

Synthesis, characterization, and ethylene polymerization behavior of $[(RR'-admpzp)_2Ti(OPr^i)_2]$ complexes ($RR'-admpzp = 1$ -dialkylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-olate)

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Received 19 March 2007; received in revised form 23 August 2007; accepted 23 August 2007

Available online 11 September 2007

Abstract

$[(RR'-admpzp)_2Ti(OPr^i)_2]$ complexes (**2a–c**), synthesized from reaction of $Ti(OPr^i)_3Cl$ (0.5 equiv) with 1-dialkylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ol compounds in the presence of triethylamine (0.5 equiv), are pseudo-octahedral with each $RR'-admpzp$ ligand κ^2 -*O,N*(pyrazolyl) coordinated to the titanium center. In solution, **2a–c** adopt isomeric structures that are in dynamic equilibrium. At 23 °C, **2a–c**/1000 MAO catalyst systems furnished high molecular weight polymers with narrow molecular weight distributions ($M_w/M_n = 2.7–2.8$). At 100 °C, **2a–c**/MAO catalyst systems exhibited increased polymerization activity and **2c**/1000 MAO system furnished high molecular weight polyethylene with a molecular weight distribution ($M_w/M_n = 2.1$) that is close to that found for single-site catalysts.

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Keywords: Olefin polymerization; Titanium(IV) catalysts; 1-Dialkylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-olate ligands

1. Introduction

The discovery of single-site ethylene and α -olefin polymerization catalyst systems based on Cp_2MX_2 [1] and $(CpSiR_2NR)MX_2$ [2] complexes of the group 4 metals has stimulated investigation of the potential of a diverse array of non-cyclopentadienyl ligand environments in early transition metal chemistry. These studies have established that steric and electronic properties of ancillary ligands greatly influence reactivity of transition metal complexes, and some highly active (and sometimes living) olefin polymerization catalysts have been generated via activation of group 4 metal complexes supported by chelating di(amide)-[3], amine-bis(phenolate)- [4], bis(phenoxy-imine)- [5], or phosphinimide [6] ligation. As part of our program aimed

at further developing the potential of non-cyclopentadienyl ligand arrays in early transition metal chemistry, we recently initiated a study of titanium(IV) complexes supported by 1-dialkylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-olate ligands ($RR'-admpzp$). The modular nature of this ligand framework is especially attractive since it should facilitate easy modification of ligand properties. Also, while $RR'-admpzp$ ligands are potentially multidentate, dissimilar steric and electronic properties of the amine- and pyrazol-1-yl donor groups may facilitate flexible ligation behavior and thereby allow different molecular geometries to be realized. In this regard, both κ^2 -*O,N* coordination of $RR'-admpzp$ ligands (analogous to phenoxy-imines in Ti-FI catalysts, Fig. 1) [5] and κ^3 -*O,N,N* coordination (analogous to heteroscorpionate ligands in which a pyrazolyl group of a tris(pyrazol-1-yl)methane system has been replaced with an oxygen donor group, Fig. 1) [7,8] are possible. Herein we describe the synthesis and structural characterization of $[(RR'-admpzp)_2Ti(OPr^i)_2]$ complexes (**2a**, $R = R' = Pr^i$; **2b**, $R = R' = Bn$; **2c**,

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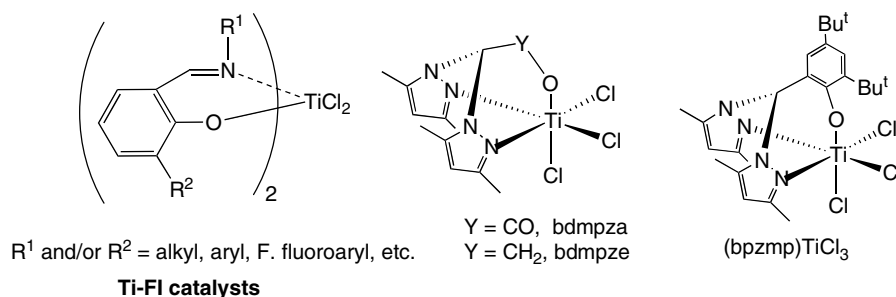


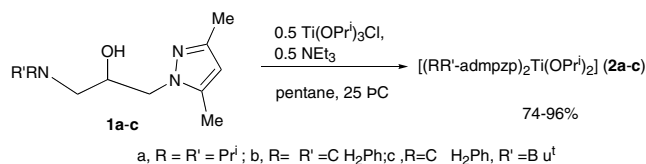
Fig. 1. Ti-FI catalysts.

$R = \text{Bn}$, $R' = \text{Bu}^t$, as well as results from a preliminary study of the ethylene polymerization behavior of catalysts generated upon MAO-activation of the complexes (MAO = methylalumoxane).

2. Results and discussion

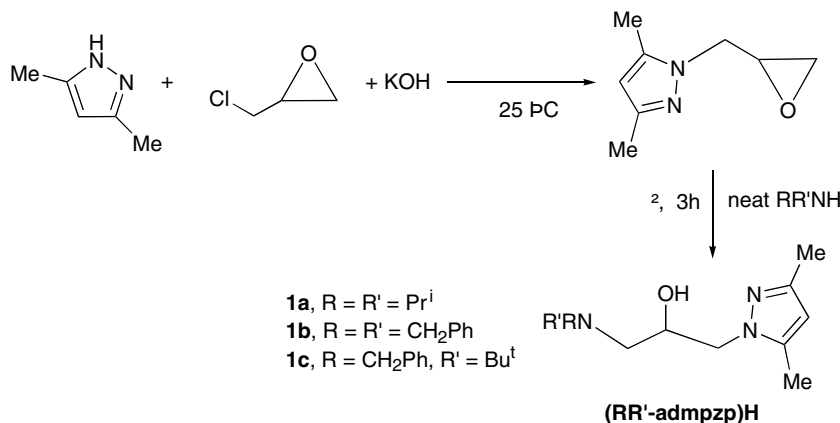
2.1. Synthesis and characterization of $[(\text{RR}'\text{-admpzp})_2\text{-Ti}(\text{OPr}^i)_2]$ complexes (**2a–c**)

The new 1-dialkylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ol compounds $\{(\text{RR}'\text{-admpzp})\text{H}$, **1a–c**, Scheme 1} were prepared by modification of the method reported by Darbinyan et al. [9] (see Section 4). Reaction of $\text{Ti}(\text{OPr}^i)_3\text{Cl}$ (0.5 equiv) with **1a–c** in the presence of triethylamine (0.5 equiv) produced **2a–c** in good to excellent yield (Eq. 1). Both $[(\text{Pr}^i_2\text{-admpzp})_2\text{Ti}(\text{OPr}^i)_2]$ (**2a**) and $[(\text{Bn}_2\text{-admpzp})_2\text{Ti}(\text{OPr}^i)_2]$ (**2b**) were isolated as colorless oils while $[(\text{Bu}^t\text{Bn-admpzp})_2\text{Ti}(\text{OPr}^i)_2]$ (**2c**) was obtained as a white crystalline solid. All of the compounds are highly sensitive to hydrolysis and oxidation (even in the solid-state) hence they are best stored for extended periods of time under N_2 atmosphere. The compounds are highly soluble in diethyl ether, THF, and most aliphatic and aromatic hydrocarbon solvents, including hexane, benzene, and toluene. However, while **2a** and **2b** are highly soluble in pentane, **2c** is moderately soluble in pentane and could be recrystallized from pentane at low temperatures.



(1)

The formulation and molecular structure of $[(\text{RR}'\text{-admpzp})_2\text{Ti}(\text{OPr}^i)_2]$ complexes (**2a–c**) were characterized by means of microanalysis and spectroscopic (IR, ^1H and ^{13}C NMR, along with 2D ^{13}C – ^1H HSQC) experiments, as well as by single crystal X-ray diffraction study of $[(\text{Bu}^t\text{Bn-admpzp})_2\text{Ti}(\text{OPr}^i)_2]$ (**2c**). The molecular structure of **2c** is shown in Fig. 2, and crystallographic data and selected metrical parameters are collected in Tables 1 and 2. Each $\text{Bu}^t\text{Bn-admpzp}$ ligand is coordinated via the alkoxide group and the pyrazolyl nitrogen. The compound adopts a distorted octahedral structure with two mutually *cis* isopropoxide ligands and two mutually *cis* pyrazolyl ligands coordinated in the equatorial plane. The distortion from idealized octahedral geometry results from acute bite angles of chelating $\text{Bu}^t\text{Bn-admpzp}$ ligands {ca. 79.2° for $\text{O}(1)\text{--Ti}(1)\text{--N}(1)$ and ca. 79.6° for $\text{O}(2)\text{--Ti}(1)\text{--N}(4)$ }, as well as steric constraints imposed by *cis*-orientation of bulky isopropoxide ligands { $\text{O}(4)\text{--Ti}(1)\text{--O}(3)$ ca. 101° }. The Ti–O bond distances {average = $1.864(2) \text{ \AA}$ } [10] are shorter than the Ti–O sigma-bond distance predicted on the basis of covalent radii (ca. $1.99\text{--}2.05 \text{ \AA}$) [11] but longer than Ti–O bond lengths reported for more highly



Scheme 1.

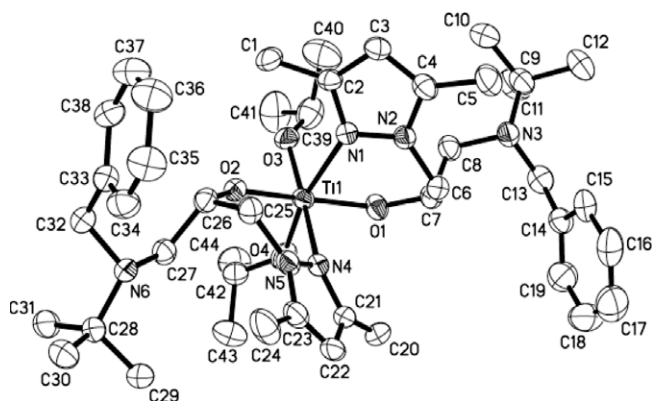


Fig. 2. Molecular structure of $[(\text{Bu}'\text{Bn-admpzp})_2\text{Ti}(\text{OPr}')_2]$ (**2c**) (50% probability ellipsoids).

Table 1
Summary of crystallographic data for **2c**

Empirical formula	$\text{C}_{44}\text{H}_{70}\text{N}_6\text{O}_4\text{Ti}$
Formula weight	794.96
T (K)	90.0(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
a (Å)	12.7297(7)
b (Å)	12.8371(6)
c (Å)	14.2719(7)
α (°)	90.494(2)
β (°)	96.845(2)
γ (°)	108.088(2)
V (Å ³)	2198.57(19)
D_{calc} (g/cm ³)	1.201
Final R indices [$I > 2\sigma(I)$]: R_1 , wR_2	0.0592, 0.1553
wR_2 , R_1 (all data)	0.0631, 0.1578

Table 2
Selected bond distances (Å) and angles (°) for **2c**

Ti(1)–O(4)	1.850(2)
Ti(1)–O(1)	1.8511(18)
Ti(1)–O(2)	1.8523(18)
Ti(1)–O(3)	1.904(2)
Ti(1)–N(4)	2.348(2)
Ti(1)–N(1)	2.368(2)
O(4)–Ti(1)–O(1)	91.36(9)
O(4)–Ti(1)–O(2)	99.23(9)
O(1)–Ti(1)–O(2)	163.60(9)
O(4)–Ti(1)–O(3)	100.95(9)
O(1)–Ti(1)–O(3)	98.76(9)
O(2)–Ti(1)–O(3)	91.53(9)
O(4)–Ti(1)–N(4)	89.74(9)
O(1)–Ti(1)–N(4)	88.05(8)
O(2)–Ti(1)–N(4)	79.56(8)
O(3)–Ti(1)–N(4)	167.12(9)
O(4)–Ti(1)–N(1)	167.81(8)
O(1)–Ti(1)–N(1)	79.19(8)
O(2)–Ti(1)–N(1)	88.47(8)
O(3)–Ti(1)–N(1)	88.19(8)
N(4)–Ti(1)–N(1)	82.33(7)
C(7)–O(1)–Ti(1)	143.20(17)
C(26)–O(2)–Ti(1)	143.24(16)
C(39)–O(3)–Ti(1)	137.7(2)
C(42)–O(4)–Ti(1)	133.39(18)

electron-deficient Ti(IV) alkoxides, such as $[(2,6\text{-Ph}_2\text{-C}_6\text{H}_3\text{O})_2\text{TiCl}_2]$ (1.73 Å) [12] and $[(2\text{-Bu}'\text{-C}_6\text{H}_4\text{O})_4\text{Ti}]$ (1.78 Å) [13]. The short Ti–O bond distances observed for **2c** likely reflect partial Ti–O π -bonding. Also consistent with existence of partial Ti–O double bond character, the Ti–O–C units in **2c** are bent (Ti–O–C range from ca. 133–143°) hence the oxygens are sp^2 -hybridized and each oxygen has one p orbital available for O–Ti π bonding; similar observations and interpretation have been reported for related $[(\text{pyCAR}_2\text{O})_2\text{M}(\text{NMe}_2)_2]$ complexes (pyCAR₂O = chelating pyridine-alkoxide ligand; M = Ti, Zr, or Hf) [11]. The Ti–N bond distances in **2c** are long {average = 2.358(2) Å} due to strong *trans* influence of the isopropoxide ligands; comparable Ti–N bond distances have been observed for a Ti(IV) heteroscorpionate complex that has a strong *trans*-influence ligand bound opposite a pyrazolyl donor $[(\text{bpzmp})\text{Ti}(\text{NMe}_2)_3]$ (average Ti–N(pyrazolyl) = 2.392(2) Å) [8e].

It is important to note that five idealized octahedral structures (A–E, Chart 1) are possible for $\kappa^2\text{-O,N}(\text{pyrazolyl})$ coordinated $[(\text{RR}'\text{-admpzp})_2\text{Ti}(\text{OPr}')_2]$ complexes, based on consideration of first coordination sphere atoms only; the number of possible idealized octahedral structures increases to 15 when the orientation (axial/equatorial) of pendant $\text{CH}_2\text{NRR}'$ groups is also considered. Even though X-ray crystallography clearly established $\kappa^2\text{-O,N}(\text{pyrazolyl})$ coordination of the Bu'Bn-admpzp ligands and the pseudo-octahedral solid-state structure (Fig. 2) corresponding to structure A (Chart 1) for $[(\text{Bu}'\text{Bn-admpzp})_2\text{Ti}(\text{OPr}')_2]$ (**2c**), structures A–C are expected to be comparable in energy because in each structure, two short Ti–O bonds are *trans* to each other, two strong *trans*-influence alkoxide groups are *trans* to weak pyrazolyl donors, and the alkoxide oxygens can participate in O–Ti– π bonding with different metal d orbitals [11,14]. However, structures D and E should be disfavored by *trans* arrangement of all of the alkoxide ligands and because the alkoxides must share a single metal d orbital for O–Ti π donation. In solution, $[(\text{RR}'\text{-admpzp})_2\text{Ti}(\text{OPr}')_2]$ complexes (**2a–c**) show multiple sets of ¹H and ¹³C NMR resonances for the RR'-admpzp and isopropoxide ligands; when dissolved in solution, single-crystals of $[(\text{Bu}'\text{Bn-admpzp})_2\text{Ti}(\text{OPr}')_2]$ (**2c**) produced identical ¹H and ¹³C NMR spectra as the bulk material. The intensities of the observed resonances are temperature dependent and a single isomer does not prevail in solution (for **2a–c**) in the 213–373 K temperature range. The data suggests low coordination energy of the pyrazolyl nitrogen to the titanium center and the existence of a dynamic equilibrium between at least two isomeric structures [15,16]. Thus, the room temperature ¹H NMR spectrum of $[(\text{Bu}'\text{Bn-admpzp})_2\text{Ti}(\text{OPr}')_2]$ (**2c**) showed a broad multiplet (ostensibly composed of overlapping broad singlet resonances and integrating as two protons) between δ 5.70 and 5.50 for protons at the pyrazolyl 4-position (pyz-4). A multiplet resonance (composed of broad singlets and integrating as six protons) was observed in the δ 2.65–2.15 range for methyl groups at the pyrazolyl 3-position

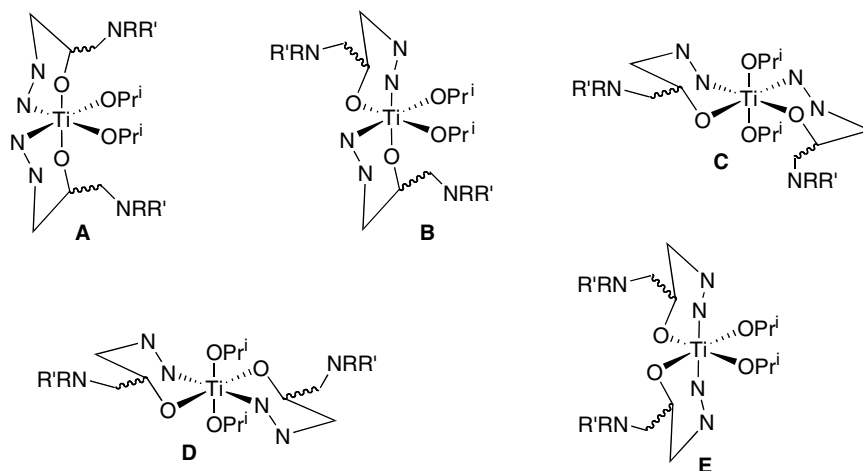


Chart 1.

(pyz-3) while methyl groups at the pyrazolyl 5-position (pyz-5) showed as a multiplet (integrating as six protons) in the δ 2.14–1.68 range. The Ti–OCHMe₂ methyl protons were observed as a multiplet in the δ 1.51–1.17 range (integrating as 12 protons). In the ¹³C NMR spectrum, each carbon atom is observed as a set of closely spaced singlet resonances (only the most intense peak is reported in Section 4). The pyz-3 carbon showed in the δ 148.0–147.4 range with the most intense peak at δ 148.0 while the pyz-5 carbon showed in the δ 139.5–138.8 range with the most intense peak at δ 139.1. The pyz-4 carbon is observed in the δ 105.5–104.6 range with the most intense peak at δ 105.0. The methyl substituent at the pyrazolyl 3-position is observed in the δ 14.4–13.8 range with the most intense peak at δ 14.3 while the methyl substituent at the pyrazolyl 5-position is observed in the δ 11.3–10.8 range with the most intense peak at δ 11.1. While RR'-admpzp ligands possess amine- and pyrazol-1-yl donor groups with dissimilar steric and electronic properties, and hence can possibly bind titanium through either amine or pyrazolyl donor, we believe that [(Pr₂-admpzp)₂Ti(OPrⁱ)₂] (**2a**) and [(Bn₂-admpzp)₂Ti(OPrⁱ)₂] (**2b**) adopt pseudo-octahedral geometry with each RR'-admpzp ligand κ^2 -O,N(pyrazolyl) coordinated to the titanium center, similar to **2c**. This belief finds strong support in the observation of parallel ¹H and ¹³C NMR data for **2a–c** (see Section 4) and in the fact that coordination of amine nitrogen will produce a 5-membered chelate ring that is more strained than the 6-membered chelate ring formed on pyrazolyl nitrogen coordination; and acute bite angles are present in 6-membered chelate rings of **2c** (*vide supra*). In addition, although the –NRR' group is more basic than the pyrazolyl group, its coordination at the crowded titanium center should be disfavored (relative to pyrazolyl) because of its substantially greater steric demand.

2.2. Ethylene polymerization behavior of [(RR'-admpzp)₂Ti(OPrⁱ)₂] complexes (**2a–c**)

Studies of ethylene polymerization catalyzed by MAO-activated [(RR'-admpzp)₂Ti(OPrⁱ)₂] complexes (**2a–c**) were

conducted at 23 °C and 100 °C for 30 min, using different Al/Ti ratios under 10 bar ethylene pressure. The data from the studies are collected in Table 3. At 23 °C and Al/Ti ratio of 500 or 1000, all of the catalyst systems (**2a–c**/MAO) furnished high molecular weight polyethylenes ($M_w \geq 1.1 \times 10^6$ g/mol) that showed narrow molecular weight distributions ($M_w/M_n = 2.7–3.3$; Table 3, entries 1–6) although the polydispersities are broader than those ($M_w/M_n \leq 2.0$) typical of single-site catalysts. In contrast to related group 4 metal heteroscorpionate complexes which typically achieve maximum polymerization activity at low temperatures (≤ 35 °C) [8], **2a–c**/1000 MAO catalyst systems exhibited increased polymerization activity at 100 °C (Table 3) although polyethylenes obtained showed lower molecular weights (up to $M_w = 2.8 \times 10^6$ g/mol, Table 3, entries 10–12) than those obtained at 23 °C and generally possessed broader multimodal molecular weight distributions ($M_w/M_n = 3.5–5.9$); the exception being the polyethylene produced by using the **2c**/1000 MAO at

Table 3
Summary of ethylene polymerization results

Entry	Precatalyst ^a	Temperature (°C)	Al/Ti	Activity [kg PE/(mol Ti h bar)] ^b	M_w^c (g mol ⁻¹)	M_w/M_n
1	2a	23	500	7.1	1.11×10^6	3.3
2	2b	23	500	6.4	1.38×10^6	2.7
3	2c	23	500	7.1	1.34×10^6	3.0
4	2a	23	1000	8.6	1.36×10^6	2.7
5	2b	23	1000	13.5	1.50×10^6	2.8
6	2c	23	1000	6.8	1.50×10^6	2.7
7	2a	100	500	18.4	5.9×10^4	6.3
8	2b	100	500	12.1	1.07×10^5	4.1
9	2c	100	500	13.8	2.63×10^5	4.0
10	2a	100	1000	28.6	2.84×10^5	5.9
11	2b	100	1000	22.3	2.76×10^5	3.6
12	2c	100	1000	19.0	1.46×10^5	2.1

^a Polymerizations conditions (unless stated otherwise): glass reactor; in toluene; 10 bar pressure of ethylene; 10 μ mol of precatalyst; (MAO solution in toluene, 10% wt% total Al); reaction time = 30 min.

^b Average activity from three experiments.

^c Molecular weight data were determined by GPC and measured relative to linear polystyrene standards.

100 °C, its molecular weight distribution ($M_w/M_n = 2.1$) is close to that found for single-site catalysts. The close parallel in ethylene polymerization behavior of **2a–c**/MAO catalyst systems suggests that similar Ti^{4+} active species are generated from these precatalysts. Hence pyrazolyl coordination to titanium is likely maintained in the putative active cationic titanium species [17], and slight differences observed in ethylene polymerization behavior of the catalysts likely reflect differences in inductive and steric effects of amine moieties of the RR' -admpzp ligands.

3. Conclusions

Preliminary studies of the ethylene polymerization behavior of catalysts generated via MAO activation of $[(RR'-admpzp)_2Ti(OPr^f)_2]$ complexes (**2a–c**) indicate that they exhibit modest ethylene polymerization activity and provide inferior control of ethylene polymerization in comparison to extensively developed Ti–FI catalysts (Fig. 1) [5]. However, **2a–c**/MAO catalysts display good thermal stability and given that $[(RR'-admpzp)_2Ti(OPr^f)_2]$ complexes are structurally related to Ti–FI catalysts and that the modular nature of 1-dialkylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-olate ligands (RR' -admpzp) should facilitate facile modification of the electronic and geometric structure of $[(RR'-admpzp)_2Ti(OPr^f)_2]$ complexes, further investigation of the ligation properties of RR' -admpzp and related ligands in titanium chemistry is of interest. Hence studies aimed at determining the nature of the active catalyst species generated in **2a–c**/MAO systems and tailoring catalyst properties through systematic modification of the ligand framework are currently underway in our laboratory in hopes of developing more active and thermally stable catalysts that provide excellent control of polymer properties.

4. Experimental

4.1. General

All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. glovebox. Solvents were dried and distilled by standard methods before use [18]. All solvents were stored in the glovebox over 4A molecular sieves that were dried in a vacuum oven at 150 °C for at least 48 h prior to use. Unless otherwise stated, all reagents were purchased from Aldrich Chemical Company. 3,5-Dimethylpyrazole was purchased from Alfa Aesar and dried under vacuum at 60 °C for 3 h prior to use. Epichlorohydrin was dried overnight over anhydrous Na_2SO_4 prior to use. Ethylene (99.9% purity) was purchased from Scott-Gross Co. or Matheson Tri-Gas Inc. 1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at room temperature unless otherwise stated. 1H and ^{13}C chemical shifts were referenced to residual solvent peaks. Infrared spectra were recorded on a Nicolet Magna 560 spectrometer. GC–

MS analyses were performed on a Hewlett Packard 5890 series II gas chromatograph with a Hewlett Packard 5972 series mass selective detector at an ionizing potential of 70 eV. Gel permeation chromatography experiments were performed at Cornell Center for Materials Research, Ithaca, NY. All molecular weights were measured relative to linear polystyrene standards. Elemental analyses were performed by Complete Analysis Laboratories Inc., Parsippany, NJ.

4.2. General synthesis of 1-dialkylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ols (**1a–c**)

NaOH pellets (7.50 g, 0.188 mol) were added into a slightly heterogeneous mixture of 3,5-dimethylpyrazole (15.0 g, 0.156 mol) and epichlorohydrin (250 ml, 3.19 mol). After stirring for several minutes, NaCl began to precipitate and the reaction mixture was stirred at room temperature for 24 h. The resulting suspension was then filtered and the filtrate was evaporated under reduced pressure to give 3,5-dimethyl-1-oxiranylmethyl-1H-pyrazole as a viscous oil. This crude product, which contained 5–10% (by GC–MS) of 1,3-bis(3,5-dimethyl-1H-pyrazol-1-yl)propan-2-ol, was used in the preparation of **1a–c** without purification.

4.2.1. 1-Diisopropylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ol (**1a**)

Distilled water (2.00 mL, 0.156 mol) and Pr_2NH (65.6 mL, 0.468 mol) were added to the viscous oil of 3,5-dimethyl-1-oxiranylmethyl-1H-pyrazole and the resulting solution was stirred at reflux for 3 h. After cooling to room temperature, the solution was concentrated under reduced pressure to give a brown-yellow viscous oil. This crude product was purified by column chromatography using a 35:4:1 ethyl acetate–hexane–triethylamine mixture as eluent. The solution was evaporated under reduced pressure to give **1a** as a white powder. Yield: 21.7 g, 55%. 1H NMR (C_6D_6): δ 5.71 (s, 1H, pyz-4), 4.39 (s, 1H, CH–OH), 4.03 (dd, $^2J = 13.8$ Hz, $^3J = 4$ Hz, 1H, H_A of $-CH_2pyz$), 3.91 (m, 1H, HO–CH), 3.73 (dd, $^2J = 13.8$ Hz, $^3J = 8.5$ Hz, 1H, H_B of $-CH_2pyz$), 2.72 (sept, $^3J = 8.5$ Hz, 2H, $N\{CHMe_2\}_2$), 2.44 (dd, $^2J = 17$ Hz, 1H, H_A of $-CH_2NPr_2$), 2.42 (dd, $J = 17$ Hz, 1H, H_B of $-CH_2NPr_2$), 2.25 (s, 3H, CH_3 at pyz-3), 2.07 (s 3H, CH_3 at pyz-5), 0.81 (d, $^3J = 8.5$ Hz, 6H, $N-CHMe_2$), 0.77 (d, 6H, $^3J = 8.5$ Hz, $N-CHMe_2$). ^{13}C NMR (C_6D_6): δ 147.0 (pyz-3), 139.7 (pyz-5), 104.8 (pyz-4), 68.6 (CH–OH), 52.6 (CH_2pyz), 48.4 ($N\{CHMe_2\}_2$), 48.3 (CH_2NPr_2), 21.4 ($N-CHMe_2$), 20.3 ($N-CHMe_2$), 13.8 (CH_3 at pyz-3), 11.1 (CH_3 at pyz-5). IR (Nujol, cm^{-1}): 3136, 1552, 1465, 1384, 1360, 1333, 1296, 1191, 1176, 1128, 1096, 974, 885, 787. GC–MS(EI): M^+ (253).

4.2.2. 1-Dibenzylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ol (**1b**)

Prepared as described for **1a** except using dibenzylamine (30 mL, 0.156 mol) and heating the reaction mixture at

80 °C for 3 h. Compound **1b** was isolated as a white powder. Yield: 30.5 g, 56%. ¹H NMR (C₆D₆): δ 7.22–7.04 (m, 10H, N(CH₂Ph)₂), 5.64 (s, 1H, pyz-4), 4.61 (d, ³J = 2.5 Hz, 1H, CH–OH), 4.12 (m, 1H, HO–CH), 3.82 (dd, ²J = 17 Hz, ³J = 3.5 Hz, 1H, H_A of –CH₂pyz), 3.56 (dd, ²J = 17 Hz, ³J = 9.5 Hz, 1H, H_B of –CH₂pyz), 3.43 (d, ²J = 17 Hz, 2H, H_A of CH₂Ph), 3.39 (d, ²J = 17 Hz, 2H, H_B of CH₂Ph), 2.54 (dd, ²J = 16.5 Hz, 1H, H_A of –CH₂NPr₂ⁱ), 2.52 (dd, ²J = 16.5 Hz, 1H, H_B of –CH₂NPr₂ⁱ), 2.20 (s, 3H, CH₃ at pyz-3), 1.82 (s, 3H, CH₃ at pyz-5). ¹³C NMR (C₆D₆): δ 147.4 (pyz-3), 139.5 (pyz-5), 139.3, 129.3, 128.5, 127.3, 104.8 (pyz-4), 69.1 (CH–OH), 59.1 (CH₂Ph), 57.0 (CH₂N(CH₂Ph)₂), 52.1 (CH₂pyz), 13.7 (CH₃ at pyz-3), 10.5 (CH₃ at pyz-5). IR (Nujol, cm⁻¹): 3174, 1548, 1461, 1377, 1359, 1123, 1092, 1077, 1047, 1032, 910, 860, 782, 751, 736, 699. GC–MS(EI): M⁺ (349).

4.2.3. 1-(Benzyl-tert-butyl-amino)-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ol (**1c**)

Prepared as described for **1b** using benzyl-tert-butylamine (28.3 mL, 0.156 mol). Compound **1c** was isolated as a yellow liquid. Yield: 18.7 g, 38%. ¹H NMR (C₆D₆): δ 7.20–6.98 (m, 5H, CH₂Ph) 5.60 (s, 1H, pyz-4), 4.24 (br s, 1H, CH–OH), 3.83 (dd, ²J = 17 Hz, ³J = 4 Hz, 1H, H_A of –CH₂pyz), 3.64 (m, 1H, HO–CH), 3.41 (dd, ²J = 17 Hz, ³J = 8.5 Hz, 1H, H_B of –CH₂pyz), 3.46 (d, ²J = 18.5 Hz, 1H, H_A of CH₂Ph), 3.35 (d, ²J = 18.5 Hz, 1H, H_B of CH₂Ph), 2.74 (dd, ²J = 17 Hz, ³J = 9 Hz, 1H, H_A of CH₂NBu^tBn), 2.52 (dd, ²J = 17 Hz, ³J = 8.5 Hz, 1H, H_B of CH₂NBu^tBn), 2.13 (s, 3H, CH₃ at pyz-3), 1.85 (s, 3H, CH₃ at pyz-5), 0.89 (s, 9H, Bu^t). ¹³C NMR (C₆D₆): δ 147.0 (pyz-3), 139.5 (pyz-5), 142.9, 128.5, 128.1, 126.8, 104.7 (pyz-4), 70.0 (CH–OH), 55.9 (CH₂Ph), 55.5 (N–CMe₃), 55.1 (CH₂NBu^tBn), 52.0 (CH₂pyz), 27.2 (N–CMe₃), 13.7 (CH₃ at pyz-3), 11.0 (CH₃ at pyz-5). IR (Neat, cm⁻¹): 3381, 3027, 2970, 2870, 1553, 1493, 1467, 1425, 1391, 1364, 1258, 1245, 1199, 1123, 1055, 1026, 948, 900, 842, 774, 750, 735, 715, 699. GC–MS(EI): M⁺ (315).

4.3. Synthesis of [(Prⁱ₂-admpzp)₂Ti(OPri)₂] (**2a**)

Into a pentane (20 mL) solution of Ti(OPrⁱ)₃Cl (0.500 g, 1.92 mmol) was added dropwise a pentane (20 mL) solution of 1-diisopropylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ol (**1a**, 0.490 g, 1.92 mmol) and NEt₃ (0.194 g, 1.92 mmol). Next, another equivalent of **1a** (0.490 g, 1.92 mmol) in pentane (20 mL) was slowly added. The reaction mixture was let stir for 2 h at room temperature, during which time [HNEt₃]Cl precipitated. After filtering off the precipitate, the yellow filtrate was evaporated under reduced pressure to give **2a** as a yellow oily liquid. This product could be obtained as a colorless oil following dissolution in pentane, filtration through a plug of dry activated carbon, and evaporation of the solvent. Yield 1.24 g, 96%. ¹H (C₆D₆) δ: 5.68 (br s, 2H, pyz-4), 5.12–4.46 (br m, 4H, Ti–OCH–), 4.44–4.10 (m, 2H, H_A of

–CH₂pyz), 3.82–3.54, (m, 2H, H_B of –CH₂pyz), 3.07–2.78 (br m, 4H, N(CHMe₂)₂) 2.93–2.70 {m, 2H, H_A of –CH₂NPr₂ⁱ}, 2.63–2.38 (m, 6H, CH₃ at pyz-3), 2.38–2.25 (m, 2H, H_B of –CH₂NPr₂ⁱ), 2.20–1.87 {m, 6H, (CH₃ at pyz-5)}, 1.45–1.24 (m, 12H, Ti–OCHMe₂), 1.07–0.72 (br m, 24 H, {N(CHMe₂)₂}. ¹³C (C₆D₆) δ: 147.8 (pyz-3), 147.3 (pyz-3), 139.2 (pyz-5), 105.0 (pyz-4), 81.7 (Ti–OCH–), 80.8 (Ti–OCH–), 77.0 (Ti–OCH–), 52.7 (–CH₂pyz), 50.5 (CH₂NPr₂ⁱ), 48.6 (CH₂NPr₂ⁱ), 26.7 (Ti–OCHMe₂), 22.3 {N(CHMe₂)₂}, 19.9 {N(CHMe₂)₂}, 14.2 (CH₃ at pyz-3), 11.0 (CH₃ at pyz-5). IR (neat, cm⁻¹): 2965, 2928, 2867, 2617, 1553, 1464, 1425, 1385, 1362, 1324, 1260, 1207, 1123, 1045, 987, 930, 886, 809, 775, 738, 696, 632. Anal. Calc. for C₃₄H₆₆N₆O₄Ti: C, 60.88; H, 9.92; N, 12.53. Found: C, 61.11; H, 9.81; N, 12.63%.

4.4. Synthesis of [(Bn₂-admpzp)₂Ti(OPri)₂] (**2b**)

Into a pentane (20 mL) solution of Ti(OPrⁱ)₃Cl (0.500 g, 1.92 mmol) was slowly added (dropwise) a pentane (40 mL) solution of 1-dibenzylamino-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ol (**1b**, 0.670 g, 1.92 mmol) and NEt₃ (0.194 g, 1.92 mmol). Next, another equivalent of **1b** (0.670 g, 1.92 mmol) in pentane (40 mL) was slowly added. The reaction mixture was let stir for 2 h at room temperature, during which time [HNEt₃]Cl precipitated. After the precipitate was filtered off, the yellow filtrate was cooled at –30 °C overnight. The bottom layer of the resulting biphasic mixture was collected and dried under vacuum for 4 h to give **2b** as a viscous yellow liquid. A colorless oil could be obtained via dissolution in pentane, filtration through a plug of dry activated carbon, and evaporation of the solvent. Yield: 1.56 g, 94%. ¹H (C₆D₆) δ: 7.50–6.98 (m, 20H, {PhCH₂})₂N}, 5.55 (br s, 2H, pyz-4), 4.95–4.60 (br m, 4H, Ti–OCH–), 4.22–4.00 (m, 2H, H_A of CH₂pyz), 3.93–3.67 (m, 4H, H_A of (PhCH₂)₂N), 3.67–3.26 (m, 2H, H_B of CH₂pyz), 3.47–3.26 (m, 4H, H_B of (PhCH₂)₂N), 2.81–2.50 (br m, 4H, –CH₂NBn₂), 2.47–2.08 (m, 6H, CH₃ at pyz-3), 2.06–1.67 (m, 6H, (CH₃ at pyz-5), 1.45–0.80 (br m, 12H, Ti–OCHMe₂). ¹³C (C₆D₆) δ: 147.8 (pyz-3), 140.1 (pyz-5), 139.2, 129.4, 128.4, 127.1 {(PhCH₂)₂N}, 105.0 (pyz-4), 79.4 (Ti–OCH–), 77.4 (Ti–OCH–), 59.4 {(PhCH₂)₂N}, 59.0 (–CH₂NBn₂), 52.8 (CH₂pyz), 26.5 (Ti–OCHMe₂), 14.2 (CH₃ at pyz-3), 11.1 (CH₃ at pyz-5). IR (neat, cm⁻¹): 3084, 3061, 3027, 2963, 2853, 2792, 2714, 2617, 1948, 1877, 1809, 1754, 1602, 1585, 1553, 1494, 1454, 1373, 1240, 1097, 1018, 933, 847, 780, 747, 698. Anal. Calc. for C₅₀H₆₆N₆O₄Ti: C, 69.59; H, 7.71; N, 9.74. Found: C, 69.65; H, 7.91; N, 9.80%.

4.5. Synthesis of [(Bu^tBn-admpzp)₂Ti(OPri)₂] (**2c**)

Into a pentane (20 mL) solution of Ti(OPrⁱ)₃Cl (0.500 g, 1.92 mmol) was slowly added (dropwise) a pentane (20 mL) solution of 1-(benzyl-tert-butyl-amino)-3-(3,5-dimethyl-pyrazol-1-yl)-propan-2-ol (**1c**, 0.610 g, 1.92 mmol) and NEt₃ (0.194 g, 1.92 mmol). Next, another equivalent of **1c**

(0.610 g, 1.92 mmol) in pentane (20 mL) was slowly added. The reaction mixture was let stir for 2 h at room temperature, during which time $[\text{HNET}_3]\text{Cl}$ precipitated. After the precipitate was filtered off, the filtrate was concentrated under reduced pressure to ~ 20 mL and cooled at -30 °C overnight. The resulting yellowish-white crystals were collected, recrystallized from hot pentane by cooling a saturated solution at -30 °C for several days, and then dried under vacuum to give **2c**. Yield: 1.13 g, 74%. ^1H (C_6D_6) δ : 7.62–6.99 (m, 10H, $\text{Bu}^i(\text{PhCH}_2)\text{N}$), 5.60 (br m, 2H, pyz-4), 5.16–4.32 (br m, 4H, $\text{Ti}-\text{OCH}-$), 4.12–3.82 (m, 2H, H_A of CH_2pyz), 3.83–3.50, (m, 4H, $\text{Bu}^i(\text{PhCH}_2)\text{N}$), 3.50–3.31 (m, 2H, H_B of CH_2pyz), 3.05–2.64 (br m, 4H, $-\text{CH}_2\text{NBnBu}^i$), 2.65–2.15 (m, 6H, CH_3 at pyz-3), 2.14–1.68 (m, 6H, CH_3 at pyz-5), 1.51–1.17 (m, 12H, $\text{Ti}-\text{OCHMe}_2$), 1.15–0.85 (m, 18H, Bu^i). ^{13}C (C_6D_6) δ : 148.0 (pyz-3), 144.1 ($\text{Bu}^i(\text{PhCH}_2)\text{N}$), 139.0 (pyz-5), 128.4 ($\text{Bu}^i(\text{PhCH}_2)\text{N}$), 127.1 ($\text{Bu}^i(\text{PhCH}_2)\text{N}$), 126.5 ($\text{Bu}^i(\text{PhCH}_2)\text{N}$), 105.0 (pyz-4), 80.7 ($\text{Ti}-\text{OCH}-$), 76.9 ($\text{Ti}-\text{OCH}-$), 57.0 ($\text{Bn}(\text{Me}_3\text{C})\text{N}$), 56.1 ($-\text{CH}_2\text{NBnBu}^i$), 55.5 ($\text{Bu}^i(\text{PhCH}_2)\text{N}$), 52.3 (CH_2pyz), 27.3 ($\text{Ti}-\text{OCHMe}_2$), 26.5 ($\text{Bn}(\text{CH}_3)_3\text{CN}$), 14.3 (CH_3 at pyz-3), 11.1 (CH_3 at pyz-5). IR (Nujol, cm^{-1}): 1551, 1465, 1367, 1323, 1296, 1201, 1160, 1135, 1092, 989, 931, 843, 734, 699. Anal. Calc. for $\text{C}_{44}\text{H}_{70}\text{N}_6\text{O}_4\text{Ti}$: C, 66.48; H, 8.88; N, 10.57. Found: C, 66.33; H, 8.75; N, 10.69%.

4.6. General procedure for ethylene polymerization reactions

Toluene (35 ml) was charged into a 90 ml Swagelok glass-tube reactor under N_2 atmosphere in a glovebox. The reactor was maintained at the desired temperature for 20 min. Next, 10 μmol of catalyst precursor (2.5 mL of 0.004 M solution in toluene) was added followed by an excess of MAO (Al/Ti ratio = 500/1 or 1000/1) and the solution was stirred for 5 min. The N_2 atmosphere was replaced with ethylene and the reactor was maintained at the pressure of 145 psi (10 bar). The polymerization was carried out for 30 min. The reactor was vented and the polymerizations were quenched with ethanol (25 mL) and then 1 M HCl solution (25 mL). The resulting suspension was vigorously stirred until both layers were colorless and clearly separated (~ 1 h). Polyethylene was filtered off, washed with 1 M HCl, and repeatedly rinsed twice with ethanol on a glass frit. The polymer was then dried at 70 °C for 72 h.

4.7. Crystallographic study

Single crystals of $[(\text{Bu}^i\text{Bn-admpzp})_2\text{Ti}(\text{OPri})_2]$ (**2c**) suitable for X-ray crystallographic analysis were obtained by low temperature (-30 °C) crystallization of a saturated pentane solution of **2c** (obtained by dissolution of **2c** in hot pentane). The crystal data for **2c** are collected in Table 1. Further details of the crystallographic study are given in the Supplementary material.

Acknowledgements

Thanks are expressed to the US National Science Foundation (Grant No. CHE-0416098) for financial support of this work. NMR instruments utilized in this research were funded in part by the CRIF program of the US National Science Foundation (Grant No. CHE-9974810). This work made use of the materials characterization facility of the Cornell Center for Materials Research (CCMR) with support from the National Science Foundation Materials Research Science and Engineering Centers (MRSEC) Program (DMR 0520404).

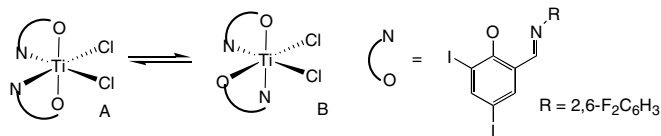
Appendix A. Supplementary material

Full crystallographic data for compound **2c**, as well as ^1H , ^{13}C , and 2D $^{13}\text{C}-^1\text{H}$ HSQC NMR spectra for compounds **1a–c** and **2a–c** (34 pages). Crystallographic data for **2c** has been deposited with the Cambridge Crystallographic Data Centre. CCDC 662008 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.040.

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