ORGANOMETALLICS

Zirconium and Titanium Propylene Polymerization Precatalysts Supported by a Fluxional C₂-Symmetric Bis(anilide)pyridine Ligand

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Supporting Information

ABSTRACT: Titanium and zirconium complexes supported by a bis(anilide)pyridine ligand (NNN = pyridine-2,6-bis(*N*mesitylanilide)) have been synthesized and crystallographically characterized. C_2 -symmetric bis(dimethylamide) complexes were generated from aminolysis of $M(NMe_2)_4$ with the neutral, diprotonated NNN ligand or by salt metathesis of the dipotassium salt of NNN with $M(NMe_2)_2Cl_2$. In contrast to the case for previously reported pyridine bis(phenoxide) complexes, the ligand geometry of these complexes appears to be dictated by chelate ring strain rather than metal-ligand π bonding. The crystal structures of the five-coordinate dihalide



complexes (NNN)MCl₂ (M = Ti, Zr) display a C_1 -symmetric geometry with a stabilizing ipso interaction between the metal and the anilido ligand. Coordination of THF to (NNN)ZrCl₂ generates a six-coordinate C_2 -symmetric complex. Facile antipode interconversion of the C_2 complexes, possibly via flat $C_{2\nu}$ intermediates, has been investigated by variable-temperature ¹H NMR spectroscopy for (NNN)MX₂(THF)_n (M = Ti, Zr; X = NMe₂, Cl) and (NNN)Zr(CH₂Ph)₂. These complexes were tested as propylene polymerization precatalysts, with most complexes giving low to moderate activities (10^2-10^4 g/(mol h)) for the formation of stereoirregular polypropylene.

INTRODUCTION

The chemistry of the early transition metals has, to a large extent, been advanced by the use of bent-metallocene frameworks. However, there has been increased interest in using well-defined mono- and polydentate "non-metallocene" or "post-metallocene" ligand sets to support a diverse range of organometallic complexes and transformations, catalysis, and small-molecule activation studies.¹⁻³³ Recently, our group^{34,35} and others^{36–38} have been

Recently, our group^{34,35} and others^{36–38} have been investigating the use of arene- and heterocycle-linked bis-(phenolate)donor ligand sets (heterocycle = pyridine, furan, thiophene) to support titanium, zirconium, and vanadium polymerization catalysts³⁴ and as ancillary ligands for other early transition metals³⁵ to explore other organometallic transformations. These nonmetallocene ligands are connected through rigid sp²–sp² aryl–aryl linkages instead of more flexible sp³–sp³ linkages, imparting increased rigidity of the backbone, which could result in more thermally robust catalysts that are less prone to undergo ligand C–H activation.

We have found that transition-metal complexes based on this class of ligands are capable of adopting C_1 , C_s , $C_{2\nu}$, or C_2 symmetry.^{34,35} While these symmetries are observed in the solid state, propylene polymerization using C_2 -symmetric bis(phenolate) early-transition-metal precatalysts nonetheless yields stereoirregular, essentially atactic (or mixtures of atactic and isotactic) polypropylene.³⁴ An investigation into the electronics of six-coordinate tantalum complexes supported

by an ONO (ONO = bis(phenolate)pyridine) ligand has revealed that the preference for ligand geometry (either C_s or C_2) is controlled by a delicate competition between phenolate oxygen to metal π bonding (favoring C_s) and six-memberedring strain (favoring C_2) within the (ONO)M chelate fragment.35c The barrier for interconversion between geometries was found to be low (<5 kcal/mol) for (ONO)Ir complexes.³⁹ We have therefore begun investigating related ligand frameworks, where either electronic factors or ring strain might completely dominate and thus dictate a more rigid geometry. Catalysts with better defined and predictable geometric preferences should allow for enantiomorphic sitecontrolled propylene polymerization. Herein we report the synthesis and structural characterization of group 4 complexes supported by a bis(anilide)pyridine ligand and preliminary results of their use as propylene polymerization precatalysts.

RESULTS AND DISCUSSION

Preparation and Characterization of (NNN)MX₂ Complexes. The bis(aniline)pyridine ligand 1-H₂ was synthesized by following a previously reported⁴⁰ two-step reaction sequence. Both titanium and zirconium bis(dimethylamide) complexes of 1 can be generated through salt metathesis of the potassium salt 1-K₂, with MCl₂(NMe₂)₂(THF)_n (M = Ti, n =

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0; M = Zr, n = 2) (eq 1). X-ray-quality orange-red crystals of (NNN)Ti(NMe₂)₂ (2) and (NNN)Zr(NMe₂)₂ (3) were



obtained by layering pentane over concentrated THF solutions of 2 or 3 and cooling to -30 °C overnight. The bis(anilide)pyridine ligand in **2** is bound in a highly twisted, C_2 -symmetric fashion, with the two anilide arms occupying the axial positions of a distorted trigonal bipyramid (Figure 1). The dihedral angle between the two anilide aryl rings connected to the pyridine is 81.8° , which is substantially larger (by $30-40^{\circ}$) than those observed in C2-symmetric complexes of the related ONO ligand system (ONO = pyridine-2,6-bis(4,6-di-tert-butylphenoxide)).^{35c} Although the anilide nitrogens are essentially planar, the titanium-anilide distances (2.078(2) and 2.080(2) Å) are substantially longer than a typical titanium amide double bond. By comparison, the Ti-N distances for the doubly bonded dimethylamido ligands in 2 are significantly shorter (1.881(2) and 1.892(2) Å). As a result, there is likely no Ti–N double-bond character in the titanium-anilide bond and the nitrogen planarity is due to the steric crowding of the bulky diarylamine and resonance of the nitrogen lone pair into the

aryl rings. DFT calculations performed on **2** and **3** agree with this assessment—there was no obvious $M-N \pi$ bonding in any of the molecular orbitals, and in both the Ti and Zr cases we could identify orbitals containing the nitrogen lone pair delocalized across the aryl rings rather than into the metal center (Figure 2).



Figure 2. DFT calculated HOMO of $(NNN)Ti(NMe_2)_2$ (**2**; top-down view) showing nitrogen lone pair delocalization into the aryl backbone.

Interestingly, the complex $(ONO)Ti(NMe_2)_{2}$, the bis-(phenoxide) analogue of **2**, exhibits a C_s symmetry in its crystal structure.⁴¹ We attribute this difference to the steric bulk of the *N*-mesityl groups, which likely forces **2** to adopt the more sterically accommodating C_2 symmetry. The overall structural features of the Zr analogue **3** are very similar to those described above for **2**.



Figure 1. Drawings of **2** (left) and **3** (right) with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å): complex **2**, Ti1–N1 = 2.0781(23), Ti1–N2 = 2.1170(19), Ti1–N3 = 2.0803(24), Ti1–N4 = 1.8807(19), Ti1–N5 = 1.8922(20); complex **3**, Zr1–N1 = 2.2096(10), Zr1–N2 = 2.3140(10), Zr1–N3 = 2.1799(10), Zr1–N4 = 2.0264(10), Zr1–N5 = 2.0281(10). H atoms are omitted for clarity.

The Zr complex $(NNN)Zr(NMe_2)_2$ (3) could alternately be generated via aminolysis between the protonated ligand $1-H_2$ and $Zr(NMe_2)_4$; however, $(NNN)Ti(NMe_2)_2$ could not be synthesized via this pathway, even under significant heating and extended reaction times (eq 2). By switching to a less bulky



ligand (^{tBu}NNN)H₂, where the mesityl groups are replaced by (3,5-^tBu₂-C₆H₃), the aminolysis is successful for both Ti and Zr and proceeds at much lower (55 °C) temperatures.

Reaction of 2 or 3 with 2.3 equiv of Me_3SiCl in toluene quantitatively generates the dichloride complexes (NNN)TiCl₂ (4) and (NNN)ZrCl₂ (5) (eq 3). Both 4 and 5 are highly



insoluble and crystallize out of the reaction mixture. 4 and 5 have been characterized by X-ray crystallography (Figure 3). As is apparent, the NNN ligand for 4 is bound unsymmetrically. In addition to the typical tridentate LX₂ binding of the NNN ligand, there is a stabilizing ipso interaction between one of the anilide arms and the metal center. The Ti1-C17 bond length is 2.584(1) Å, more than 0.4 Å shorter than the distance to the ipso carbon on the other anilide arm (Ti1-C1 = 3.009 Å). This ipso interaction is likely necessary to stabilize the highly electrophilic 14-electron Ti center. The Zr analogue 5 is structurally very similar to 4 and also contains an unsymmetrically bound NNN ligand with an ipso interaction. Complexes 2 and 3, on the other hand, are significantly more electron-rich as a consequence of the π -donating dimethylamido ligands and do not require the ipso interaction to stabilize the metal center. Since both 4 and 5 appear symmetric by NMR spectroscopy, it is likely that in solution the ipso interaction is rapidly interchanging between the two anilide arms.

If 3 is treated with 2.3 equiv of Me₃SiCl in THF rather than toluene, the THF adduct (NNN)ZrCl₂(THF) (6) crystallizes (eq 3). Unlike the case for 4 and 5, the solid-state structure of 6 is C_2 symmetric and has no stabilizing ipso interaction with the NNN ligand aryl rings (Figure 4), likely a result of the increased electron count around the THF-coordinated Zr. The C_2 -symmetric structure of 6 is significant because, in the related bis(phenoxide)pyridine complexes, the addition of a sixth ligand to the coordination sphere shifts the solid-state geometry of the complexes from C_2 to C_s . In the bis(anilide)pyridine case, however, a change in coordination number does not affect the solid-state geometry; thus, **6** further confirms our hypothesis that the new bis(anilide)pyridine ligand set imparts greater geometric control. Binding of THF in **6** is reversible, and successive washings of **6** with toluene remove the THF to generate **5**. The analogous Ti complex, (NNN)TiCl₂(THF), is not generated upon reaction of **2** with excess Me₃SiCl in THF, likely a result of a smaller titanium center that does not readily accommodate a sixth ligand in its coordination sphere.

Reaction of $1-H_2$ with $ZrBn_4$ or $TiBn_4$ led only to decomposition products. However, protonolysis of $ZrBn_4$ with the less bulky (^{tBu}NNN)H₂ yielded (^{tBu}NNN)ZrBn₂ (7) after heating at 90 °C for 24 h (eq 4). 7 is light sensitive and



decomposes over the course of days when exposed to ambient light. 7 was crystallized from a saturated pentane solution and is roughly C_s symmetric in the solid state (Figure 5). However, in solution the structure appears fluxional; the ¹H NMR for the benzylic protons of 7 appear as a singlet at room temperature (vide infra). The related (ONO)ZrBn₂ complex is, in contrast, C_2 symmetric in solution and the solid state, and this unexpected discrepancy shows that the energy differences between the possible conformations of the (t^{Bu}NNN) framework are likely very small in comparison to the more bulky mesitylene-substituted (NNN) framework.

NMR Studies of the Mechanism of Fluxionality. In complexes 2–6, the *o*-methyl groups of the *N*-mesityl substituents appear as a broad signal in the ¹H NMR at room temperature. In a C_2 -symmetric molecule, the *o*-methyl groups on each mesityl ring are pairwise equivalent (Scheme 1) with two pointing toward the X substituents and two pointing more toward the pyridine. The broadening could be a result of two possible processes: (1) inversion at the metal center effecting interconversion between the two C_2 antipodes thereby exchanging the sites of the *o*-methyls and (2) rotation about the N–mesityl bond (without inversion) to interconvert the two *o*-methyls.

Variable-temperature ¹H NMR studies were carried out on complexes 2–5 and 7 to determine the nature of the *o*-methyl fluxionality and barriers for methyl interconversion. Figure 6 shows the VT ¹H NMR spectra of 5 in toluene- d_8 from 25 to -90 °C; similar VT NMR spectra are observed for 2–4. At room temperature, the mesityl *o*-methyls appear as a singlet at 1.80 ppm. Upon cooling, this singlet broadens, disappears at -60 °C, and at -90 °C splits into two equal-intensity singlets at 2.59 and 1.05 ppm. From the coalescence rate constant (k_c) and coalescence temperature (T_c), the free energy of activation, ΔG^{\ddagger} , was determined to be 9.2 kcal/mol at the coalescence temperature for 5 (213 K). All four complexes (2–5) exhibit activation free energies between 9 and 11 kcal/mol (Table 1).⁴² In complex 7, which is ligated by ^{tBu}NNN, the ¹H NMR

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Figure 3. Drawings of 4 (left) and 5 (right) with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å): complex 4, Ti1–N1 = 1.891(1), Ti1–N2 = 2.129(1), Ti1–N3 = 1.9263(9), Ti1–Cl1 = 2.3717(1), Ti1–Cl2 = 2.3323(1), Ti1–Cl7 = 2.584(1); complex 5, Zr1–N1 = 2.033(1), Zr1–N2 = 2.262(1), Zr1–N3 = 2.066(1), Zr1–Cl1 = 2.4692(1), Zr1–Cl2 = 2.4638(1), Zr1–Cl7 = 2.654(1). Solvents of crystallization and H atoms are omitted for clarity.



Figure 4. Drawings of **6** with thermal ellipsoids at the 50% probability level showing front (left) and top-down views (right). Selected bond lengths (Å): Zr-N1 = 2.133(1), Zr-N2 = 2.3103(8), Zr-N3 = 2.152(1), Zr-Cl1 = 2.4498(3), Zr-Cl2 = 2.4496(3), Zr-O1 = 2.2432(7). H atoms are omitted for clarity.

spectrum displays a singlet at room temperature for the benzylic hydrogens (Figure 7). When a toluene sample of 7 is cooled to -95 °C, the peak corresponding to the benzylic protons shifts upfield, broadens, and disappears into the baseline.

As shown in Scheme 1, both possible mechanisms for *o*-methyl exchange of the anilide mesityl groups for 2-5 involve some degree of rotation about the N– C_{ipso} bond. Thus, a clear distinction between the two processes is difficult. However, some evidence may support antipode interconversion (process 1) as the operative fluxional process. For example, the

measured barriers are substantially less than those reported by Mislow and co-workers⁴² for trimesitylamine and related amines (18–22 kcal/mol) for N–C_{ipso} rotation. Additionally, Carpentier has observed barriers similar to those measured for the (NNN)MX₂ complexes for the interconversion of *rac* and *meso* stereoisomers of some related group 4 bis(naphthoxy)pyridine complexes.^{38b} Moreover, for the (NNN)MX₂ complexes partial rotation coupled to inversion at metal might well be more facile, if substantial steric clashes of the methyls with the X substituents contribute to the barrier for N–C_{ipso} rotation. Space-filling and DFT models of the N–C_{ipso}



Figure 5. Drawings of 7 with thermal ellipsoids at the 50% probability level. The C53 benzyl group has been darkened for contrast. Selected bond lengths (Å): Zr-N1 = 2.079(1), Zr-N2 = 2.385(1), Zr-N3 = 2.031(1), Zr-C46 = 2.261(2), Zr-C53 = 2.322(2). Solvent of crystallization and H atoms are omitted for clarity.

Scheme 1



2. N-Cipso bond rotation without inversion



bond rotation in **2** reveal that the mesitylene ring cannot rotate through a full 180° (i.e., through a N–M–N plane of the NNN ligand framework), because the *o*-methyl group movement is blocked by an NMe₂ group. Thus, we favor C_2 antipode interconversion (process 1) as the mechanism for *o*-methyl interconversion.

In C_s -symmetric 7, the two benzyl groups should be chemically inequivalent on the basis of the solid-state structure. However, the benzyl groups are found to be averaged in the ¹H NMR spectra at room temperature. Furthermore, the chemical shift of the averaged benzylic hydrogen peak changes with temperature, suggesting that another stereoisomer, possibly the C_2 isomer, may be in a temperature-dependent equilibrium



Figure 6. Variable-temperature NMR spectra of (NNN)ZrCl₂ (5) in toluene- d_8 . The decoalesced *o*-methyl peaks appear at 2.60 and 1.05 ppm at -90 °C.

Table 1. Experimentally Determined Barriers of o-MethylInterconversion in Complexes 2–5

complex	$T_{\rm c}$ (K)	$\Delta G^{\ddagger}_{T_c}$ (kcal/mol)	k_{T_c} (s ⁻¹)
$(NNN)Ti(NMe_2)_2$	243	10.8	900
$(NNN)Zr(NMe_2)_2$	233	10.4	900
(NNN)TiCl ₂	253	10.9	1900
(NNN)ZrCl ₂	213	9.2	1700

with C_s 7. Much like the case for 2–5, there are a number of potential mechanisms that would lead to an averaging of the benzyl groups in 7. For example, there could be inversion at the metal center of (possibly through a $C_{2\nu}$ intermediate) that reverses the sense of folding of the C_s isomers and hence exchanges the inequivalent benzyl groups. Alternatively, Berry pseudorotations of five-coordinate 7 could exchange the positions of the benzyl groups. However, unlike the case for 2-5, the benzylic averaging could *not* be a result of solely N-Cipso bond rotation as depicted in Scheme 1 and must involve some sort of geometric reorganization of the NNN framework. Since the rates of interconversion of 2-5 and 7 are all similarly fast at room temperature, the observation of NNN geometry distortion in 7 could provide further support for C_2 antipode interconversion (process 1) as the fluxional process operative for the $(NNN)MX_2$ complexes.

Propylene Polymerization. Complexes 2-6 were tested as propylene polymerization precatalysts. Test polymerizations were run in 35 mL of propylene at 0 °C with 500–2000 equiv of MAO as an activator (Table 2). Under these conditions, most of the precatalysts yielded poor to moderate $(10^2-10^4 \text{ g/} (\text{mol h}))$ activities for polymerization.

Surprisingly, the most active catalyst tested was the bis(amide)pyridine titanium complex **2**, which yielded activities on the order of 10^4 g/(mol h). This result is in contrast to the bis(phenolate)pyridine-based catalyst systems, for which the Zr precatalysts were typically 3 orders of magnitude more active than their Ti analogues.³⁴ As **2** was the most active precatalyst, the polymers generated from it were examined to determine tacticity, molecular weight distribution, and activator effects. Activities for propylene polymerization using **2** are maintained over the course of at least 3 h and appear to increase slightly with increasing amounts of MAO. Increasing the catalyst loading does not lead to increased activity, indicating that there is not an initial sacrifice of catalyst when these highly sensitive precatalysts are introduced to the reaction mixture.

Polymers generated by 2 activated with 500, 1000, or 2000 equiv of MAO were examined by ¹³C NMR. The polymers are stereoirregular and essentially atactic with slight enrichment of the *mmmm* pentad. There are no isobutyl or olefinic peaks visible by NMR, and changing the concentration of MAO does not appreciably change the spectrum. The lack of visible end groups in the ¹³C NMR spectrum is due to the extremely high molecular weights of the polymers—GPC analysis shows molecular weights of 10⁶, albeit with very broad PDIs. Such high PDIs are atypical of single-site catalysis, and as such precatalyst 2 may generate a multimetallic species or decompose into a mixture of different active species upon activation with MAO. We were optimistic that by employing precatalysts which could fluctuate between C_2 -symmetric



Table 2. Propylene Polymerization Results Obtained with Precatalysts $2-6^{a}$

entry	precat.	cat. loading (mmol)	MAO (equiv)	time (h)	mass of polymer (mg)	activity (10^4 g/(mol h))	$M_{\rm w}~(10^6)$	$M_{\rm n}~(10^6)$	PDI
1	2	0.007	1000	0.5	34.9	0.997			
2	2	0.007	1000	3	242.2	1.15			
3	2	0.007	2000	3	239.9	1.14			
4	2	0.05	500	3	474	0.316	1.037	0.03322	31.2
5	2	0.05	1000	2.5	1160	0.928	0.821	0.1674	4.9
6	2	0.05	2000	2	1780	1.78	1.151	0.2062	5.6
7	3	0.007	1000	1	n.d.	n.d.			
8	4	0.007	1000	1	6	0.0857			
9	5	0.007	1000	1	17.7	0.253			
10	5	0.007	2000	1	28.9	0.413			
11	6	0.007	1000	1	1.7	0.024			
^a Conditions: 0 °C, 30–40 mL of propylene, 2.7 mL of toluene distilled from "Cp ₂ TiH".									

enantiomers we could generate stereoblock isotactic polypropylene,⁴³ but it appears that the active species may be significantly changed from the precatalyst.

While the ¹³C NMR of polypropylene generated by 2 appears stereoirregular, the polymers are solids that exhibit thermoplastic elastomeric properties, and the slight *mmmm* enrichment does not appear to result in any measurable crystallinity. The elastomeric nature of these polymers could be due to entanglement from their high molecular weights, or it could be a result of a significant amount of regioerrors that are evident in the ¹³C NMR between 30 and 46 ppm (2,1- and 3,1- enchainments) that might give rise to methylene runs long enough to give some crystallites in the polymeryl chain. Further investigation into these interesting macroscopic polymer properties and their relationship to the polymer microstructure are ongoing using related ligand sets.

CONCLUSIONS

A series of group 4 complexes based on a bis(anilide)pyridine ligand set have been synthesized. These complexes are fluxional in solution, likely as a consequence of inversion at the metal center, thus interconverting the C_2 -symmetric antipodes, with barriers of approximately 10 kcal/mol. Unlike the related bis(phenolate) complexes these complexes do not exhibit C_s symmetry upon coordination of a sixth ligand, which indicates that the bis(anilide)pyridine ligand imparts a greater geometric preference for the C2-symmetric isomer as compared to the bis(phenolate)pyridine analogues. These complexes were tested as propylene polymerization precatalysts and yielded poor to moderate $(10^2-10^4 \text{ g/(mol h)})$ polymerization activities. Disappointingly, the most active precatalyst (NNN)Ti(NMe₂)₂ yielded only slightly isotactically enriched high-molecularweight polypropylene with a very broad polydispersity index. Despite the limited success in using these complexes for propylene polymerization, understanding the solution-state fluxional processes that these complexes undergo will allow

for the development of new catalysts for stereoselective transformations with well-understood geometric preferences.

EXPERIMENTAL SECTION

General Considerations and Instrumentation. All air- and moisture-sensitive compounds were manipulated using standard high-vacuum and Schlenk techniques or manipulated in a glovebox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl and stored over titanocene where compatible or dried by the method of Grubbs.⁴⁴ (NNN)H₂ (1),⁴⁰ TiCl₂(NMe₂)₂,⁴⁵ and ZrCl₂(NMe₂)₂(THF)₂,⁴⁶ were prepared following literature procedures. Benzene-*d*₆, toluene-*d*₈, and THF-*d*₈ were purchased from Cambridge Isotopes and dried over sodium benzophenone ketyl. CD₂Cl₂ was distilled from CaH₂ and run through a plug of activated alumina prior to use. ¹H and ¹³C spectra were recorded on Varian Mercury 300 or Varian INOVA 500 spectrometers, and chemical shifts are reported with respect to residual protio solvent impurity for ¹H (s, 7.16 ppm for C₆D₅H₃ t, 5.32 ppm for CDHCl₂) and solvent carbons for ¹³C (t, 128.39 ppm for C₆H₆; p, 53.84 ppm for CD₂Cl₂).

Computational Details. Density functional calculations were carried out using Gaussian 03 Revision D.01.⁴⁷ Calculations were performed using the nonlocal exchange correction by Becke^{48,49} and nonlocal correlation corrections by Perdew,⁵⁰ as implemented using the B3LYP^{51,52} keyword in Gaussian. The following basis sets were used: LANL2DZ^{53–55} for Ti and Zr atoms and 6-31G** basis set for all other atoms. Pseudopotentials were utilized for Ti and Zr atoms using the LANL2DZ ECP. All optimized structures were verified using frequency calculations and did not contain any imaginary frequencies. Isosurface plots were made using the Gaussian 03 Revision D.01 program.⁴⁷

X-ray Crystal Data: General Procedure. Crystals were removed quickly from a scintillation vial to a microscope slide coated with Paratone N oil. Samples were selected and mounted on a glass fiber with Paratone N oil. Data collection was carried out on a Bruker KAPPA APEX II diffractometer with a 0.710 73 Å MoK α source. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Details regarding refined data and cell parameters are available in Table S1 in the Supporting Information.

Synthesis of (NNN)Ti(NMe₂)₂ (2). A 10 mL toluene solution of bis(aniline)pyridine 1 (602.5 mg, 1.210 mmol) was added to a 20 mL toluene suspension of KBn (314.6 mg, 2.420 mmol) and stirred for 2 h. After 2 h, a 10 mL toluene solution of TiCl₂(NMe₂)₂ (251 mg, 1.210 mmol) was added. The mixture was stirred for 12 h, and the resulting dark red solution was filtered through Celite to remove salts. The toluene was then removed in vacuo, giving 687 mg (90%) of 2 as a red solid. Further purification and X-ray-quality crystals were obtained by layering pentane over a saturated THF solution of 2 and cooling to -30 °C overnight. ¹H NMR (500 MHz, C₆D₆; δ , ppm): 1.97 (br s, 12H, NCH₃), 2.18 (s, 6H, p-CH₃), 2.50 (s, 12H, o-CH₃), 6.56 (dd, J = 8.5, 1.1 Hz, 2H) 6.70 (ddd, J = 8.0, 6.9, 1.2 Hz, 2H), 6.82 (s, 4H, *m*-mesityl), 7.08 (ddd, *J* = 8.5, 6.9, 1.7 Hz, 2H), 7.16, (t, *J* = 7.9 Hz, 1H, p-py), 7.26 (d, J = 7.9 Hz, 3,5-py, 2H), 7.60 (dd, J = 7.9, 1.6 Hz, 2H). ¹³C NMR (125 MHz, C₆D₆; δ , ppm): 19.4 (CH₃), 21.3 (CH₃), 44.4 (NCH₃), 116.5, 116.6, 123.5, 123.6, 129.2, 129.4, 131.1, 132.7, 134.8, 136.4, 151.4, 151.4, 154.6 (aryl). Anal. Calcd for C₃₉H₄₅N₅Ti: C, 74.15; H, 7.18; N, 11.09. Found: C, 73.37; H, 7.31; N,

Synthesis of $(NNN)Zr(NMe_2)_2$ (3). Route A: Salt Metathesis. Using a procedure identical to the synthesis of 2 starting with $Zr(NMe_2)_2Cl_2(THF)_2$ yielded 3 as yellow crystals.

Route B: Aminolysis. In a glovebox, a 100 mL bomb fitted with a Kontes valve was charged with a stirbar, 393 mg (0.79 mmol) of 1, and 211.6 mg (0.79 mmol) of $Zr(NMe_2)_4$ and the vessel was then evacuated on a high-vacuum line. Twenty milliliters of benzene was vacuum-transferred onto the solid mixture, and then the vessel was heated to 90 °C and stirred overnight. The vessel was degassed and then heated at 90 °C for a further 12 h. Solvent was then removed in vacuo, and the resulting yellow residue was recrystallized from a

concentrated THF solution that was layered with pentane and cooled to -30 °C overnight. Yield: 346 mg of **3** as yellow crystals (65%). ¹H NMR (300 MHz, CD₂Cl₂; δ , ppm): 1.82 (br s, 12H, *o*-CH₃), 2.09 (s, 12H, N(CH₃)₂), 2.18 (s, 6H, *p*-CH₃), 6.33 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.70 (dd, *J* = 7.9, 1.0 Hz, 4H), 6.77 (s, 4H, *m*-mesityl), 7.13 (ddd, *J* = 8.5, 7.0, 1.6 Hz, 2H), 7.64 (d, *J* = 8 Hz, 2H, 3,5-py), 7.71 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.96 (t, *J* = 7.9 Hz, 1H, *p*-py). ¹³C NMR (125 MHz, C₆D₆; δ , ppm): 19.1 (CH₃), 21.3 (CH₃), 39.5 (NCH₃), 116.6, 118.0, 122.6, 124.2, 129.3, 130.3, 131.9, 132.6, 134.9, 137.4, 149.0, 150.7, 154.8 (aryl). Anal. Calcd for C₃₉H₄₅N₅Zr: C, 69.39; H, 6.72; N, 10.37. Found: C, 69.14; H, 6.73; N, 10.09.

Synthesis of (NNN)TiCl₂ (4). Me₃SiCl (210 μ L, 1.65 mmol) was added by syringe to a CH₂Cl₂ solution (20 mL) containing bisamide **2** (200 mg, 0.317 mmol). The reaction was stirred for 3 h, and then volatiles were removed in vacuo. The red residue was recrystallized from a concentrated toluene solution cooled to -30 °C, giving 175 mg (90%) of 4 as red crystals. ¹H NMR (300 MHz, CD₂Cl₂; δ , ppm): 1.49 (br s, 12H, *o*-CH₃), 2.29 (s, 6H, *p*-CH₃), 6.51 (d, *J* = 8.3 Hz, 2H), 6.71 (s, 4H, *m*-mesityl), 7.38 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 8.09 (d, *J* = 8.1 Hz, 2H), 8.15 (d, *J* = 7.9 Hz, 2H), 8.26 (t, *J* = 7.8 Hz, 1H, *p*-py). ¹³C NMR (125 MHz, CD₂Cl₂; δ , ppm): 20.1 (CH₃), 26.0 (CH₃), 120.1, 123.3, 123.9, 126.5, 129.6, 130.1, 133.4, 136.9, 138.7, 139.8, 142.2, 143.6, 151.3 (aryl). Satisfactory combustion analysis could not be obtained for this compound due to cocrystallized solvent molecules.

Synthesis of (NNN)ZrCl₂ (5). Me₃SiCl (210 μ L, 1.65 mmol) was added via syringe to a CH₂Cl₂ solution (20 mL) containing bisamide **3** (223 mg, 0.330 mmol). The reaction mixture was stirred for 10 min, and then volatiles were removed in vacuo to yield a yellow residue. Recrystallization from a toluene solution of **5** at -30 °C yielded yellow crystals of **5** (179 mg, 83% yield) over the course of 2 days. ¹H NMR (300 MHz, CD₂Cl₂; δ , ppm): 1.59 (s, 12H, *o*-CH₃), 2.30 (s, 6H, *p*-CH₃), 6.61 (d, *J* = 8.3 Hz, 2H), 6.78 (s, 4H, *m*-mesityl), 7.26 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 8.19 (t, *J* = 7.8 Hz, 1H, *p*-py). ¹³C NMR (125 MHz, CD₂Cl₂; δ , ppm): 19.4 (CH₃), 21.1 (CH₃), 122.4, 122.7, 123.7, 124.3, 130.3, 131.1, 133.8, 138.4, 139.7, 140.2, 143.0, 152.4 (aryl). Satisfactory combustion analysis could not be obtained for this compound due to cocrystallized solvent molecules.

Synthesis of (^{tBu}NNN)ZrBn₂ (7). (^{tBu}NNN)H₂ (44.2 mg, 0.07 mmol) and ZrBn₄ (31.6 mg, 0.07 mmol) were dissolved in 0.7 mL of C₆D₆ and sealed in a J. Young NMR tube. The tube was shielded from light using aluminum foil and heated to 90 °C in an oil bath. Reaction progress was monitored via NMR, and after 24 h volatiles were removed in vacuo, yielding a red-orange residue. This residue was dissolved in a minimal amount of pentane and cooled to -30 °C, yielding yellow crystals of 7 (45%). ¹H NMR (500 MHz, CD₂Cl₂; δ , ppm): 1.16 (s, 36H, C(CH₃)₃), 1.97 (s, 4H, PhCH₂), 6.34 (d, J = 7.1 Hz, 4H), 6.61 (t, J = 7.3 Hz, 2H), 6.73 (t, J = 2.3 Hz, 4H, o- $C_6H_3(^{t}Bu)_2$, 6.79 (t, J = 7.7 Hz, 4H), 7.01 (dd, J = 8.3, 1.1 Hz, 2H), 7.07 (t, J = 1.7 Hz, 2H, p-C₆ $H_3({}^{t}Bu)_2$), 7.15 (dt, J = 12.7, 2.9 Hz, 2H), 7.36 (m, 2H), 7.48 (dd, J = 7.9, 1.6 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H, *m*-py), 7.91 (t, J = 8.0 Hz, 1H, *p*-py). ¹³C NMR (125 MHz, CD₂Cl₂; δ , ppm): 31.2 (C(CH₃)₃), 34.7 (C(CH₃)₃), 68.4 (PhCH₂), 117.8, 119.4, 120.1, 123.0, 123.5, 125.7, 126.7, 127.7, 129.3, 131.0, 131.4, 139.2, 142.7, 148.0, 148.1, 151.6, 154.6 (aryl). Satisfactory combustion analysis could not be obtained for this compound due to cocrystallized solvent molecules.

General Polymerization Protocol. A high-pressure glass reactor was charged with solid MAO (0.207-0.828 mg, 500-2000 equiv), and toluene (3 mL, distilled from " Cp_2TiH_2 ") was added. The vessel was sealed and attached to a propylene tank and purged. Upon cooling to 0 °C, propylene (35-39 mL) was condensed in. Zirconium or titanium precatalysts were added via syringe as a toluene solution (0.7 mL). The reaction mixture was stirred vigorously at 0 °C for the desired amount of time. Excess propylene was carefully vented. Then the cold bath was removed, and a MeOH/HCl solution (10:1, 50 mL) was added slowly. The resulting mixture was transferred to an Erlenmeyer flask, additional MeOH/HCl solution was added (50 mL), and the mixture was stirred at room temperature overnight. The methanol

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solution was decanted, and the polymer was rinsed with methanol. When the methanol was decanted, the polymer was transferred to a vial, and volatile materials were removed by placing the vial under vacuum and heating to 80 °C overnight. The resulting materials were investigated by NMR spectroscopy and GPC. Polymer NMR spectroscopy data were acquired at 120 °C in tetrachloroethane. No polymer was formed without titanium or zirconium precatalyst addition or in just the presence of the NNN ligand.

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving full experimental and crystallographic details for the synthesis of $({}^{tBu}NNN)H_2$, spectroscopic data and variable-temperature NMR spectra for **2–5**, and 7, ¹³C NMR and GPC traces of polymers generated from **2**, bond lengths, angles, and anisotropic displacement parameters for the presented solid-state structures, and X-ray crystallographic data of compounds **2–7**. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data for compounds **2–7** have also been deposited with the Cambridge Crystallographic Data Center and can be obtained by requesting the deposition numbers.

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Notes

The authors declare no competing financial interest.

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