

High-Temperature Single-Site Ethylene Polymerization Behavior of Titanate Complexes Supported by 1,3-Bis(3,5-dialkylpyrazol-1-yl)propan-2-olate Ligand

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Titanate(1–) complexes $\text{Na}[(\text{THF})(\kappa^1\text{-O-bdbpzp})\text{TiCl}_4]$ (**1**) and $\text{Na}[(\text{THF})(\kappa^1\text{-O-bdmpzp})\text{TiCl}_4]$ (**2**) and titanate(2–) complexes $[\text{Na}(\text{THF})]_2[(\kappa^1\text{-O-bdbpzp})_2\text{TiCl}_4]$ (**4**) and $[\text{Na}(\text{THF})]_2[(\kappa^1\text{-O-bdmpzp})_2\text{TiCl}_4]$ (**5**) were obtained in good yield from reaction of $\text{Na}[\text{bdbpzp}]$ or $\text{Na}[\text{bdmpzp}]$ (sodium salt of 1,3-bis(3,5-di-tert-butylpyrazol-1-yl)propan-2-ol or 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol) with TiCl_4 (in the appropriate molar ratio) at 0–25 °C. Protonolysis of TiCl_4 with 1 equiv of bdmpzpH furnished related zwitterionic titanate(1–) complex **3** that possessed a $\kappa^2\text{-N,O}$ -coordinated pyrazolyl-alkoxide with pendant pyrazolium group. Methylalumoxane (MAO) activation of **1–5** under high-temperature solution polymerization conditions produced active single-site ethylene polymerization catalysts that exhibit considerably higher thermal stability (especially **2/MAO**, **3/MAO**, and **5/MAO**) than previously reported for $\text{Cp}_2\text{TiCl}_2/\text{MAO}$ or Ti catalysts supported by related heteroscorpionate or scorpionate ligation.

Introduction

The discovery of Group 4 metal-containing single-site olefin polymerization catalyst systems, $\text{Cp}_2\text{MX}_2/\text{activator}^1$ and $(\text{CpSiR}_2\text{NR})\text{MX}_2/\text{activator}^2$ has inspired intense study of the potential of a diverse array of ancillary ligands in early transition metal chemistry in hopes of uncovering alternative catalyst systems that provide comparable or improved polymerization activity and control of polymer properties. These studies have helped establish the impact of ligand design on catalyst performance, and a few highly active (and sometimes living) olefin polymerization catalysts have been

obtained from activation of chelating di(amide),³ amine-bis-(phenolate),⁴ bis(salicylaldehyde),⁵ or phosphinimide⁶ complexes of the Group 4 metals. Recently, heteroscorpionate ligands⁷ that incorporate the bis(pyrazol-1-yl)methyl fragment have been attracting attention since they are capable of binding strongly to early transition metals in tridentate facial fashion (Figure 1)^{7d,e} and behaving as six-electron donors, analogous to scorpionate ligands⁸ and the ubiquitous cyclopentadienide (Cp^-) ligand and its derivatives. Additionally,

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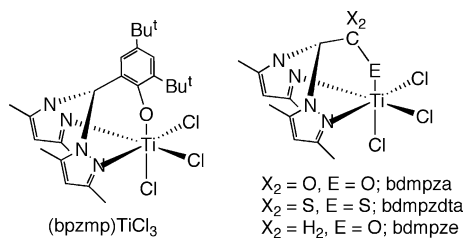
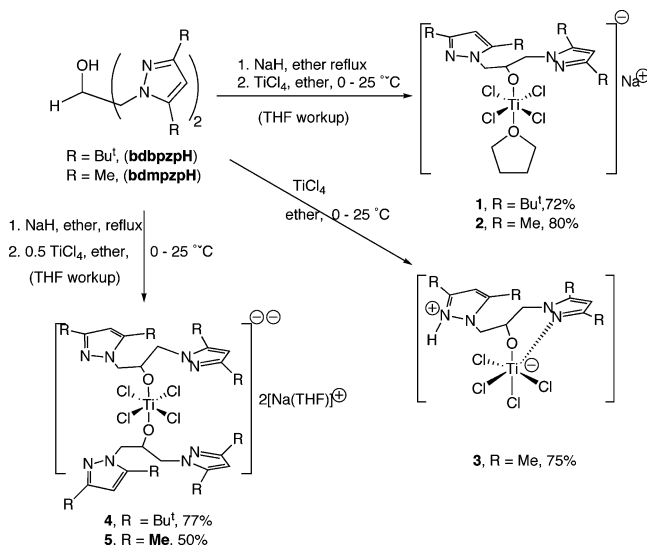


Figure 1.

coordination to hard nitrogen and oxygen donor groups may lead to better stabilization of Ti(IV) species against reduction, and reactivity of the metal complex may be modulated through tuning of electronic and steric properties of the donor groups. Several studies have shown that Group 4 metal scorpionate^{8b,c} and heteroscorpionate^{7a,b,d-f} complexes polymerize ethylene and/or α -olefins when activated with an appropriate cocatalyst, such as methylalumoxane (MAO). However, catalysts generated thus far have generally displayed low thermal stability and furnished polymers with broad molecular weight distributions, although some highly active catalysts have been found, including Tp^{Ms*}TiCl₃/MAO (Tp^{Ms*} = tris(3,5-dimesitylpyrazol-1-yl)borate)^{8b} and [(bdmpza)TiCl₃]/MAO.^{7d} As part of our program aimed at developing the potential of non-cyclopentadienyl ligand arrays in organotitanium chemistry,⁹ we recently initiated a study of the synthesis, structure, and reactivity of Ti(IV) complexes supported by 1,3-bis(pyrazol-1-yl)propan-2-olate ligation (Scheme 1). This ligand framework is attractive because of its modular nature, which should facilitate easy modification of ligand properties. In addition, while 1,3-bis-

Scheme 1



(pyrazol-1-yl)propan-2-olate ligands are potentially tridentate, incorporation of methylene bridges between the pyrazolyl and alkoxide donor groups, may facilitate flexible ligation behavior and thereby allow different molecular geometries to be realized. Herein we describe the isolation and characterization of unusual titanate complexes and results from our preliminary exploration of the ethylene polymerization behavior of catalysts generated via MAO activation of the complexes.

Results and Discussion

Synthesis and Characterization of Titanate Complexes.

1,3-Bis(3,5-di-*tert*-butylpyrazol-1-yl)propan-2-ol (**bdbpzh**) was synthesized by modification of the method previously reported for preparation of 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (**bdmpzh**).¹⁰ The formulation of **bdbpzh** was established by ¹H and ¹³C NMR, mass spectral, and microanalysis data (see Experimental Section). The EI-MS mass spectrum of **bdbpzh** is consistent with a monomeric molecular structure, which was unambiguously established by X-ray crystallography (Figure 2; selected metrics are provided in the figure caption, and crystallographic data are given in Table 1).¹¹ Syntheses of titanate complexes described in this report are summarized in Scheme 1. Titanate(1⁻) complexes Na[(κ¹-O-bdbpzp)(THF)TiCl₄] (**1**) and Na[(κ¹-O-bdmppz)(THF)TiCl₄] (**2**) were isolated in high yield from reaction of TiCl₄ in ether at 0–25 °C with 1 equiv of **Na[bdbpzh]** or **Na[bdmpzh]**, respectively; complexation of THF occurred during workup (see Experimental Section). Protonolysis of TiCl₄ with 1 equiv of **bdmpzh** furnished the related zwitterionic titanate(1⁻) complex **3** (Scheme 1), which contains a chelating pyrazolyl-alkoxide ligand with a pendant pyrazolium group. Titanate(2⁻) complexes [Na(THF)]₂[(κ¹-O-bdbpzp)₂TiCl₄] (**4**) and [Na(THF)]₂[(κ¹-O-

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(11) All of the bond distances and angles are within the expected ranges and comparable to those reported in the supporting information available online for the related heteroscorpionate ligands in [(bdmpza)-TiCl₂{O(CH₂)₄Cl}]^{7d} and [(bpzmp)TiCl₃].^{7c}

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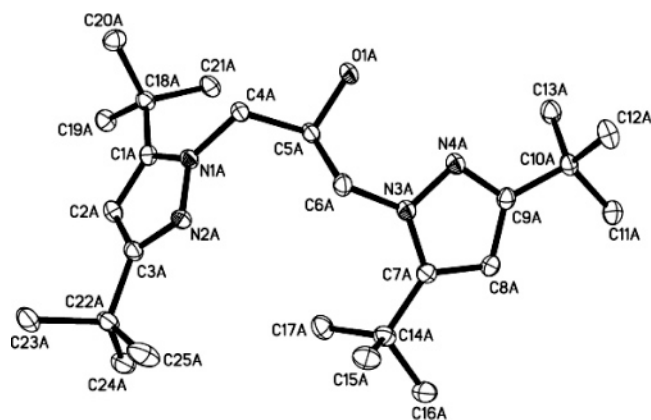


Figure 2. Molecular structure of **bdbpzzpH** (50% probability ellipsoids). Selected bond distances (Å) and angles (deg): N(1A)–N(2A), 1.3671(18); N(1A)–C(1A), 1.370(2); N(1A)–C(4A), 1.450(2); N(2A)–C(3A), 1.328(2); O(1A)–C(5A), 1.4181(18); C(1A)–C(2A), 1.373(2); C(2A)–C(3A), 1.405(2); C(4A)–C(5A), 1.528(2); N(2A)–N(1A)–C(1A), 111.82(12); N(2A)–N(1A)–C(4A), 117.43(12); C(1A)–N(1A)–C(4A), 130.75(13); C(3A)–N(2A)–N(1A), 105.29(12); C(1A)–C(2A)–C(3A), 106.51(14); N(2A)–C(3A)–C(2A), 110.72(13); N(1A)–C(4A)–C(5A), 113.06(12); O(1A)–C(5A)–C(4A), 105.91(12).

Table 1. Crystallographic Data for **bdbpzzpH** and **3**

	bdbpzzpH	3
formula	C ₂₅ H ₄₄ O	C ₁₃ H ₂₀ Cl ₄ N ₄ O ₁ Ti
fw	416.64	438.03
T, K	90.0(2)	90.0(2)
cryst syst	triclinic	monoclinic
space group	P1̄	P2 ₁ /c
Z	4	4
a, Å	9.2769(4)	9.5012(5)
b, Å	10.1816(4)	8.2886(4)
c, Å	28.9708(11)	22.4097(13)
α, (deg)	89.107(2)	90
β, (deg)	87.567	91.038(3)
γ, (deg)	66.349	90
V, Å ³	2504.30(17)	1764.51(16)
d _{calc} , g/cm ³	1.105	1.649
final R indices [I > 2σ(I)]:	0.0446, 0.1189	0.0371, 0.0820
R1, wR2		
wR2, R1 (all data)	0.0473, 0.1208	0.0547, 0.0924

bdmpzp)₂TiCl₄] (**5**) were produced via slow addition of an ether solution of **Na[bdbpzzp]** or **Na[bdmpzzp]** to 0.5 equiv of TiCl₄ in ether at 0 °C followed by overnight stirring of the heterogeneous mixture at 0–25 °C (Scheme 1). Compounds **1–5** are air- and extremely moisture-sensitive pale yellow solids.¹² All of the compounds display good solubility in THF, CH₃CN, and DMSO. However, while **1** and **4** are moderately soluble in diethyl ether, CH₂Cl₂, CHCl₃, and toluene, **2**, **3**, and **5** are just slightly soluble in these solvents. Compounds **1–5** are practically insoluble in aliphatic hydrocarbon solvents.

The formulations and structures of **1–5** (Scheme 1) were established by microanalysis, spectroscopic (¹H and ¹³C NMR, IR, and MS), and/or single-crystal X-ray diffraction experiments. Laser desorption ionization-time-of-flight (LDI-

TOF) mass spectra of **1** and **2** contained fragment ions, such as [Ti₂Cl₄{OCH(CH₂)₂}][–] (*m/z* = 295), [NaTi₂Cl₄{OCH(CH₂)₂}][–] (*m/z* = 318), [NaTi₂Cl₆{OCH(CH₂)₂}][–] (*m/z* = 388), and [Na₂Ti₂Cl₈{OCH(CH₂)₂}][–] (*m/z* = 483) for **1**, and [TiCl₄][–] (*m/z* = 190), [NaTiCl₄{OCH(CH₂)₂}][–] (*m/z* = 270), [NaTi₂Cl₈{OCH(CH₂)₂}][–] (*m/z* = 460), and [Na₂Ti₂Cl₈{OCH(CH₂)₂}][–] (*m/z* = 540) for **2**, consistent with coordination of **bdbpzzp** or **bdmpzzp** and four chlorides to titanium.¹³ Evidently, dimeric species observed in LDI-TOF mass spectra of **1** and **2** are generated during the course of the LDI-TOF experiment since ¹H and ¹³C{¹H} NMR data of **1** and **2** confirm THF coordination to titanium in solution (vide infra) and cryoscopic molecular weight measurements in chloroform indicate a monomeric solution structure for **1** and **4**.¹⁴ Additional support of a monomeric six-coordinate structure for titanate(1–) complexes **1** and **2** is found in observation of monomeric fragment ions in the EI-MS spectrum of **1**, including [(bdbpzzp)(THF)TiCl₄]⁺ (*m/z* = 677) and [(bdbpzzp)TiCl₂]⁺ (*m/z* = 533). ¹H and ¹³C{¹H} NMR spectra of **1** and **2** showed a single set of signals for the **bdbpzzp** or **bdmpzzp** ligand, indicative of symmetry-equivalent pyrazolyl groups. For example, the ¹H NMR (CDCl₃) spectrum of **1** showed two singlet resonances (each integrating as six protons) at δ 1.42 and 1.44 for *tert*-butyl substituents of the pyrazolyl rings, a singlet resonance at δ 6.10 for the two pyrazolyl protons (pyz-4), and a sharp multiplet at δ 1.92 and a broad multiplet at δ 4.20 (each integrating as four protons) for the THF ligand. In the ¹³C{¹H} (CDCl₃) NMR spectrum of **1**, the THF ligand appeared as two singlet resonances at δ 25.5 and 71.5. The related titanate(1–) complex [Et₃NH][(OPr^t)(THF)TiCl₄][–] whose molecular structure was unambiguously characterized by X-ray crystallography displayed parallel ¹H (δ 1.95 and 4.25) and ¹³C{¹H} (δ 25.3 and 72.8) NMR resonances in CDCl₃ for its THF ligand.¹⁵ Hence, our data support octahedral C_s-symmetric structure for titanate(1–) complexes **1** and **2** with the **bdbpzzp** or **bdmpzzp** ligand κ¹-O coordinated to titanium trans to THF and the chloride ligands occupying the equatorial plane, analogous to the crystallographically established structure of [(OPr^t)(THF)TiCl₄][–] and consistent with the structure of **3** (vide infra). This geometric arrangement of **1** and **2** is favored by placement of the strongest donor (alkoxide group) trans to the weakest donor (THF) and results in a substitutionally labile THF ligand.

At 25 °C, solution (CD₃CN or CD₂Cl₂) ¹H and ¹³C{¹H} NMR data for the zwitterionic titanate(1–) complex **3** (Scheme 1) indicate that proton exchange between pyrazolyl and pyrazolium groups with concomitant titanium shift is fast on the NMR time scale. In the ¹H NMR spectrum of **3** in CD₃CN, two slightly broad singlets were observed at δ 2.41 and 2.46 (each integrating as six protons) for methyl

(12) The compounds are especially susceptible to hydrolysis in solution. A white precipitate that cannot be redissolved in any solvent is deposited on standing of solutions of the compounds for ~1 h. Although the precipitate has not been identified, its lack of crystallinity and quantity strongly suggests it is not sodium chloride. However, exposure of the compounds to air for 30 min in the solid state does not appear to result in any decomposition (by ¹H NMR).

(13) The composition of the fragment ions was determined by a comparison of experimental and simulated isotope patterns using Isotope, v 1.6.8 and ChemDraw Ultra, v 7.0.1 programs (see Supporting Information).
 (14) The cryoscopic molecular weights of **1** and **4** were determined to be 710.8 g/mol ± 10% and 1248.4 g/mol ± 10%, respectively; their calculated molecular weights are 700.4 and 1211.1 g/mol.
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Table 2. Selected Bond Distances (Å) and Angles (deg) for **3**

Ti(1)–O(1)	1.817(2)
Ti(1)–N(4)	2.197(3)
Ti(1)–Cl(3)	2.3197(10)
Ti(1)–Cl(2)	2.3439(10)
Ti(1)–Cl(1)	2.3496(9)
Ti(1)–Cl(4)	2.3650(10)
N(2)–H(2)···O(1)	0.88, 2.27, 2.755(3)
N(2)–H(2)···Cl(1)	0.88, 2.37, 3.227(3)
O(1)–Ti(1)–N(4)	81.61(10)
O(1)–Ti(1)–Cl(3)	94.40(8)
N(4)–Ti(1)–Cl(3)	86.53(8)
O(1)–Ti(1)–Cl(2)	173.99(8)
N(4)–Ti(1)–Cl(2)	94.46(7)
Cl(3)–Ti(1)–Cl(2)	89.89(4)
O(1)–Ti(1)–Cl(1)	89.67(7)
N(4)–Ti(1)–Cl(1)	170.75(8)
Cl(3)–Ti(1)–Cl(1)	91.10(4)
Cl(2)–Ti(1)–Cl(1)	94.47(3)
O(1)–Ti(1)–Cl(4)	90.02(8)
N(4)–Ti(1)–Cl(4)	90.04(7)
Cl(3)–Ti(1)–Cl(4)	173.96(4)
Cl(2)–Ti(1)–Cl(4)	85.42(4)
Cl(1)–Ti(1)–Cl(4)	93.05(4)
C(7)–O(1)–Ti(1)	142.0(2)
N(2)–H(2)···O(1)	114.3
N(2)–H(2)···Cl(1)	166.2

substituents of the pyrazolyl/pyrazolium rings and a slightly broad singlet at δ 6.28 was observed for the two pyrazolyl/pyrazolium ring protons (pyz-4), consistent with facile equilibration of the pyrazolyl and pyrazolium groups. A variable-temperature ^1H NMR study of **3** in CD_2Cl_2 from 298 to 193 K did not permit observation of a rigid structure on the NMR time scale; resonances in the NMR spectrum sharpened somewhat as the temperature was lowered, and only minor resonances grew in alongside those observed at room temperature. Consistent with the presence of a pyrazolium group, the IR (KBr) spectrum of **3** showed a complex series of N–H stretching absorptions in the 2800–2000 cm^{-1} region; similar data have been reported for other pyrazolium salts.¹⁶ As shown in Figure 3, X-ray analysis of single crystals of **3** confirmed that the compound adopts a distorted octahedral structure with the titanium coordinated to a chelating alkoxide-pyrazolyl ligand that bears a pendant pyrazolium group. Crystallographic data and selected metrics for **3** are given in Tables 1 and 2, respectively. The distortion from idealized octahedral geometry arises from the acute bite angle of the bidentate alkoxide-pyrazolyl ligand [$\text{O}(1)\text{--Ti--N}(4) = \text{ca. } 82^\circ$]. The Ti–O bond distance (ca. 1.82 Å) is much shorter than the Ti–O σ -bond distance predicted on the basis of covalent radii (ca. 1.99–2.05 Å) and probably reflects partial Ti–O π -bonding.¹⁷ Additional evidence in favor of this explanation can be found in the Ti–O(1)–C(7) angle of ca. 142°, which is suggestive of an sp^2 -hybridized oxygen with one p orbital available for O–Ti π -bonding.

All of the Ti–Cl bond distances are within the expected range and comparable to those (2.33–2.37 Å) observed for the related titanate(1–) complex $[\text{Et}_3\text{NH}][(\text{OPr}^i)(\text{THF})\text{--TiCl}_4]$.¹⁵ The pendant pyrazolium unit of **3** participates in good intramolecular N–H···O {N(2)···O(1) = ca. 2.76 Å}¹⁸ and somewhat weaker N–H···Cl {N(2)···Cl(1) = ca. 3.73 Å}¹⁹ hydrogen bonds, and the N(2)–H(2)···O(1) angle of ca. 114° facilitates formation of a thermodynamically favorable six-membered ring.

EI-MS mass spectra of titanate(2–) complexes **4** and **5** contained fragment ions, such as $[(\text{bdbpzp})_2\text{TiCl}]^+$ ($m/z = 913$) and $[(\text{bdmpzp})_2\text{TiCl}]^+$ ($m/z = 577$), consistent with coordination of two 1,3-bis(pyrazol-1-yl)propan-2-olate ligands to titanium. In addition, their LDI-TOF mass spectra contained fragment ions, such as $[\text{TiCl}_4]^-$ ($m/z = 190$), $[\text{NaTiCl}_4\{\text{OCH}(\text{CH}_2)_2\}]^-$ ($m/z = 270$), $[\text{NaTi}_2\text{Cl}_8\{\text{OCH}(\text{CH}_2)_2\}]^-$ ($m/z = 460$), and $[\text{Na}_2\text{Ti}_2\text{Cl}_8\{\text{OCH}(\text{CH}_2)_2\}_2]^-$ ($m/z = 540$) for **4** and $[\text{Ti}_2\text{Cl}_4\{\text{OCH}(\text{CH}_2)_2\}]^-$ ($m/z = 295$), $[\text{NaTi}_2\text{Cl}_7\{\text{OCH}(\text{CH}_2)_2\}]^-$ ($m/z = 423$), and $[\text{Na}_2\text{Ti}_2\text{Cl}_8\{\text{OCH}(\text{CH}_2)_2\}_2]^-$ ($m/z = 540$) for **5**, which establish coordination of four chlorides about titanium. As mentioned before, cryoscopic molecular weight measurements in chloroform showed that **4** is monomeric in solution. Hence, analogous to **1** and **2** (vide supra), dimeric species observed in LDI-TOF mass spectra of **4** and **5** are generated during the course of the LDI-TOF experiments. A monomeric six-coordinate structure in which the alkoxide oxygens of the two 1,3-bis(pyrazol-1-yl)propan-2-olate ligands are mutually trans is proposed for **4** and **5** (Scheme 1). This structure is expected to be favored over the alternative structure in which alkoxide oxygens are mutually cis because alkoxide oxygens can participate in O–Ti π -bonding with different metal d orbitals when mutually trans while they must share a single metal d orbital when mutually cis.^{17,20} Consistent with their proposed structure, both **4** and **5** show a single set of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR signals for two symmetry-equivalent 1,3-bis(pyrazol-1-yl)propan-2-olate ligands. For example, the *tert*-butyl groups of the pyrazolyl rings of **bdbpzp** appear as two singlets at δ 1.34 and 1.37 in the room-temperature ^1H NMR spectrum of **4** and protons at the 4-position of the pyrazolyl rings appear as one singlet (δ 5.96). Unfortunately, we have so far been unsuccessful in obtaining single crystals of **4** or **5** suitable for X-ray diffraction studies. However, trans κ^1 -O coordination of the aryloxide donors has been established by crystallography for the related titanate (2–) complex $[\{2\text{-(RHN}^+\text{=CH)C}_6\text{H}_4\text{O}\}_2\text{--TiCl}_4]$ (R = 2,6-Pr¹₂-C₆H₃).²¹

That reactions described in Scheme 1 resulted in formation of titanate complexes **1–5** indicates that **bdbpzp** and

(16) See for example: (a) Luis, P. A. L.; Martin-Zarza, P.; Sanchez, A.; Ruiz-Perez, C.; Hernandez-Molina, M.; Solans, X.; Gili, P. *Inorg. Chim. Acta* **1998**, *277*, 139. (b) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975; pp 278, 290, 318.

(17) Parallel observations and interpretation have been made for related $[(\text{pyCAr}_2\text{O})_2\text{M}(\text{NMe}_2)_2]$ complexes (pyCAr₂O = chelating pyridne-alkoxide ligand; M = Ti, Zr, or Hf); see, Kim, I.; Nishihara, Y.; Jordan, R. F.; Rogers, R. D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1997**, *16*, 3314.

(18) For typical N···O separation in N–H···O hydrogen bonds, see for example: (a) Sonar, V. N.; Parkin, S.; Crooks, P. A. *Acta Crystallogr.* **2005**, *C61*, o527. (b) Li, L.; Zhu, M.-L.; Lu, L.-P. *Acta Crystallogr.* **2006**, *C62*, m227.

(19) For typical N···Cl separation in N–H···Cl hydrogen bonds, see for example: (a) Trotter, J.; Whitlow, S. H. *J. Chem. Soc. A* **1970**, 455. (b) Kaluderovic, G. N.; Bogdanovic, G. A.; Sabo, T. J. *J. Coord. Chem.* **2002**, *55*, 817.

(20) Keppert, D. L. In *Progress in Inorganic Chemistry*; Lippard, S. L., Ed.; John Wiley and Sons: New York, 1977; Vol. 23, Chapter 1.

(21) Strauch, J.; Warren, T. H.; Erker, G.; Frolich, R.; Saarenketo, P. *Inorg. Chim. Acta* **2000**, *300–302*, 810.

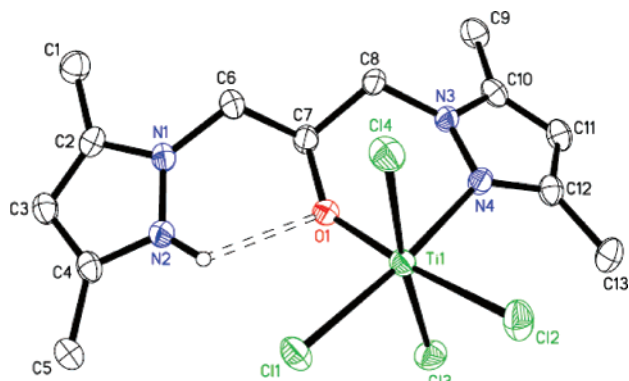


Figure 3. Molecular structure of **3** (50% probability ellipsoids).

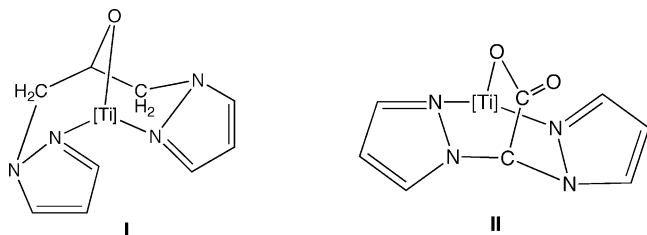


Figure 4. Pyrazolyl substituents omitted for clarity.

bdmpzp ligands have somewhat lower propensity for multidentate coordination than related monoanionic heteroscorpionate ligands that incorporate the bis(pyrazol-1-yl)methyl fragment. For instance, a number of neutral group 4 metal complexes that contain monoanionic, κ^3 -N,N,O-bound **bdmpza** or **bpzmp** ligands have been reported, such as [(**bdmpza**)TiCl₃],^{7d} [(**bpzmp**)TiCl₃],^{7e} and [(**bpzmp**)Ti(NMe₂)₃],^{7e} and solid-state structures of the latter two compounds were characterized by X-ray crystallography.^{7e} Both kinetic and thermodynamic factors presumably favor production of **1–5**. Since pyrazolyl groups of **bdmpzp** (or **bdbpzb**) are bridged to the alkoxide donor by different methylene units, they can act with greater independence of one another than pyrazolyl groups of **bdmpza** or **bpzmp**, which are bound to the same carbon atom. Thus, coordination of **bdmpzp** (or **bdbpzb**) to titanium via the alkoxide donor does not constrain pyrazolyl groups of **bdmpzp** (or **bdbpzb**) as close to the metal center as does analogous coordination of **bdmpza** or **bpzmp** (Figure 4). Moreover, κ^3 -N,N,O coordination of **bdmpzp** or **bdbpzb** to titanium results in a metallabicyclo[3.3.1]nonane-like structure (I, Figure 4) which is likely less stable than the metallabicyclo[2.2.2]octane-like structure (II, Figure 4) produced by κ^3 -N,N,O coordination of **bdmpza**.

Ethylene Polymerization Studies. A preliminary study of the ethylene polymerization behavior of catalysts generated by MAO (1000 equiv) activation of titanate complexes **1–5** in toluene revealed that **1/MAO–5/MAO** exhibit moderate activity in the 23–100 °C temperature range. Remarkably, their polymerization activities at 100 °C are comparable to or greater than their room-temperature activities (Table 3).²² Gel permeation chromatography (GPC)

analyses of the polyethylenes obtained indicate that they possess narrow molecular weight distributions ($M_w/M_n = 1.6–2.4$) with the polyethylenes produced at 100 °C showing molecular weights of ca. 100 000 and reproducibly exhibiting molecular weight distributions less than 2, as expected for single-site catalysts. Differential scanning calorimetry (DSC) analyses demonstrated that the polyethylenes are essentially linear and show melting points of ca. 135 °C. As evident from the data in Table 3, active catalysts generated by MAO activation of titanate complexes that possess one or more **bdmpzp** ligands (**2/MAO**, **3/MAO**, and **5/MAO**) are quite robust under the reaction conditions; their activity data are consistent with a stable polymerization profile and modest catalyst decay at 100 °C. Conversely, MAO activation of titanate complexes supported by more bulky **bdbpzb** ligand(s) furnishes catalysts (**1/MAO** and **4/MAO**) that undergo fast deactivation,²³ as indicated by a steep drop in polymerization activity with an increase in reaction time (Table 3, entry 10 vs 11). This suggests that as the steric bulk around the titanium center is increased, the catalyst becomes shorter-lived; similar reactivity trends involving substituted metallocene catalysts have been observed.^{24,25} While **1/MAO–5/MAO** are less active than Cp₂TiCl₂/MAO at room temperature (Table 3, entries 1–3 vs 16), they display similar or significantly higher ethylene polymerization activity than Cp₂TiCl₂/MAO at 100 °C (Table 3, entries 7, 8, 11, and 13 vs 14). Although examples of more active titanium-based catalyst systems that operate at 130 °C and above have been reported,^{2e,26} both high thermal stability and single-site behavior of Ti catalysts containing **bdmpzp** ligand(s) is of significant interest because related Group 4 metal heteroscorpionate complexes⁷ and titanocenes^{24,25} typically achieve maximum polymerization activity at low temperatures (≤ 35 °C, Table 3, entries 14–19)²⁷ and/or furnish polymers with broad molecular weight distributions at high temperatures.^{7d,8b} The putative active catalyst generated by MAO activation of L_nMX₂ compounds is a cationic L_nMR⁺ species,²⁸ hence multidentate (κ^3 -N,N,O or κ^2 -N,O) coordination of **bdmpzp** ligand(s) in the active cationic species likely contributes to both high thermal stability and single-site behavior of

(23) Ethylene uptake is noticeably faster for (**bdbpzb**)_nTi-based catalysts (such as **1/MAO**) than for (**bdmbp**)_nTi-based catalysts (such as **2/MAO**). Also, (**bdbpzb**)_nTi-based catalysts ($n = 1$ or 2) give a higher initial exotherm.

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(25) Mallin, D. T.; Rausch, M. D.; Mintz, E. A.; Rheingold, A. L. *J. Organomet. Chem.* **1990**, *381*, 35.

(26) See for example: (a) Klosin, J.; Kruper, W. J.; Nickias, P. N.; Roof, G. R.; De Waele, P.; Abbound, K. A. *Organometallics* **2001**, *20*, 2663. (b) Klosin, J.; Kruper, W. J.; Nickias, P. N.; Patton, J. T.; Wilson, D. R. WO 9806728, 1998.

(27) The marked decrease in activity described for the Cp₂TiCl₂/activator systems at temperatures greater than 50 °C is believed to result from an increase in the reduction of Ti(IV) to Ti(II). See: (a) Tait, P. J. *Polym. Mater. Encycl.* **1996**, 4169. (b) Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* **1959**, *81*, 81. (c) Chien, J. C. W. *J. Am. Chem. Soc.* **1959**, *81*, 86. (d) Ewen, J. A.; Zambelli, A.; Longo, P.; Sullivan, J. M. *Macromol. Rapid Commun.* **1998**, *19*, 71.

(28) Guram, A. S.; Jordan, R. F. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Lappert, M. F., Ed.; Pergamon/Elsevier: Oxford, 1995; Vol. 4, p 589, and references therein.

(22) Higher activities were obtained using lower precatalyst loadings due to low solubility of **1–5** in toluene. Attempts to obtain more soluble precatalysts are currently in progress.

Table 3. Summary of Ethylene Polymerization Results

no.	precat.	Al/Ti	T (°C)	t (min)	activity [kg PE/(mol Ti·h·bar)] ^d	10 ⁻³ M _w ^e	M _w /M _n ^e	ref
1	1 ^{a,b}	1000	23	30	18	1472	2.3	
2	1 ^{a,b}	1000	100	30	17	97	1.7	
3	1 ^{a,c}	1000	100	5	70			
4	2 ^{a,b}	1000	100	30	10	107	1.6	
5	2 ^{a,c}	1000	100	30	62			
6	3 ^{a,b}	1000	100	30	25			
7	4 ^{a,b}	1000	23	30	14	1368	2.4	
8	5 ^{a,b}	1000	23	30	15			
9	4 ^{a,b}	1000	100	30	27	106	1.7	
10	4 ^{a,c}	1000	100	5	62			
11	4 ^{a,c}	1000	100	30	36			
12	5 ^{a,b}	1000	100	30	19	105	1.7	
13	5 ^{a,c}	1000	100	30	124			
14	Cp ₂ TiCl ₂ ^{a,c}	1000	100	30	42			
15	Cp ₂ TiCl ₂ ^f	2155	50	120	41			27
16	Cp ₂ TiCl ₂ ^f	2155	25	120	220			27
17	[(bdmpza)TiCl ₂ OR] ^g	1000	25	30	103			7d
18	[(bdmpza)TiCl ₂ OR] ^g	2000	25	30	565			7d
18	[(bdmpza)TiCl ₂ OR] ^g	2000	35	30	690		4.5	7d
19	[(bdmpza)TiCl ₂ OR] ^g	2000	45	30	400		8.2	7d

^a 600 mL stainless steel Parr reactor; MAO solution in toluene, 10 wt % total Al. ^b Experimental conditions: 18 μmol of Ti; P(C₂H₄) = 10 bar; solvent = toluene (100 mL total). ^c Experimental conditions: 1 μmol of Ti; P(C₂H₄) = 10 bar; solvent = toluene (100 mL total). ^d Average of three runs. ^e Determined by GPC. ^f Experimental conditions: 2 μmol of Ti; P(C₂H₄) = 1.31 bar; 100 mL toluene; stainless steel Parr reactor. ^g R = (CH₂)₄Cl.

catalysts produced by MAO activation of **bdmpzp**-based titanate complexes (**2**, **3**, and **5**).²⁹

Conclusions

MAO activation of titanate complexes (**1–5**) supported by 1,3-bis(pyrazol-1-yl)propan-2-olate ligation furnished rare examples of titanium-based ethylene polymerization catalysts that exhibit single-site behavior under high-temperature solution conditions. Both the unusual thermal stability and single-site ethylene polymerization behavior displayed by catalysts generated from titanate complexes that bear one or two **bdmpzp** ligands (**2**/MAO, **3**/MAO, and **5**/MAO) are presumably due to the hard donor environment imposed at titanium upon multidentate coordination of **bdmpzp** ligand(s) in the active catalyst species. These results and the modular nature of 1,3-bis(pyrazol-1-yl)propan-2-olate ligands, which should facilitate easy modification of ligand properties, make further investigation of ligation properties of 1,3-bis(pyrazol-1-yl)propan-2-olate and related ligands in titanium chemistry of great interest. Current studies are aimed at determining the nature of the active catalysts generated in this study and tailoring of catalyst properties through systematic modification of the ligand framework in hopes developing more active and thermally stable catalysts. We are also exploring the potential of these titanate and related complexes as precatalysts for styrene polymerization and for copolymerization of ethylene with α-olefins.

Experimental Section

General Details. 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.³⁰ All solvents were stored in the glovebox over 4 Å 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 Co. Ethylene (99.9% purity) was purchased from Scott-Gross Co. or Matheson Tri-Gas, Inc. 1,3-Bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (**bdmpzpH**)¹⁰ was prepared according to the published procedure. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at room temperature unless otherwise stated. ¹H and ¹³C 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. Laser desorption/ionization mass spectrometry (no matrix) experiments were performed at University of Kentucky Mass Spectrometry Center on a Bruker Daltonics Autoflex spectrometer. EI-MS experiments were performed on a Thermo Finnigan (San Jose, CA) Polaris Q (quadrupole ion trap) or JEOL JMS-700T MStation spectrometer. GPC and DSC were performed at Cornell Center for Materials Research, Ithaca, NY or at Symyx Technologies, Inc., Santa Clara, CA.³¹ All molecular weights were measured relative to linear polystyrene standards. Elemental analyses were performed by Robertson Microlit Laboratories Inc., Madison, NJ.

1,3-Bis(3,5-di-*tert*-butylpyrazol-1-yl)propan-2-ol (bdbpzh). 3,5-Di-*tert*-butyl-1H-pyrazole (20.0 g, 111 mmol) was added slowly to a suspension of sodium hydride (4.39 g, 183 mmol) in diethyl ether (200 mL) at 0 °C. The reaction mixture was refluxed with stirring for 1 h then cooled to 0 °C. 1,3-Dichloropropan-2-ol (5.30 mL, 55.0 mmol) was added dropwise, and the mixture was refluxed for 3 days. The reaction mixture was cooled to 0 °C, quenched by the addition of water (5 mL), and extracted with diethyl ether (5 × 20 mL). The ether extracts were combined and washed with water

(29) Enhanced electrophilicity and steric unsaturation of cationic Ti(IV) should facilitate multidentate coordination of **bdmpzp** (or **bdbpzh**) ligand(s).

(30) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, 1988.

(31) Boussie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M.; Lund, C.; Murphy, V.; Shoemaker, J. A. W.; Tracht, U.; Turner, H.; Zhang, J.; Uno, T.; Rosen, R. K.; Stevens, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 4306.

followed by brine. The ether solution was dried over anhydrous MgSO_4 , filtered, and then concentrated to dryness. 1,3-Bis(3,5-*tert*-butylpyrazol-1-yl)propan-2-ol was isolated as a white powder following flash chromatography on silica using 3% CH_2Cl_2 in methanol as eluent. Yield: 12.6 g, 55%. ^1H (CDCl_3): δ 1.26 (s, 36H, Bu^t), 4.17–4.28 (m, 3H, CH_2 , CH), 4.46–4.58 (m, 2H, CH_2), 5.80 (s, 2H, pyz-4), 6.25 (br s, 1H, OH). ^{13}C (CDCl_3): δ 30.1 (CMe_3), 30.5 (CMe_3), 31.2 (CMe_3), 31.9 (CMe_3), 53.3 ($\text{OCH}(\text{CH}_2\text{-pyz}_2)$), 71.7 ($\text{OCH}(\text{CH}_2\text{-pyz}_2)$), 99.5 (pyz-4-CH), 152.0, 160.1. MS (EI, 70 eV) m/z : 398 [$\text{M} - \text{H}_2\text{O}$]⁺.

$[\text{Na}(\kappa^1\text{-O-bdbppz})(\text{THF})\text{TiCl}_4]$ (1). To a suspension of sodium hydride (58.0 mg, 2.40 mmol) in ether (50 mL) was added 1,3-bis(3,5-*tert*-butylpyrazol-1-yl)propan-2-ol (1.00 g, 2.40 mmol). The reaction was refluxed for 2 h then cooled to room temperature, and the suspension was transferred into an addition funnel. The suspension was added dropwise to a cold (0 °C) solution of TiCl_4 (0.45 g, 2.40 mmol) in ether (50 mL). After the addition was complete, the reaction mixture was stirred for 1 h at 0 °C then allowed to warm gradually to ambient temperature and let stir overnight. The suspension was concentrated to dryness and the residue was exhaustively extracted with THF (~100 mL). The solvent was removed under reduced pressure, and the pale yellow solid was dried under vacuum. Yield: 1.08 g, 71.6%. ^1H (CDCl_3): δ 1.42 (s, 18H, Bu^t), 1.44 (s, 18H, Bu^t), 1.92 (m, 4H, THF), 4.20 (br m, 4H, THF), 4.53–5.41 (br m, 5H, CH_2 , CH), 6.10 (s, 2H, pyz-4). ^{13}C (CDCl_3): δ 25.5 (THF), 30.1 (CMe_3), 30.3 (CMe_3), 32.4 (CMe_3), 32.5 (CMe_3), 52.8 ($\text{OCH}(\text{CH}_2\text{-pyz}_2)$), 71.5 (THF), 102.6 (pyz-4-CH), 157.0, 159.1. LDI-TOF MS (negative ion mode, m/z): 518 [$\text{C}_3\text{H}_5\text{Cl}_6\text{Na}_2\text{OTi}_2$]⁻, 483 [$\text{C}_3\text{H}_5\text{Cl}_8\text{Na}_2\text{OTi}_2$]⁻, 388 [$\text{C}_3\text{H}_5\text{Cl}_6\text{NaOTi}_2$]⁻, 353 [$\text{C}_3\text{H}_5\text{Cl}_5\text{NaOTi}_2$]⁻, 295 [$\text{C}_3\text{H}_5\text{Cl}_4\text{OTi}_2$]⁻, 258 [$\text{C}_3\text{H}_5\text{Cl}_3\text{OTi}_2$]⁻, 223 [$\text{C}_3\text{H}_5\text{Cl}_2\text{OTi}_2$]⁻. Anal. Calcd for $\text{C}_{20}\text{H}_{51}\text{-Cl}_4\text{N}_4\text{NaO}_2\text{Ti}$: C, 49.73; H, 7.34; N, 8.00. Found: C, 49.17; H, 7.40; N, 7.49.

$[\text{Na}(\kappa^1\text{-O-bdmpzp})(\text{THF})\text{TiCl}_4]$ (2). To a diethyl ether (100 mL) suspension of sodium hydride (0.090 g, 3.75 mmol) was added 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (0.93 g, 3.75 mmol). The reaction mixture was heated at reflux for 2 h then cooled to room temperature, and the suspension was transferred into an addition funnel. The suspension was added dropwise to a cold (0 °C) solution of TiCl_4 (0.73 g, 3.75 mmol) in diethyl ether (50 mL). After the addition was complete, the reaction was stirred for 1 h at 0 °C then allowed to warm gradually to ambient temperature and let stir overnight. The suspension was concentrated to dryness and the residue was exhaustively extracted with THF (~100 mL). The solvent was removed under reduced pressure, and the pale yellow solid was dried under vacuum. Yield: 1.38 g, 80.0%. ^1H ($\text{CD}_3\text{-CN}$): δ 1.79 (m, 4H, THF), 2.40 (br s, 6H, CH_3), 2.42 (br s, 6H, CH_3), 3.66 (m, 4H, THF), 4.35–4.91 (m, 5H, CH_2 , CH), 6.23 (s, 2H, pyz-4). ^{13}C ($\text{CD}_3\text{-CN}$): δ 11.8 (Me), 26.3 (THF), 51.5 ($\text{OCH}(\text{CH}_2\text{-pyz}_2)$), 68.5 (THF), 108.3 (pyz-4-CH), 147.2. IR ($\text{CH}_3\text{-CN}$, cm^{-1}): $\nu(\text{Ti}-\text{O})$ 688. LDI-TOF MS (negative ion mode, m/z): 540 [$\text{Na}_2\text{Ti}_2\text{Cl}_8\{\text{OCH}(\text{CH}_2)_2\}_2$]⁻, 460 [$\text{NaTi}_2\text{Cl}_8\{\text{OCH}(\text{CH}_2)_2\}$]⁻, 404 [$\text{C}_3\text{H}_5\text{Cl}_6\text{NaO}_2\text{Ti}_2$]⁻, 324 [Cl_6OTi_2]⁻, 305 [$\text{Cl}_5\text{O}_2\text{Ti}_2$]⁻, 270 [$\text{C}_3\text{H}_5\text{Cl}_4\text{NaOTi}$]⁻, 190 [TiCl_4]⁻, 169 [Cl_3OTi]⁻. Anal. Calcd for $\text{C}_{17}\text{H}_{27}\text{Cl}_4\text{N}_4\text{NaO}_2\text{-Ti}$: C, 38.37; H, 5.11; N, 10.53. Found: C, 39.03; H, 5.39; N, 9.89.

Synthesis of Titanate(1-) Zwitterion 3. A diethyl ether solution (3 mL) of 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (0.226 g, 0.910 mmol) was added dropwise to a cold (0 °C) solution of TiCl_4 (0.173 g, 0.910 mmol) in diethyl ether (3 mL). The reaction mixture was allowed to warm to room temperature and let stir for 18 h. The yellow suspension was concentrated to dryness under reduced pressure and the residue was dissolved in CH_2Cl_2 (5 mL). After

filtering the yellow solution through celite, the solvent was removed in vacuo and the yellow solid was dried under vacuum at ambient temperature for 24 h. Yield: 0.299 g, 75%. ^1H ($\text{CD}_3\text{-CN}$): δ 2.41 (br s, 6H, CH_3), 2.46 (br s, 6H, CH_3), 4.40–4.85 (br m, 5H, CH_2 , OCH), 6.28 (br s, 2H, pyz-4). ^{13}C ($\text{CD}_3\text{-CN}$): δ 10.7 (Me), 50.8 ($\text{OCH}(\text{CH}_2\text{-pyz}_2)$), 107.5 (pyz-4-CH), 145.7, 147.0. IR (KBr, cm^{-1}): 3128, 2966, 2859, 1631, 1589, 1433, 1291, 1128, 1095. Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{Cl}_4\text{N}_4\text{OTi}$: C, 35.65; H, 4.60; N, 12.79; Found C, 35.72; H, 4.65; N, 12.56.

$[\text{Na}(\text{THF})_2](\kappa^1\text{-O-bdbppz})_2\text{TiCl}_4$ (4). To a suspension of sodium hydride (0.058 g, 2.40 mmol) in ether (50 mL) was added 1,3-bis(3,5-*tert*-butylpyrazol-1-yl)propan-2-ol (1.00 g, 2.40 mmol). The reaction was refluxed for 2 h then cooled to room temperature, and the suspension was transferred into an addition funnel. The suspension was added dropwise to a cold (0 °C) solution of TiCl_4 (0.225 g, 1.19 mmol) in ether (50 mL). After the addition was complete, the reaction mixture was stirred for 1 h at 0 °C then allowed to warm gradually to ambient temperature and let stir overnight. The suspension was concentrated to dryness and the residue was exhaustively extracted with THF (~100 mL). The solvent was removed under reduced pressure and the pale yellow solid was dried under vacuum. Yield: 0.955 g, 77.3%. ^1H (CDCl_3): δ : 1.34 (s, 36H, Bu^t), 1.37 (36H, Bu^t), 1.83 (m, 4H, THF), 3.81 (br m, 4H, THF), 4.32–5.13 (br m, 10H, CH_2 , CH), 5.96 (s, 4H, pyz-4). ^{13}C (CDCl_3): δ : 25.8 (THF), 30.0 (CMe_3), 30.1 (CMe_3), 31.7 (CMe_3), 32.1 (CMe_3), 53.0 ($\text{OCH}(\text{CH}_2\text{-pyz}_2)$), 69.9 (THF), 101.0 (pyz-4-CH), 155.0, 159.4. EI-MS (m/z): 913 [$(\text{bdbppz})_2\text{TiCl}_4$]⁺; LDI-TOF MS (negative ion mode, m/z): [TiCl_4]⁻ ($m/z = 190$), [$\text{NaTiCl}_4\{\text{OCH}(\text{CH}_2)_2\}$]⁻ ($m/z = 270$), [$\text{NaTi}_2\text{Cl}_8\{\text{OCH}(\text{CH}_2)_2\}_2$]⁻ ($m/z = 460$), and [$\text{Na}_2\text{Ti}_2\text{Cl}_8\{\text{OCH}(\text{CH}_2)_2\}_2$]⁻ ($m/z = 540$). Anal. Calcd for $\text{C}_{58}\text{H}_{102}\text{Cl}_4\text{N}_8\text{Na}_2\text{O}_4\text{Ti}$: C, 57.52; H, 8.49; N, 9.25. Found: C, 57.65; H, 8.84; N, 9.44.

$[\text{Na}(\text{THF})_2](\kappa^1\text{-bdmpzp})_2\text{TiCl}_4$ (5). To a diethyl ether (100 mL) suspension of sodium hydride (0.097 g, 4.04 mmol) was added 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-ol (1.00 g, 4.03 mmol). The reaction mixture was heated at reflux for 2 h then cooled to room temperature, and the suspension was transferred into an addition funnel. The suspension was added dropwise to a cold (0 °C) solution of TiCl_4 (0.38 g, 2.01 mmol) in diethyl ether (50 mL). After the addition was complete, the reaction was stirred for 1 h at 0 °C then allowed to warm gradually to ambient temperature and let stir overnight. The suspension was concentrated to dryness and the residue was exhaustively extracted with THF (~100 mL). The solvent was removed under reduced pressure and the pale yellow solid was dried under vacuum. Yield: 0.75 g, 50.1%. ^1H (CDCl_3 , 50 °C): δ : 1.82 (m, 4H, THF), 2.28 (br s, 24H, CH_3), 3.70 (m, 4H, THF), 4.20–5.43 (br overlapping m, 10H, CH_2 , CH), 5.93 (br s, 4H, pyz-4). ^1H (CDCl_3 , 50 °C): δ : 1.80 (m, 4H, THF), 2.28 (br s, 12H, CH_3), 2.42 (br s, 12H, CH_3), 3.73 (m, 4H, THF), 4.40–5.30 (br overlapping m, 10H, CH_2 , CH), 5.95 (s, 4H, pyz-4). ^{13}C ($\text{CH}_3\text{-CN}$): 11.8 (Me), 26.2 (THF), 51.5 ($\text{OCH}(\text{CH}_2\text{-pyz}_2)$), 68.4 (THF), 108.3 (pyz-4-CH), 147.1 (br s). Anal. Calcd for $\text{C}_{34}\text{H}_{54}\text{Cl}_4\text{N}_8\text{Na}_2\text{O}_4\text{Ti}$: C, 46.70; H, 6.22; N, 12.81. Found: C, 46.49; H, 5.90; N, 14.33. EI-MS (m/z): 577 [$(\text{bdmpzp})_2\text{TiCl}_4$]⁺; LDI-TOF MS (negative ion mode, m/z): [$\text{Ti}_2\text{Cl}_4\{\text{OCH}(\text{CH}_2)_2\}_2$]⁻ ($m/z = 295$), [$\text{NaTi}_2\text{Cl}_7\{\text{OCH}(\text{CH}_2)_2\}$]⁻ ($m/z = 423$), and [$\text{Na}_2\text{Ti}_2\text{Cl}_8\{\text{OCH}(\text{CH}_2)_2\}_2$]⁻ ($m/z = 540$).

Typical Procedure for Ethylene Polymerization. Toluene (82 mL) was charged into a 600 mL Parr reactor equipped with a mechanical stirrer. Next, a 10% by weight toluene solution of MAO (13.26 mL, 20 mmol) was added. The precatalyst (typically, 5 mL of 3.6 mM solution, 18 μmol) was charged into an isolated catalyst addition chamber in the reactor. The reactor was sealed under N_2

atmosphere and then charged with ethylene to 7 bar pressure and maintained at the desired temperature for 20 min. The catalyst was charged into the reaction mixture using a stream of ethylene at 10 bar pressure, and the pressure inside the chamber was maintained at 10 bar pressure throughout the course of the reaction (usually 30 min). After the required time, the reactor was vented, and the reaction quenched with ethanol (30 mL) and then a 1 M HCl solution (30 mL). The resulting suspension was vigorously stirred until both layers were colorless and clearly separated (~10 min). Polyethylene was filtered off, washed with 1 M HCl and ethanol, and then dried in a vacuum oven at 60 °C for 24 h.

Crystallographic Study. The crystal data for **bdbpzpH** and **3** are collected in Table 1, and selected metrical parameters are presented in Figure 2 and Table 2, respectively. Further details of the crystallographic study are given in the Supporting Information.

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Supporting Information Available: Experimental and characterization details for **1–5** and GPC charts for polymers obtained. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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