Synthesis and ethylene polymerization behavior of {MeB(3-Ph-pyrazolyl)₃}TiCl₃

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ABSTRACT

The new methyl-tris(pyrazolyl)borate reagents Li[MeTp^{Ph}] (**1**) [MeTp^{Ph}]$^-$ = MeB(3-Ph-pyrazolyl)$_3^-$) and Tl[MeTp^{Ph}] (**2**) react with TiCl₄ to afford (MeTp^{Ph})TiCl₃ (**3**) in 77% and 81% yield respectively. **2** reacts with ZrCl₄ and HfCl₄ to yield mixtures of products. The reaction of **1** with TiCl₃(THF)₃ proceeds with B—N bond cleavage to afford TiCl₃(3-Ph-pyrazole)(THF)₂ as the major product (30%). The reaction of **3** with MeLi (3 equiv) yields **1** (60%) and reduced Ti species, via apparent displacement of [MeTp^{Ph}]$^-$ and generation of unstable TiCl₄Me$_{4-x}$ species. Under MAO activation conditions (MAO = methylalumoxane), **3** polymerizes ethylene to linear polyethylene. **3**/MAO is significantly more active in ethylene polymerization than the hydrido-tris(pyrazolyl)borate analogue {HB(3-Ph-pyrazolyl)₃}TiCl₃/MAO.

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1. Introduction

Group 4 metal Tp′MCl₃ tris(pyrazolyl)borate complexes (Tp′ = generic tris(pyrazolyl)borate) react with methylalumoxane (MAO) to produce active olefin polymerization catalysts [1–4]. The performance of these catalysts is very sensitive to the steric properties of the Tp′M unit, and Tp′MCl₃ complexes that contain bulky pyrazolyl units, such as HB(3-mesityl-pyrazolyl)₃$^-$ ([Tp^{Ms}]$^-$) or HB(3-mesityl-pyrazolyl)₂(5-mesityl-pyrazolyl)$^-$ ([Tp^{Ms*}]$^-$), exhibit very high productivity in MAO-activated ethylene polymerization and ethylene/hexene copolymerization.[1] The catalytically active metal alkyl species in these systems have not been identified and the chemistry of group 4 metal Tp′M alkyl compounds is not well explored, due part to the fact that Tp′MCl₃ species are difficult to alkylate [5–7]. However, based on results for other MAO-activated group 4 metal catalysts, cationic Tp′MR$_n$X$_{2-n}^+$ species (n = 1, 2; X = Cl or anionic ligand derived from MAO) may play a key role in Tp′MCl₃/MAO catalysts. We reported the synthesis of Tp*Zr(CH₂Ph)₂$^+$ ([Tp*]$^-$ = HB(3,5-Me₂-pz)₃)$^-$; pz = pyrazolyl) via reaction of K[Tp*] with Zr(CH₂Ph)₄ to generate Tp*Zr(CH₂Ph)₃ followed by abstraction of a benzyl ligand by Ph₃C$^+$ [8,9]. The Tp*Zr(CH₂Ph)₂$^+$ cation rearranges at 0 °C to the bis(pyrazolyl)borate species {(PhCH₂)B(μ-H)(μ-3,5-Me₂-pz)₂}Zr(η²-3,5-Me₂-pz)(CH₂Ph)$^+$, which is stabilized by a B—H⋯Zr agostic interaction. Both Tp*Zr(CH₂Ph)₂$^+$ and {(PhCH₂)B(μ-H)(μ-3,5-Me₂-pz)₂}Zr(η²-3,5-Me₂-pz)(CH₂Ph)$^+$ polymerize ethylene at −60 °C to linear polyethylene (PE) [10].

An alternative approach to modifying the structure and reactivity of Tp′MCl₃-based catalysts is to replace the B—H unit with a B—R unit [11]. Steric interactions between the B—R and pyrazolyl groups in {RB(pyrazolyl)₃}M compounds may inhibit 1,2-borotropic shifts and may influence the rigidity and bite angle of the alkyl-tris(pyrazolyl) borate ligand. Furthermore, {RB(pyrazolyl)₃}M compounds may be more resistant to rearrangement to bis(pyrazolyl)borate species, and in general may be more stable than analogous {HB(pyrazolyl)₃}M compounds due to the absence of a potentially reactive B—H bond [12,13]. However, analogous {HB(pyrazolyl)₃}M and {RB(pyrazolyl)₃}M compounds are expected to have very similar electronic properties. For example, the carbonyl stretching frequencies of [Tp^{CF3}]AgCO ([Tp^{CF3}]$^-$ = HB(3-CF₃-pyrazolyl)₃$^-$; ν_{CO} = 2100 cm^{-1}) and [MeTp^{CF3}]AgCO (ν_{CO} = 2099 cm^{-1}), and [Tp^{Ms}]CuCO (ν_{CO} = 2079 cm^{-1}) and [MeTp^{Ms}]CuCO (ν_{CO} = 2075 cm^{-1}), are very similar [14,15]. Previously we found that TpTiCl₃ and {^{n}BuB(pz)₃} TiCl₃ both exhibit low activity in ethylene polymerization under MAO activation conditions [1a]. In the present work we investigate the use of MeB(3-Ph-pyrazolyl)₃$^-$ ([MeTp^{Ph}]$^-$) as an ancillary ligand for group 4 metal catalysts.

2. Results and discussion

2.1. Li[MeTp^{Ph}] (1), Tl[MeTp^{Ph}] (2) and (MeTp^{Ph})TiCl₃ (3)

The reaction of Li[MeBH₃] with 3 equiv of 3-Ph-pyrazole (pz^{Ph}H) at 180 °C affords Li[MeTp^{Ph}] (**1**) in 95% yield as a white solid (Scheme 1). The reaction of **1** with TlOAc in THF at room temperature affords Tl

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Scheme 1.

Fig. 2. (a) Molecular structure of (MeTp^{Ph})TiCl$_3$ (3). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg) for 3: N(1)–Ti(1) 2.188(4), Cl(1)–Ti(1) 2.2262(16), B(1)–N(2) 1.547(5), B(1)–C(1) 1.599(13), N(1A)–Ti(1)–N(1) 82.33(16), Cl(1A)–Ti(1)–Cl(1B) 97.03(7), N(1A)–Ti(1)–Cl(1A) 87.56(12), N(1)–Ti(1)–Cl(1A) 92.23(11), N(1B)–Ti(1)–Cl(1A) 169.06(13), N(2)–N(1)–Ti(1) 120.4(3).
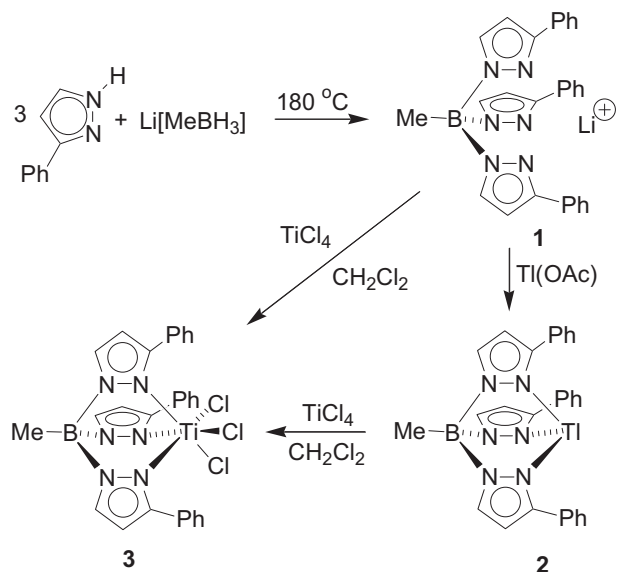
[MeTp^{Ph}] (**2**) in 86% yield. The reaction of **2** with 1 equiv TiCl$_4$ in CH$_2$Cl$_2$ affords (MeTp^{Ph})TiCl$_3$ (**3**) in 81% yield as a yellow solid. The direct reaction of **1** with 1 equiv TiCl$_4$ also generates **3** (77%). **1**–**3** are stable in toluene for more than 1 week at 110 °C, and no rearrangement products derived from 1,2-borotropic shifts were observed.

In contrast, the reaction of **2** with 1 equiv of ZrCl$_4$ or HfCl$_4$ results in the consumption of **2** and formation of a mixture of products (six singlets were observed in the B–Me region of the ^{1}H NMR spectrum of the reaction mixture), which could not be identified or isolated. Similar results were observed in the reactions of Tl[MeTp^{Ms}] and Tl[MeTp^{tBu}] ([MeTp^{tBu}]$^-$ = MeB(3-^{t}Bu-pz)$_3^-$) with MCl$_4$ (M = Ti, Zr, Hf).

2.2. Molecular structures of **2** and **3**

The molecular structures of **2** and **3** were determined by X-ray diffraction (Figs. 1 and 2). Complex **2** exhibits pyramidal geometry at thallium. The Tl and B substituents on a given pyrazolyl ring are markedly staggered, such that the Tl–N–N–B dihedral angles are in the range 17.0–35.3° (average 27.6°). Two ortho hydrogens of the phenyl groups, H(14) and H(27), make close contact with the thallium centre (3.04 Å; sum of van der Waals radii of Tl and H = 3.16 Å), consistent with the presence of CH···Tl agostic interactions. For comparison, the agostic BH···Tl distance in Tl[MeHB(3-mesityl-pyrazolyl)$_2$] is 3.06 Å and that in Tl[H$_2$B(pz)$_2$] is 2.7 Å) [16,17]. In contrast, no such distortion of the pyrazolyl rings or agostic interactions were observed in the structures of Tl[MeTp^{tBu}]

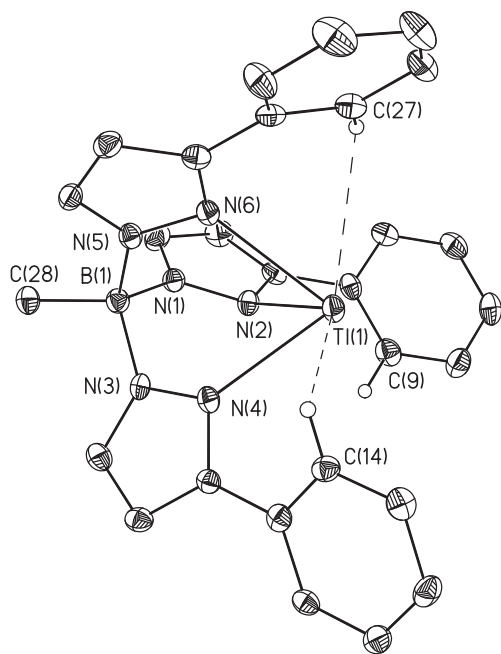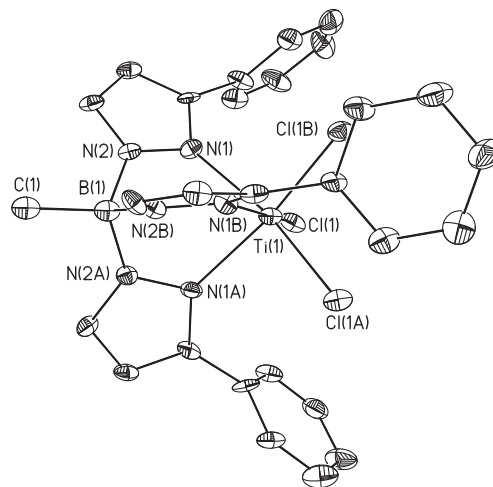**Fig. 1.** Molecular structure of Tl[MeTp^{Ph}] (2). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): N(2)–Tl(1) 2.593(3), N(4)–Tl(1) 2.546(3), N(6)–Tl(1) 2.636(3), N(4)–Tl(1)–N(2) 74.13(9), N(4)–Tl(1)–N(6) 70.85(9), N(2)–Tl(1)–N(6) 76.73(9).
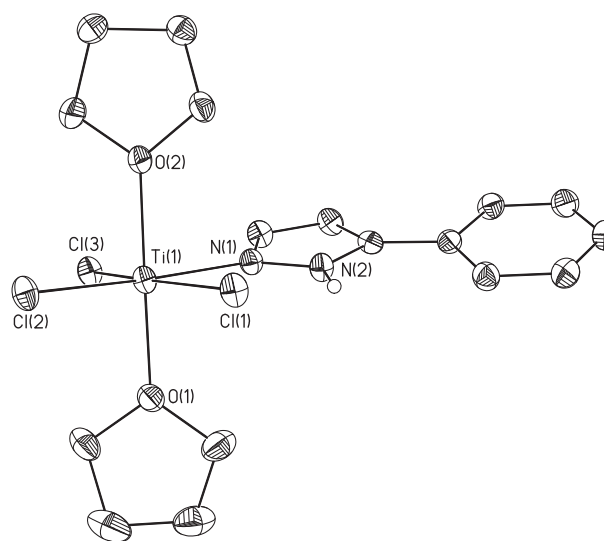
Fig. 3. Molecular structure of TiCl$_3$(pz^{Ph}H)(THF)$_2$ (4). Hydrogen atoms except H(2) are omitted. Selected bond lengths (Å) and angles (deg) for 4: Cl(1)–Ti(1) 2.4288(6), Cl(2)–Ti(1) 2.3436(7), Cl(3)–Ti(1) 2.3460(6), N(1)–Ti(1) 2.2291(14), O(1)–Ti(1) 2.0836(12), N(1)–Ti(1)–Cl(3) 85.67(3), Cl(2)–Ti(1)–Cl(3) 98.316(18), N(1)–Ti(1)–Cl(1) 83.49(3), Cl(2)–Ti(1)–Cl(1) 92.612(17).

Table 1
Ethylene Polymerization Behavior of (Tp^{Ph})TiCl$_3$, **3** and Tp$^{Ms^*}$TiCl$_3$[a].

Entry	Precatalyst	Precatalyst loading(μmol)	Equiv MAO	Time (min)	Polymer yield (g)[b]	P[c]	T$_m$(°C)
1	Tp^{Ph}TiCl$_3$[d]	10	500	60	0.085	2.8	132
2	**3**	10	500	60	1.76	58.6	131.8
3	**3**	1	500	30	0.263	175	132.9
4	**3**	1	500, D[e]	30	0.716	477	136.2
5	**3**	1	500, D[e]	2	0.528	5280	134.5
6	Tp$^{Ms^*}$TiCl[f]	1	1000,D[e]	6	1.29	4300	–

[a] Polymerization conditions: glass Fischer–Porter bottle, polymerization temperature 60 °C, 60 mL toluene, P_{C2H4} = 3.0 atm, MAO solution in toluene (10 wt. % total Al).
[b] The reported yield is the average of two runs.
[c] P = productivity in units of (kg of polymer)/(mol of precatalyst·atm·h).
[d] results from Ref. 2d.
[e] Dried MAO used.
[f] results from Ref. 1a.

and Tl[MeTp^{Ms}][15]. Complex **3** exhibits distorted octahedral coordination at Ti. The Tl–N–N–B dihedral angles are 10.6°, much smaller than those in **2**. The metrical parameters for **3** are very similar to those for Tp$^{Ms^*}$TiCl$_3$ and Tp^{Ms}TiCl$_3$ [1a,18].

2.3. Attempted synthesis of (MeTp^{Ph})TiMe$_3$

The reaction of **3** with MeLi (3 equiv) in CH$_2$Cl$_2$ at −20 °C resulted in a change in the color of the solution from yellow to blue and finally black, which is typical for the reduction of Ti(IV) species to lower oxidation state species. Li[MeTp^{Ph}] was identified as a major product (60%) of this reaction by NMR and ESI-MS analysis. These results suggest that this reaction proceeds by substitution of the MeTp^{Ph-} ligand and possibly chloride ligands to yield thermally unstable TiCl$_x$Me$_{4-x}$ species[19,20]. Similar displacements of [Tp′]$^-$ ligands in reactions with Li reagents have been observed in group 3 and lanthanide tris(pyrazolyl)borate complexes[21]. The reaction of **3** with the milder alkylating reagents AlMe$_3$, MgMe$_2$ or ZnEt$_2$ also resulted in a change in the color of the solution from yellow to blue and finally black, and no reaction was observed between **3** and SnMe$_4$, even at 60 °C.

Fujita and coworkers prepared {(C$_6$F$_5$)N=CH(2-O-3-^{t}Bu–C$_6$H$_3$)}$_2$TiMe$_2$ by the reaction of TiMe$_3$Cl with (C$_6$F$_5$)N=CH(2-ONa-3-^{t}Bu–C$_6$H$_3$),[22] whereas this complex could not be prepared by alkylation of {(C$_6$F$_5$)N=CH(2-O-3-^{t}Bu–C$_6$H$_3$)}$_2$TiCl$_2$. However, this approach was unsuccessful with the (MeTp^{Ph})Ti system. The reaction of in-situ-generated TiMe$_3$Cl or TiMe$_4$[19] with **2** resulted in the consumption of **2** and a change in the color

of the solution from yellow to blue and finally black, and no products could be identified.

An alternative possible route to Ti(IV) alkyls is alkylation of Ti(III) precursors followed by oxidation to Ti(IV)[23]. However, the reaction of TiCl$_3$(THF)$_3$ with 1 equiv of **1** in THF generated TiCl$_3$(pz^{Ph}H)(THF)$_2$ (**4**) as the major product (30%). Similar B–N bond cleavage reactions have been observed previously in the synthesis and derivatization of Tp′ complexes of both early and late transition metals[24,25]. The molecular structure of **4** was determined by X-ray diffraction and is shown in Fig. 3. **4** adopts a distorted octahedral geometry, with two THF molecules trans to each other. The Ti–N bond distance (2.23 Å) in **4** is similar to those in other Ti(III) complexes, such as Tp$^{Ms^*}$TiCl$_2$(pz^{Ms}H)[24]. The source of the 2-phenyl-pyrazolyl N–H atom (H(2)) in **4** is unknown.

2.4. Ethylene polymerization by **3**/MAO

The ethylene polymerization performance of **3** under MAO activation conditions is compared with that of the hydrido-tris(pyrazolyl)borate analogues Tp^{Ph}TiCl$_3$ and Tp$^{Ms^*}$TiCl$_3$ in Table 1. At 60 °C in toluene with [Ti] = 0.16 mM, **3**/MAO is at least 20 times more active than Tp^{Ph}TiCl$_3$/MAO (entry 1 vs 2). Under these conditions, the activity of **3**/MAO is mass transport-limited, and decreasing the precatalyst loading and shortening the reaction time results in an increase in productivity (entry 3). The use of dried MAO (DMAO), from which much of the AlMe$_3$ has been removed, also results in an increase in activity of **3** (entry 3 vs 4). This effect may result from binding of AlMe$_3$ to the active catalyst species,[1a]

Table 2
Summary of X-Ray Diffraction Data for **2**, **3** and **4**.

	2·toluene	3·(1.5 toluene)	4·toluene
formula	C$_{35}$H$_{32}$BN$_6$Tl	C$_{38.5}$H$_{36}$BCl$_3$N$_6$Ti	C$_{24}$H$_{32}$Cl$_3$N$_2$O$_2$Ti
formula wt	707.75	747.79	534.77
crystl syst	Triclinic	Trigonal	Triclinic
space group	P1(bar)	P3(bar)c1	P1(bar)
a (Å)	8.583(4)	13.680(3)	9.865(3)
b (Å)	8.757(4)	13.680(3)	11.470(3)
c (Å)	18.945(9)	23.080(4)	12.037(3)
α (o)	97.920(7)		91.051(4)
β (o)	94.623(7)		105.039(4)
γ (o)	91.459(7)	120	99.282(4)
V (Å^3)	1404.8(11)	3740.6(13)	1295.6(6)
Z	2	4	2
T (K)	100	100	100
crystal color, habit	clear, fragment	yellow, irregular	green, fragment
GOF on F^2	0.881	1.044	1.000
R indices [I > 2σ(I)][a]	R1 = 0.0292 wR2 = 0.0582	R1 = 0.0730 wR2 = 0.1287	R1 = 0.0333 wR2 = 0.0854
R indices (all data)[a]	R1 = 0.0333 wR2 = 0.0592	R1 = 0.1352 wR2 = 0.1508	R1 = 0.0402 wR2 = 0.0881

[a] R1 = $\sum ||F_o| - |F_c||/\sum |F_o|$; wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where w = q$[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$

or from $AlMe_3$-induced catalyst decomposition (vide supra). The activity of 3/DMAO is similar to that of $Tp^{Ms^*}TiCl_3$/DMAO, one of the most active $Tp'TiCl_3$ catalysts studied previously (entry 5 vs 6). The polyethylene generated by 3 under these conditions is highly linear and could not be dissolved in 1,2,4-trichlorobenzene for GPC analysis, suggesting that it has a very high molecular weight.

3. Conclusions

The reaction of $Li[MeTp^{Ph}]$ (1) or $Tl[MeTp^{Ph}]$ (2) with $TiCl_4$ affords $(MeTp^{Ph})TiCl_3$ (3) in high yield, whereas the reactions of 2 with $ZrCl_4$ and $HfCl_4$ yield mixtures of products. The reaction of 1 with $TiCl_3(THF)_3$ proceeds with B–N bond cleavage to afford $TiCl_3$(3-Ph-pyrazole)$(THF)_2$ as the major product (30%). The reaction of 3 with MeLi yields 1 (60%) and reduced Ti species, via apparent displacement of $[MeTp^{Ph}]^-$ and generation of unstable $TiCl_4Me_{4-x}$ species. 3/MAO (MAO = methylalumoxane) polymerizes ethylene to linear polyethylene and is significantly more active than the hydrido-tris(pyrazolyl)borate analogue {HB(3-Ph-pyrazolyl)$TiCl_3$/MAO.

4. Experiment section

4.1. General procedures

All manipulations were performed using standard vacuum line, Schlenk, or glove box techniques under a purified N_2 atmosphere. THF was distilled from sodium benzophenone ketyl. Toluene, benzene, pentane, and hexanes were dried by passage through activated alumina and BASF R3-11 oxygen scavenger. CH_2Cl_2 was dried over CaH_2 and distilled. Solvents were stored under N_2 or vacuum prior to use. $pz^{Ph}H$, $TiCl_4$ and $TiCl_3(THF)_3$ were purchased from Aldrich and used as received. $Li[MeBH_3]$, $Tl[MeTp^{tBu}]$ and Tl$[MeTp^{Ms}]$ were prepared by literature procedures [26,15]. MAO was obtained as a 10 wt. % Al solution in toluene from Aldrich, stored at room temperature, and used without further purification. This solution was dried under vacuum to remove the toluene and a substantial fraction of the $AlMe_3$, to produce "dried MAO" (DMAO).

NMR spectra were recorded on Bruker DMX-500 or DMX-400 spectrometers in Teflon-valved NMR tubes. Chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. [11]B chemical shifts are reported relative to external $BF_3 \cdot Et_2O$. Coupling constants are reported in Hertz. Elemental analyses were performed by Midwest Microlab. EPR experiments were performed at room temperature in a Varian TE_{102} resonance cavity attached to a modified Bruker ER041 MR bridge equipped with a GAs FET microwave preamplifier operating at X-band with 20 ns time resolution.

4.1.1. $Li[MeTp^{Ph}]$ (1)

A flask was charged with $pz^{Ph}H$ (2.65 g, 18.4 mmol) and Li$[MeBH_3]$ (0.220 g, 6.13 mmol). The mixture was stirred at 180 °C for 8 h. The solid was washed with hexanes (3 × 10 mL) and dried under vacuum to give a white solid (2.69 g, 95%). ^{1}H NMR (CD_2Cl_2): δ 7.81 (d, $J = 2$, 3H, 5-pz), 7.59 (d, $J = 7$, 6H, H_{ortho}), 7.36 (t, $J = 7$, 6H, H_{meta}), 7.29 (t, $J = 7$, 3H, H_{para}), 6.40 (d, $J = 2$, 3H, pz), 1.12 (s, 3H, BCH_3). ^{11}B NMR (CD_2Cl_2): δ −4.8. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 154.1 (pz), 137.7, 133.4, 131.1, 128.4, 128.3, 105.2 (pz), 4.5 (br, BCH_3).

4.1.2. $Tl[MeTp^{Ph}]$ (2)

A flask was charged with 1 (2.68 g, 5.80 mmol), Tl(OAc) (1.63 g, 6.13 mmol) and THF (60 ml). The mixture was stirred overnight at 23 °C. The mixture was filtered through Celite and the colorless filtrate was dried under vacuum to give a white solid. The solid was washed with hexanes (3 × 10 mL) and dried under vacuum to yield a white solid (3.46 g, 86%). Anal. Calcd for $C_{28}H_{24}BN_6Tl$: C, 50.97; H, 3.66; N, 12.74. Found: C, 50.76; H, 3.82; N, 12.52. ^{1}H NMR (CD_2Cl_2): δ 7.84 (d, $J = 2$, 3H, pz), 7.61 (d, $J = 7$, 6H, H_{ortho}), 7.39 (t, $J = 7$, 6H, H_{meta}), 7.31 (d, $J = 7$, 3H, H_{para}), 6.54 (d, $J = 2$, 3H, pz), 1.10 (s, 3H, BCH_3). ^{11}B NMR (CD_2Cl_2): δ −0.3. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 153.7 (pz), 135.4, 134.2, 129.4, 128.3, 127.5, 104.1 (pz), 6.5 (br, BCH_3).

4.1.3. $(MeTp^{Ph})TiCl_3$ (3)

A flask was charged with $TiCl_4$ (0.417 g, 2.20 mmol) and 2 (1.45 g, 2.20 mmol). CH_2Cl_2 (80 mL) was added by vacuum transfer at −78 °C. The mixture was warmed to room temperature over 2 h, and the resulting white suspension was stirred for 6 h. The mixture was filtered through Celite to yield a yellow filtrate. The volatiles were removed from the filtrate under vacuum yielding a yellow solid. The solid was washed with hexanes (3 × 10 mL) and dried under vacuum to yield a yellow solid (1.26 g, 81%). Anal. Calcd for $C_{28}H_{24}BN_6Li$: C, 55.26; H, 3.95; N, 13.82. Found: C, 54.86; H, 4.06; N, 13.44. ^{1}H NMR (CD_2Cl_2): δ 7.89 (d, $J = 2$, 3H, pz), 7.40 (d, $J = 7$, 6H, H_{ortho}), 7.34 (t, $J = 7$, 3H, H_{para}), 7.30 (t, $J = 7$, 6H, H_{meta}), 6.22 (d, $J = 2$, 3H, pz), 1.12 (s, 3H, BCH_3). ^{11}B NMR (CD_2Cl_2): δ −2.1. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 159.1 (pz), 134.8, 134.0, 131.6, 128.8, 127.5, 108.7 (pz), 3.6 (br, BCH_3).

4.1.4. $TiCl_3(pz^{Ph}H)(THF)_2$ (4)

A flask was charged with $TiCl_3(THF)_3$ (0.800 g, 2.16 mmol) and 1 (1.00 g, 2.16 mmol). THF (50 mL) was added to by vacuum transfer at −78 °C. The mixture was slowly warmed to room temperature, and the resulting white suspension was stirred for 1 day. The mixture was filtered through Celite and the green filtrate was concentrated to ca. 15 ml. Green crystals were obtained by slow diffusion of hexanes into the concentrated THF solution at −35 °C (0.285 g, 30% based on Ti). Anal. Calcd for $C_{17}H_{25}N_2O_2Cl_3Ti$: C, 46.03; H, 5.68; N, 6.31. Found: C, 45.93; H, 5.24; N, 6.29. EPR (toluene, 23 °C) $g = 1.925$.

4.2. Ethylene polymerization (Table 1)

Polymerization reactions were performed in a 200 mL Fischer–Porter bottle equipped with a magnetic stir bar and a stainless steel pressure head fitted with inlet and outlet needle valves, a septum-capped ball valve for injections, a check valve for safety, and a pressure gauge. In a glove box, the bottle was charged with MAO and toluene (50 mL), and sealed. The bottle was removed from the glove box and attached to a stainless steel double manifold (vacuum/ethylene) line. The nitrogen atmosphere was removed by vacuum, and the solution was saturated with ethylene at 1.4 atm and thermally equilibrated at polymerization temperature for 15 min. The polymerization reactions were started by addition of a solution of 3 in toluene (10 mL), followed by an immediate increase of the ethylene pressure to 3.0 atm. The total volume of the reaction mixture was 60 mL for all polymerization reactions. The total pressure was kept constant by feeding ethylene on demand. After the specified reaction time, the polymerization was stopped by quenching with methanol. The polymer was collected by filtration and washed with acidic methanol for several hours, then washed with methanol and dried under vacuum for 12 h.

4.3. X-Ray crystallography

Crystallographic data are summarized in Table 2. Data were collected on a Bruker Smart Apex diffractometer using Mo Kα radiation (0.71073 Å). Non-hydrogen atoms were refined with anisotropic displacement coefficients. All terminal hydrogen atoms were included in the structure factor calculation at idealized

positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Hydrogen atoms and solvent molecules are omitted from the ORTEP diagrams. All ORTEP diagrams have been drawn with 50% probability ellipsoids. Single crystals of **2**, **3** and **4** were obtained by slow diffusion of pentane into a concentrated toluene solution at −35 °C.

Appendix A. Supplementary material

CCDC 787352; 787353; and 787354 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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