_3)$_2$), 25.9 (CH(CH_3)$_2$). IR Data (KBr pellet cm^{-1}): 3436 (m), 2967 (m), 2859 (w), 1461 (s), 1374 (w), 1312 (w), 1217 (w), 1124 (m), 1016 (m), 866 (m), 780 (w), 608 (m), 540 (w), 486 (w). Anal. Calcd. for $C_{36}H_{38}Cl_6N_2O_4Ti\cdot CH_2Cl_2$: C, 48.93; H, 4.44; N, 3.08. Found: C, 48.77; H, 4.31; N, 2.90.

Ethylene polymerization

A mechanically stirred stainless steel 400 ml autoclave was heated under vacuum for at least 1 h at 120 °C and cooled to room temperature prior to being charged with 150 ml toluene, MAO, and the **1b–6b** catalyst precursor. After addition of required amount of MAO and precursor, the reaction mixture was heated to 30 ± 1 °C; ethylene was introduced to a pressure of 88 psi. The reactor pressure was maintained at 88 ± 2 psi throughout the polymerization. At the end of the polymerization, the unreacted ethylene was vented and the reaction quenched with acidified methanol. After filtration, the polymer was washed with methanol, and then dried at 60 °C under vacuum to constant weight.

Melting points of polyethylene were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 calorimeter operating at the rate of 10 °C min^{-1}. For polymer molecular weights, gel permeation chromatography (GPC) was performed on a Polymer Laboratories PL-GPC220 High Temperature Chromatograph instrument (columns: 3 × PLgel Mixed-B 10 μm) with two detectors (viscometer and refractometer) in 1,2,4 - trichlorobenzene at flow rate of 1 mL min^{-1} at 160 °C. The system was calibrated with polystyrene standards using universal calibration. The NMR spectra were recorded on a Bruker Avance-400 spectrometer in 50% (v/v) 1,2,4-trichlorobenzene and d2-tetrachloroethane solution with 10% (w/v) at frequencies of 100 MHz for ^{13}C. A delay time of 2 s was given for recording ^{13}C{^{1}H} NMR spectra.

ESR experiment for detecting Ti(III) radical species in the catalytic cycle

In order to rule out the involvement of Ti(III) radical in the catalytic cycle we recorded an ESR spectrum of representative titanium precatalyst **2b** after activating with methylaluminoxane MAO. Specifically, in a typical experiment, MAO (300 μL, 4.52 mmol) was added to a solution of **2b** (0.015 g, 0.018 mmol) in toluene (*ca.* 2 mL) and the ESR spectrum of the resulting solution was recorded at 77 K. However, as no signal corresponding to the radical Ti(III) species was observed, the possibility of a radical pathway for the ethylene polymerization was thus ruled out.

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