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Cyclopentadienyl Titanium Imido Compounds and Their Ethylene Polymerization Capability: Control of Molecular Weight Distributions by Imido N-Substituents

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Reaction of the previously reported Cp*Ti(N^{t}Bu)Cl(py) (**1**) with bulky *ortho*-substituted anilines $ArNH_2$ afforded the corresponding aryl imido derivatives Cp*Ti(NAr)Cl(py) (Ar = 2,6-$C_6H_3{}^iPr_2$ (**2**), 2,6-$C_6H_3Br_2$ (**3**), 2-$C_6H_4{}^tBu$ (**4**), and 2-$C_6H_4{}^iPr$ (**5**)). Reaction of **2** with $B(C_6F_5)_3$ in C_6D_6 or heating in vacuo at 200 °C afforded the imido-bridged dimer $Cp^*{}_2Ti_2(\mu$-N-2,6-$C_6H_3{}^iPr_2)_2Cl_2$ (**8**). Activation of **1**−**5** with MAO gave moderately active catalyst systems for the polymerization of ethylene in contrast to the previously reported, highly active titanium imido systems Ti(Me_3[9]aneN_3)(NR)Cl_2/MAO and Ti{HC(Me_2-pz)$_3$}(NR)Cl_2/MAO, which are isolobal and isoelectronic with **1**−**5**. The Cp*-supported precatalyst productivities were sensitive to both the imido N-substituents and initial precatalyst/cocatalyst concentrations. Depending upon the imido N-substituents and initial precatalyst/cocatalyst concentrations, polyethylene with unimodal (either rather low or very high molecular weight) or bimodal molecular weight distributions can be obtained. Excess $AlMe_3$ suppresses catalyst productivity but does not affect the overall molecular weight distribution in the system evaluated (**1**/MAO). Both chain transfer to aluminum and β-hydrogen transfer appear to be active pathways for formation of the low molecular weight fractions of the polymers formed with **1**−**5**/MAO. Under otherwise identical polymerization conditions the catalyst systems **2**/MAO and **8**/MAO had comparable productivities and gave polyethylene with very similar molecular weight and molecular weight distributions, suggesting a potential role for binuclear species in the catalyst systems **1**−**5**/MAO.

Introduction

Olefin polymerization catalysis continues to be an area of considerable importance to both the academic and industrial communities, and a wide range of cyclopentadienyl- and non-cyclopentadienyl-based systems have been described.[1−12] Of particular relevance to this contribution are half-sandwich compounds of titanium, which in general have a strong track record in this area. The most notable of these are the constrained geometry catalysts (CGC)[5] and aryloxide, ketimide, guanidinate, and phosphinimide compounds of the type $Cp^RTi(X)R_2$ (Cp^R = η-C_5H_5 or substituted cyclopentadienyl, X = monoanionic O- or N-donor, R = Cl or alkyl).[12−26] Early transition metal imido compounds (general formula $L_nM{=}NR$) also have an established track record in Ziegler−Natta catalysis,[11] including non-cyclopentadienyl compounds of titanium[27−33] and cyclo-

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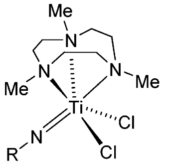
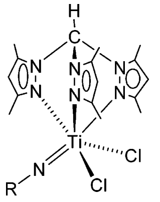
pentadienyl-supported group 5 compounds.[34−38]



I-R



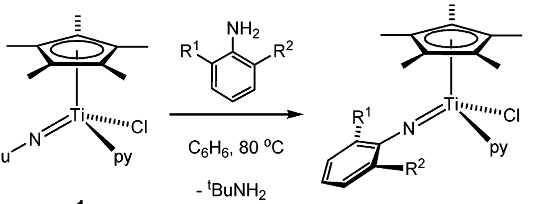
II-R

The most productive transition metal imido precatalysts so far reported are of the type Ti(TACN)(NR)Cl$_2$ (**I-R**, TACN = 1,4,7-trimethyltriazacyclononane)[29,33] and Ti(TPM)(NR)Cl$_2$ (**II-R**, TPM = tris(3,5-dimethylpyrazolyl)methane).[32] Compounds with a bulky imido R-group (e.g., ^{t}Bu, 2,6-C$_6$H$_3$^{i}Pr$_2$, 2-C$_6$H$_4$-^{t}Bu) provided the best catalyst systems. As described elsewhere,[39−42] the compounds **I-R** and **II-R** are isolobal analogues of the group 4 metallocenes Cp$^R{}_2$MCl$_2$. By analogy with the metallocene systems,[2,7,43] the active species in ethylene polymerization catalysis by **I-R** and **II-R** upon activation with MAO (methyl aluminoxanes) cocatalyst[44] are likely to be cations of the type "[Ti(*fac*-N$_3$)(NR)R′]$^+$" (*fac*-N$_3$ = TACN or TPM). These cations are themselves isolobal analogues of the group 4 metallocenium species "Cp$^R{}_2$MR$^+$", and we have reported on this aspect very recently.[42]

Conical six-electron donors such as TACN and TPM are isolobal with the [C$_5$R$_5$]$^-$ anion.[45] Replacing the *fac*-N$_3$ donors in [Ti(*fac*-N$_3$)(NR)X]$^+$ (X = alkyl or halide) by cyclopentadienide therefore gives Cp^{R}Ti(NR)X, analogues of the rare earth metallocenes Cp$^R{}_2$MR, themselves a rich source of reactivity including polymerization catalysis.[46] Jordan has previously described a similar approach in which one of the cyclopentadienide ligands of [Cp$^R{}_2$MMe]$^+$ (M = Ti, Zr, Hf) was replaced by a dianionic dicarbollide ligand to give Cp^{R}M(η^5-C$_2$B$_9$H$_{11}$)-Me, again analogues of the neutral rare earth metallocenes.[47,48] In this contribution we describe the synthesis and ethylene polymerization capability of a series of titanium cyclopentadienyl-imido compounds Cp*Ti(NR)Cl(py) and some related compounds.

Results and Discussion

Synthesis and Characterization of New Cyclopentadienyl Titanium Imido Compounds. Mono(cyclopentadienyl) titanium imido compounds have been known for over 20 years,[49,50] the first examples being Teuben's imido-bridged dimers Cp$_2$-Ti$_2$(μ-NR)$_2$Cl$_2$ (R = Et, ^{i}Pr, ^{t}Bu, Ph), prepared from CpTi-(NHR)Cl$_2$ and MeLi.[51] Roesky showed that the corresponding dehydrohalogenation reactions of Cp^{R}Ti(NH^{t}Bu)Cl$_2$ in the presence of pyridine gave monomeric terminal imido derivatives Cp^{R}Ti(N^{t}Bu)Cl(py) (Cp^R = C$_5$Me$_5$ (**1**) or C$_5$H$_4$SiMe$_3$).[52] We subsequently prepared a number of monomeric and dimeric mono(cyclopentadienyl) *tert*-butyl imido compounds, including **1**, from the useful synthons Ti(N^{t}Bu)Cl$_2$(L)$_n$ (L = py or 4-*tert*-butyl pyridine; n = 2 or 3).[53,54] Bulky cyclopentadienyl ring substituents are necessary to reduce the likelihood of the formation of imido-bridged dimers. For example, CpTi(N^{t}Bu)-Cl(py) loses pyridine to form Cp$_2$Ti$_2$(μ-N^{t}Bu)$_2$Cl$_2$ on heating in vacuo, whereas **1** is stable in this regard.[54] To explore the ethylene polymerization capability of cyclopentadienyl titanium terminal imido compounds, we therefore focused on systems containing η-C$_5$Me$_5$ (Cp*) ligands. The TACN- and TPM-supported titanium imido catalyst systems **I-R** and **II-R**) require bulky aryl imido *ortho*-substituents for higher productivities and good control of molecular weight distributions. In addition to determining the ethylene polymerization capability of **1**, we therefore targeted aryl imido compounds of the type Cp*Ti-(NAr)Cl(py), where Ar is a successful substituent from our previous studies of **I-R** and **II-R**.



(1)

1

R^1 = R^2 = ^{i}Pr (**2**) or Br (**3**)
R^1 = H, R^2 = ^{t}Bu (**4**) or ^{i}Pr (**5**)

Aryl imido titanium compounds are usually conveniently accessed by *tert*-butyl imide/aniline exchange reactions.[50,55,56] Since Cp*Ti(N^{t}Bu)Cl(py) is conveniently prepared in multigram quantities,[54] this was the route of choice. The syntheses of the new compounds Cp*Ti(NAr)Cl(py) (Ar = 2,6-C$_6$H$_3$^{i}Pr$_2$ (**2**), 2,6-C$_6$H$_3$Br$_2$ (**3**), 2-C$_6$H$_4$^{t}Bu (**4**), and 2-C$_6$H$_4$^{i}Pr (**5**)) are summarized in eq 1. Thus heating solutions of **1** with 1 equiv of the desired ArNH$_2$ for 4 days at 80 °C in benzene gave the target compounds in 30−65% isolated yields after recrystallization. All four have been crystallographically characterized (see below), and the solid-state structures are consistent with those proposed in eq 1.

The solution ^{1}H and ^{13}C NMR and other data are also consistent with the proposed structures (see Experimental

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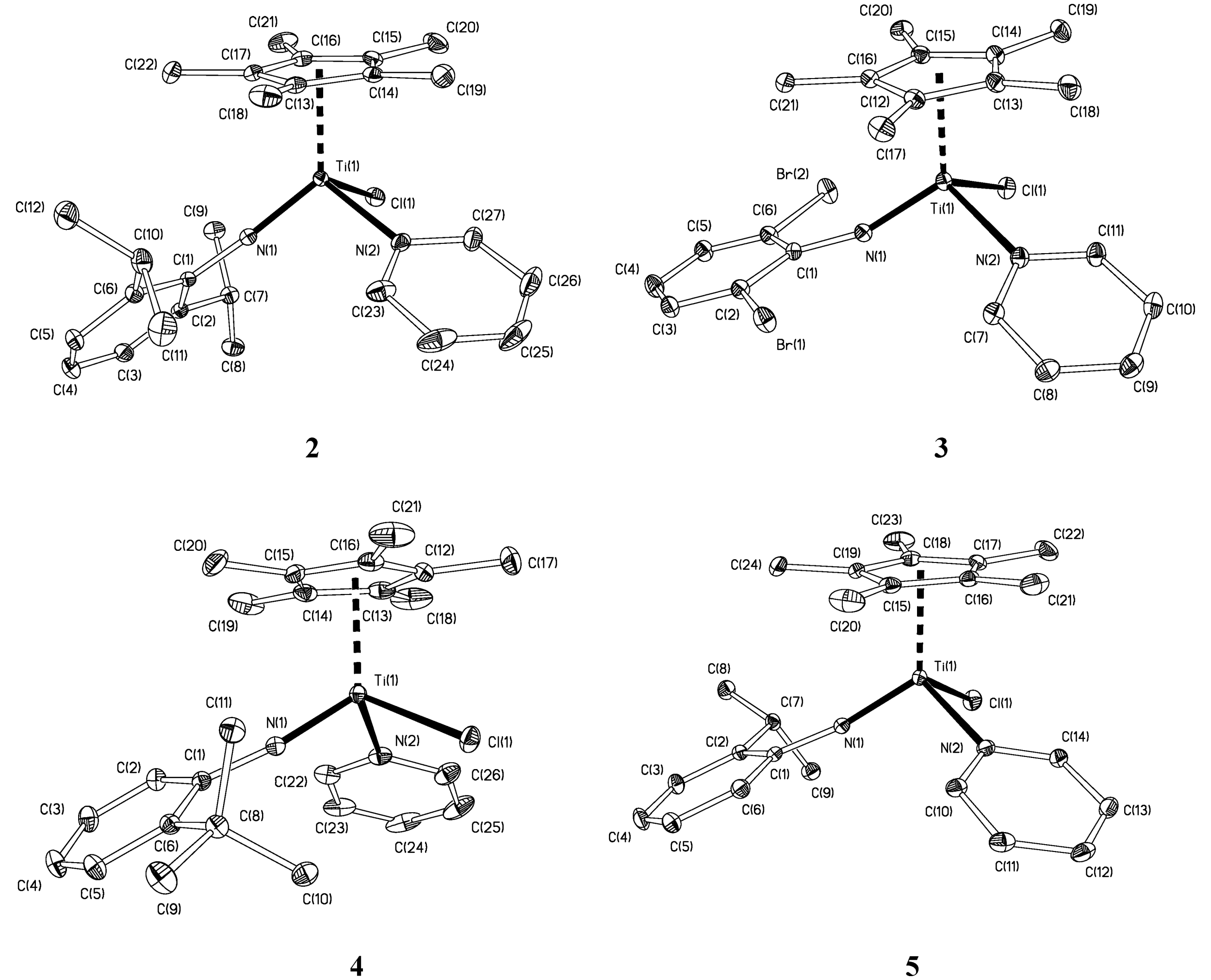

2 **3**

4 **5**

Figure 1. Molecular structures of Cp*Ti(NAr)Cl(py) (Ar = 2,6-$C_6H_3{}^iPr_2$ (**2**), 2,6-$C_6H_3Br_2$ (**3**), 2-$C_6H_4{}^tBu$ (**4**), and 2-$C_6H_4{}^iPr$ (**5**)). Displacement ellipsoids are drawn at the 25% probablility level. H atoms are omitted.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Cp*Ti(NAr)Cl(py) (Ar = 2,6-$C_6H_3{}^iPr_2$ (2), 2,6-$C_6H_3Br_2$ (3), 2-$C_6H_4{}^tBu$ (4), and 2-$C_6H_4{}^iPr$ (5))[a]

parameter	2	3	4	5
Ti(1)−Cl(1)	2.3473(6)	2.3304(8)	2.3381(5)	2.3382(7)
Ti(1)−N(1)	1.7435(16)	1.753(2)	1.7382(13)	1.7304(19)
Ti(1)−N(2)	2.1739(17)	2.169(2)	2.1793(14)	2.1761(19)
Ti(1)−Cp_{cent}	2.069	2.056	2.062	2.056
Cl(1)−Ti(1)−N(1)	106.58(5)	108.03(7)	107.53(5)	106.86(7)
Cl(1)−Ti(1)−N(2)	94.54(5)	95.60(6)	97.67(4)	99.21(6)
N(1)−Ti(1)−N(2)	99.61(7)	103.65(9)	98.39(6)	98.65(8)
Cp_{cent}−Ti(1)−Cl(1)	113.8	114.9	115.3	116.1
Cp_{cent}−Ti(1)−N(1)	125.8	120.0	122.3	120.9
Cp_{cent}−Ti(1)−N(2)	111.3	111.4	111.6	111.7
Ti(1)−N(1)−C(1)	174.48(14)	162.38(19)	169.01(11)	170.85(16)

[a] Cp_{cent} refers to the computed η-C_5Me_5 ring centroid in each case.

Section). The NMR spectra of each show resonances for η^5-coordinated C_5Me_5 ligands and an N-bound pyridine donor. The prochiral isopropyl substituents in **2** give rise to a binomial septet (integrating as 2 H per Cp* resonance) and two doublets (each 6 H per Cp*) for the methine and methyl groups, respectively. This indicates free rotation of the N-aryl group on the NMR time scale. The isopropyl group of **5** also appears as an apparent septet (1 H per Cp*) and two doublets (each 3 H).

The X-ray structures of **2**−**5** have all been determined. The molecular structures are illustrated in Figure 1, and selected bond distances and angles are listed in Table 1. Two related *tert*-butyl imido half-sandwich complexes have been structurally characterized, namely, Cp*Ti(N^tBu)Cl(L) (L = py (**1**, two molecules in the asymmetric unit)[52] and MeC(O)NMe_2).[57] The general features of **2**−**5** are similar and comparable to that of **1**. Each compound is one of a pair of enantiomers in the centrosymmetric unit cell, and the metal centers achieve a 16 valence electron count through effectively linear imido ligands (Ti−N−R > 160°). The Ti−C, Ti−Cl, and Ti−N distances are all within the previously reported ranges for these types of ligand.[58,59] The aryl substituents adopt a common orientation, namely, with the normal to the C_6 ring plane being effectively co-incident with the plane containing Ti(1), N(1), and the Cp* ring centroid. For the monosubstituted aryl imides **4** and **5** the *ortho*-substituents are oriented away from the pyridine ligand on the Ti−Cl side of the molecule.

The Ti=N_{imide} distances in **2**−**5** (range 1.7304(19)−1.753(2) Å) are significantly longer than in Cp*Ti(N^tBu)Cl(L) (1.697 Å (av) for **1** and 1.702(2) Å) as is typically the case for aryl imides in comparison with their *tert*-butyl imido homologues. In contrast the Ti−Cl distances in **2**−**5** are shorter than in Cp*Ti(N^tBu)Cl(L) (2.356 Å (av) for **1** and 2.3697(6) Å), as are the Ti−N_{py} (2.192 Å (av) for **1**) distances. This is due to the greater general labilizing effect of *tert*-butyl compared to

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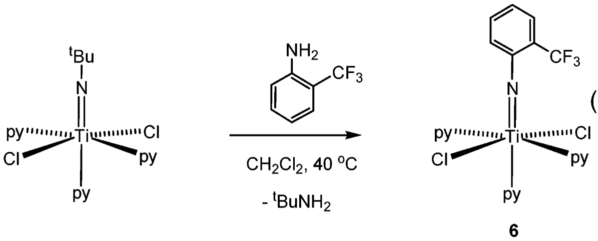
aryl imides.[49,55,58,59] Within the homologous series **2**−**5**, there is little variation in the metric parameters. The most significantly different compound within the series is Cp*Ti(N-2,6-$C_6H_3Br_2$)-Cl(py) (**3**), which features the longest Ti═N_{imide} distance and the least linear Ti═N_{imide}−Ar angle.

Surprisingly, attempts to prepare Cp*Ti(N-2-$C_6H_4CF_3$)Cl(py) (the *ortho*-CF_3 analogue of **4** and **5**) from H_2N-2-$C_6H_4CF_3$ and **1** according to the general method in eq 1 led to inseparable mixtures. Since the TACN and TPM catalyst systems containing this substituent were among the most productive at ambient temperature, further efforts were made to prepare the target cyclopentadienyl analogues.

Compound **1** itself is readily prepared from $Ti(N^tBu)Cl_2(py)_3$, and so an analogous route to Cp*Ti(N-2-$C_6H_4CF_3$)Cl(py) was attempted. The desired starting material Ti(N-2-$C_6H_4CF_3$)Cl_2-$(py)_3$ (**6**) had not been previously reported and so was synthesized in 67% yield by the stoichiometric reaction of H_2N-2-$C_6H_4CF_3$ with $Ti(N^tBu)Cl_2(py)_3$ (eq 2) according to a general method we have described previously for other compounds of the type $Ti(NAr)Cl_2(py)_3$.[55]



(2)

The NMR spectra of **6** are consistent with the structure shown in eq 2, which has been confirmed by X-ray crystallography (Figure 2, Table 2). Molecules of **6** lie across crystallographic 2-fold rotation axes (passing through N(1), Ti(1), N(2), and C(10)), and because of this, the 2-$C_6H_4CF_3$ ligand is positionally disordered (see Experimental Section for further details). The structure of **6** is analogous to the previously characterized compounds $Ti(NR)Cl_2(py)_3$ (R = ^tBu, Ph, 4-C_6H_4Me, and 4-$C_6H_4NO_2$),[55] and its Ti═N_{imide} and Ti−Cl distances are comparable to those of the aryl imido homologues. However, the bending of the imido ligand (Ti(1)−N(1)−C(1) = 165.10-(8)°) is more pronounced in **6** than in these other examples, and this is probably due to the steric demands of the *ortho*-CF_3 substituent.

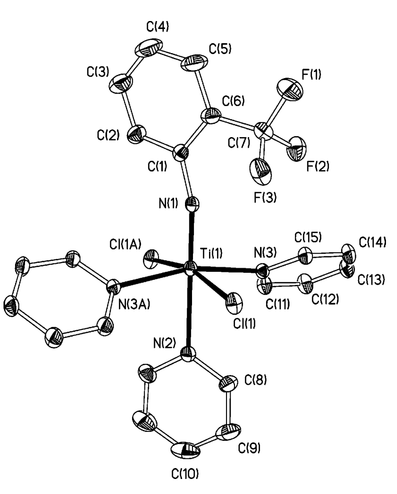


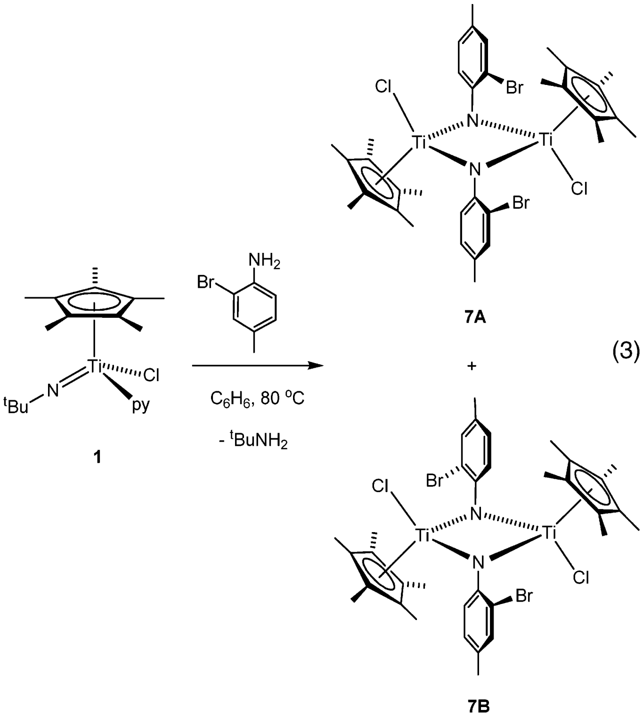
Figure 2. Molecular structure of Ti(N-2-$C_6H_4CF_3$)$Cl_2(py)_3$ (**6**). Displacement ellipsoids are drawn at the 25% probability level. H atoms are omitted and only one orientation of the disordered 2-C_6H_4-CF_3 group is shown. Atoms carrying the suffix "A" are related to their counterparts by the symmetry operator 1−*x*, *y*, 1/2−*z*.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ti(N-2-$C_6H_4CF_3$)$Cl_2(py)_3$ (6)[a]

Ti(1)−Cl(1)	2.3909(5)	Ti(1)−N(2)	2.380(2)
Ti(1)−N(1)	1.730(2)	Ti(1)−N(3)	2.2284(15)
Cl(1)−Ti(1)−Cl(1A)	164.64(3)	Cl(1)−Ti(1)−N(3)	88.27(4)
Cl(1)−Ti(1)−N(1)	97.681(17)	Cl(1)−Ti(1)−N(3A)	89.74(4)
Cl(1)−Ti(1)−N(2)	82.319(17)	N(1)−Ti(1)−N(3)	97.45(4)
N(1)−Ti(1)−N(2)	180.00	N(2)−Ti(1)−N(3)	82.55(4)
N(3)−Ti(1)−N(3A)	165.10(8)	Ti(1)−N(1)−C(1)	165.34(15)

[a] Atoms carrying the suffix "A" are related to their counterparts by the symmetry operator 1−*x*, *y*, 1/2−*z*.

Regrettably, reaction of **6** with LiCp* in THF again gave inseparable mixtures. Further experiments showed that neither **2** nor **4** could be prepared from the analogous Ti(N-2,6-C_6H_3-$^iPr_2$)$Cl_2(py)_3$[55] or Ti(N-2-$C_6H_4{}^tBu$)$Cl_2(py)_2$.[28] Further attempts to prepare Cp*Ti(N-2-$C_6H_4CF_3$)Cl(py) were discontinued.



(3)

There is no evidence of pyridine loss from **2**−**5** (e.g., to form dimeric species) under normal handling or drying in vacuo at ambient temperature. However, reaction of **1** with 2-bromo-4-methyl aniline gave the imido-bridged dimer $Cp^*{}_2Ti_2(\mu$-N-2-Br-4-$C_6H_3Me)_2Cl_2$ (**7**) along with free pyridine and $^tBuNH_2$ (as judged by NMR tube scale reactions in C_6D_6). The formation of a dimeric, pyridine-free compound in this case is attributed to the reduced steric protection at the Ti═NAr bond. Compound **7** was obtained as a mixture of two isomers, denoted **7A** and **7B**, in a ca. 2:1 ratio, respectively (eq 3). The exact ratio of **7A** and **7B** changed slightly depending on the individual sample, but did not change in solution on heating. We were not able to obtain diffraction-quality crystals of **7A** or **7B**, and their formulation as imido- rather than chloride-bridged dimers is based on a number of crystallographically characterized literature precedents, $Cp^R{}_2Ti_2(\mu\text{-}NR)_2Cl_2$ (Cp^R = C_5H_5 or substituted cyclopentadienyl, R = alkyl, aryl, or related).[51,58−60]

The ^1H NMR spectra of **7** show two sets of 2-Br-4-C_6H_3Me aryl ring protons in a ca. 2:1 ratio (for **7A** and **7B**, respectively). While two corresponding singlets for the *para*-methyl groups

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(60) Abarca, A.; Martin, A.; Mena, M.; Yelamos, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 3460.

Table 3. Ethylene Polymerization Data for Cp*Ti(N^{t}Bu)Cl(py) (1), Cp*Ti(NAr)Cl(py) (Ar = 2,6-$C_6H_3{}^iPr_2$ (2), 2,6-$C_6H_3Br_2$ (3), 2-$C_6H_4{}^tBu$ (4), and 2-$C_6H_4{}^iPr$ (5)), and Cp*$_2$Ti$_2$(μ-N-2,6-$C_6H_3{}^iPr_2$)$_2$Cl$_2$ (8)[a]

						low molecular wt fraction			higher molecular wt fraction		
entry	precatalyst	duration (min)	precatalyst loading (μmol)	PE yield (g)	productivity (kg(PE) mol(Ti)$^{-1}$ h^{-1} bar^{-1})	M_w	M_w/M_n	wt %[b]	M_w	M_w/M_n	wt %[b]
1	**1**	60	20	4.70	39	5640	2.1	92	1 345 000	2.8	8
2	**1**	60	10	1.82	30	5930	2.1	73	925 000	2.4	27
3	**1**	40	10	1.18	35	6600	2.5	87	593 000	2.0	13
4	**1**	20	10	0.40	24	6650	2.4	71	711 000	2.4	29
5	**1**	60	2.5	1.27	85	39 000	3.6	53	2 310 000[d]	1.9[d]	47
6	**1**[c]	60	10	0.22	4	3350	1.8	72	644 000	3.6	28
7	**2**	60	10	1.26	21	6490	3.0	61	1 430 000	2.7	39
8	**2**	60	2.5	0.46	20		*e*		2 010 000	2.8	*e*
9	**3**	60	10	1.02	21	4390	2.3	72	1 520 000	2.6	28
10	**3**	60	2.5	0.74	50		*e*		1 830 000	5.9	*e*
11	**4**	60	10	1.24	21	5840	3.2	53	1 380 000	2.7	47
12	**4**	60	2.5	0.96	64		*e*		2 200 000	2.9	*e*
13	**5**	60	10	1.12	19	4550	2.2	82	1 300 000	2.8	18
14	**5**	60	2.5	1.10	73		*e*		1 800 000	3.2	*e*
15	**2**[f]	60	10	1.73	29	8530	2.3	92	587 000	2.0	8
16	**8**[f]	60	5	1.88	30	8990	2.4	96	298 000	1.5	4

[a] Conditions: 6 bar of C_2H_4, Al:Ti = 1500, 250 mL of toluene, T_0 = 22−24 °C. [b] For bimodal polymer samples "wt %" refers to relative amounts of the two fractions. [c] With 1500 equiv of $AlMe_3$ added. [d] M_w and M_w/M_n probably underestimated due to truncation of peaks at high M_w. [e] No clear low molecular weight fraction. [f] The MAO used in these experiments was a more aged sample from the same batch as used in entries 1−14 (i.e., entry 15 is identical to entry 7 in all other regards).[67]

are seen (relative integrals 6H and 3H), *three* Cp* methyl group resonances are also evident, each integrating as 15 H with respect to the *para*-methyl signals. These data suggest that the dominant isomer (**7A**) has equivalent N-aryl groups but inequivalent Cp* rings, whereas the minor isomer (**7B**) has both pairs of groups chemically equivalent. The two proposed structures are illustrated in eq 3. C_s symmetric **7A** has the two *ortho*-Br substituents oriented "up" toward one Cp* ring, whereas **7B** (C_i symmetric) has them arranged in a mutually *anti* arrangement across the molecular inversion center.

Ethylene Polymerization Studies. Ethylene polymerization experiments on the monomeric precatalysts **1**−**5** were carried out using MAO cocatalyst under comparable conditions to those used for the ambient temperature studies of the TACN and TPM systems **I-R** and **II-R**. Precatalyst samples were preactivated with MAO (Al:Ti ratio = 1500:1) for 30 min, and then ethylene was admitted at 6 bar pressure for 1 h (unless otherwise stated) at ambient temperature (see the Experimental Section for further details). The results are summarized in Table 3.

Initial studies focused on the *tert*-butyl imido system Cp*Ti(N^{t}Bu)Cl(py) (**1**) (entries 1−6 in Table 3) to determine the effects of different precatalyst loadings, polymerization time, and added $AlMe_3$ (TMA). In general, **1** (and the other precatalysts listed) has "moderate" productivities (namely, in the range 10−100 kg(PE) mol(Ti)$^{-1}$ h^{-1} bar^{-1}).[6] Considering first the productivities of **1**/MAO it can be seen that at 20 and 10 μmol loading of **1** in 250 mL of toluene ([Ti] = 8×10^{-5} and 4×10^{-5} M, respectively) the productivities are comparable (4.70 and 1.82 g of isolated PE, giving figures of merit 30 and 39 kg(PE) mol(Ti)$^{-1}$ h^{-1} bar^{-1}). The productivities at 10 μmol loading at 20, 40, and 60 min polymerization times are again comparable within experimental error and suggest that this system continues to produce PE during the course of the entire experiment. These experiments also show that, for PE yields of up to ca. 4 g under these experimental conditions, mass transport limitations do not have significant effects on the productivity figures.

Reducing the precatalyst loading of **1** to 2.5 μmol ([Ti] = 1×10^{-5} M, all other parameters being the same) gave an increase in productivity to 85 kg(PE) mol(Ti)$^{-1}$ h^{-1} bar^{-1} (entry 6) compared to those for the 20 and 10 μmol loading experiments (entries 1 and 2). As established above, this is not attributable to mass transport limitations in the higher loading experiments. Instead it may reflect the higher absolute concentrations of both **1** and the MAO cocatalyst (and the TMA that it contains, ca. 20 wt % based on aluminum). To assess the effect of free TMA on the productivity of **1**/MAO, a further experiment at 10 μmol precatalyst loading was carried out (entry 6) in which 1500 equiv of TMA was added to the polymerization mixture. This experiment yielded only 0.22 g of PE (4 kg(PE) mol(Ti)$^{-1}$ h^{-1} bar^{-1}) compared to 1.82 g with no added TMA (entry 2, 30 kg(PE) mol(Ti)$^{-1}$ h^{-1} bar^{-1}). The decreased productivity is attributed to binding of $AlMe_3$ to the titanium centers of the catalytically active species as observed previously.[7,61] Additionally, the higher productivities at the lower precatalyst loadings (higher dilutions) might reflect reduced ion-pairing effects if the active species are cationic.[62]

The aryl imido catalyst systems Cp*Ti(NAr)Cl(py)/MAO (Ar = 2,6-$C_6H_3{}^iPr_2$ (**2**), 2,6-$C_6H_3Br_2$ (**3**), 2-$C_6H_4{}^tBu$ (**4**), and 2-$C_6H_4{}^iPr$ (**5**)) were first evaluated at 10 μmol precatalyst loadings (Table 3, entries 7, 9, 11, 13). The productivities were all comparable to that of **1**/MAO under these conditions. The aryl imido systems were also evaluated at 2.5 μmol precatalyst loadings (Table 3, entries 8, 10, 12, 14) and, with the exception of **2**/MAO, showed an increase in productivity compared to the 10 μmol loading experiments. This is analogous to the results found for **1**/MAO (Table 3, entries 2 and 5). At the 2.5 μmol loading level the productivities of the aryl imido systems **4**/MAO and **5**/MAO were comparable to that of **1**/MAO. The productivities of **2**/MAO and **3**/MAO were somewhat lower. These results show that although the imido substituents have some effect on the productivities of these systems, at least at the lower concentrations, the differences are rather small in comparison to the MAO-activated TACN and TPM systems **I-R** and **II-R**.[29,32,33] Furthermore, the productivities of the best of these systems (ca. 1200 kg(PE) mol(Ti)$^{-1}$ h^{-1} bar^{-1}) are some 2 orders of magnitude greater than the best of the Cp*Ti(NR)Cl(py)/MAO systems under comparable conditions. Analogous results were reported by Jordan for the carbollide systems Cp^{R}M(η^5-$C_2B_9H_{11}$)Me (M = Ti, Zr).[47,48]

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(61) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(62) D'Agnillo, L.; Soares, J. B. P.; Penlidis, A. *Macromol. Chem. Phys.* **1998**, *199*, 955.

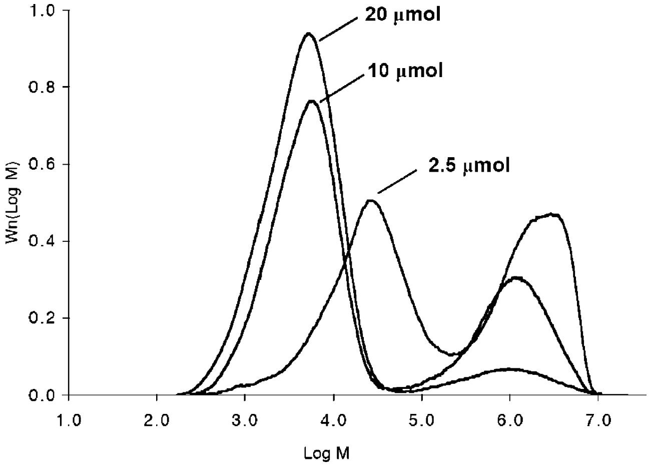

Figure 3. Molecular weight distributions determined by GPC for the polyethylenes produced by Cp*Ti(N^{t}Bu)Cl(py)/MAO (**1**/MAO) at the various precatayst loadings indicated.

The polyethylenes produced by the new catalyst systems were analyzed by GPC. Selected chromatograms are given in Figures 3 and 4, and the data are summarized in Table 3. The molecular weights and distributions all show a dependence on the imido N-substituent and catalyst loading. We consider first the Cp*Ti(N^{t}Bu)Cl(py) (**1**)/MAO catalyst systems (Table 3, entries 1−6; Figure 3). At 20 μmol precatalyst loading the polymer has one dominant low molecular weight fraction ($M_w = 5640$ g mol^{-1}, 92 wt % of total polymer) with a narrow polydispersity index (PDI, M_w/M_n) of 2.1. The narrow PDI is consistent with a single-site catalyst undergoing chain transfer processes, for which the Schultz−Flory distribution predicts a PDI of 2.0.[63] The M_n for this fraction (2690 g mol^{-1}) indicates that ca. 80 polymer chains per precatalyst metal center are formed. In addition to the low molecular weight fraction there is a higher molecular weight one ($M_w = 1\,345\,000$) with a broader PDI of 2.8, which is also consistent with single-site type behavior. As the precatalyst loading is decreased (Table 3, entries 2 and 5; Figure 3), the bimodal nature of the molecular weight distributions become more pronounced, with the lower molecular weight fraction composing only 53 wt % of the total polymer at 2.5 μmol loading of **1**.

GPC analysis of the polymer formed (10 μmol loading of **1**) after 20 and 40 min (Table 3, entries 3 and 4) showed no significant or systematic variation in the proportion of high and low molecular weight fractions. Interestingly, the proportion of high and low molecular weight polymer formed with **1**/MAO in the presence of an excess of TMA (Table 3, entry 6) was not significantly different from that formed with MAO alone (entry 2) under otherwise identical conditions, despite the very different productivities (4 and 30 kg(PE) mol^{-1}(Ti) h^{-1} bar^{-1}, respectively). However, the molecular weights of the high and low molecular fractions were somewhat lower in the presence of TMA, as would be expected if chain transfer to aluminum is important in these systems. ^{1}H NMR analysis (1,2-$C_6D_4Cl_2$, 100 °C) of the soluble part of the polymer formed with **1**/MAO (10 μmol loading, Table 3, entry 2) confirmed the product as linear polyethylene with a mixture of saturated (methyl) and unsaturated (vinyl, $-CH{=}CH_2$) end groups. The ratio of saturated: unsaturated polyethylene was ca. 3:1, showing that although the low molecular weight fraction (73 wt %) has a relatively narrow PDI (2.1), it contains polymer formed by two chain transfer processes. The soluble polymer formed with **1**/MAO/TMA (Table 3, entry 6) was almost exclusively terminated by methyl end groups (ratio of saturated:unsaturated polyethylene ca. 7:1), consistent with the greater degree of chain transfer to aluminum expected in this case.

GPC analysis of the polymers formed with the aryl imido systems **2**−**5**/MAO at 10 μmol precatalyst loading showed analogous features to that of **1**/MAO, as readily seen from the chromatograms (Figure 4) and entries 7, 9, 11, and 13 in Table 3. The relative proportions of low and high molecular weight polymer components varied with imido N-substituent from 53 (**4**/MAO) to 82 wt % (**5**/MAO). ^{1}H NMR analysis of the soluble portion of the polymer for **5**/MAO again showed a mixture of saturated and unsaturated end groups (saturated:unsaturated polyethylene ca. 3:2; PDI = 3.2). The chromatograms for the polymer formed with **2**/MAO and **4**/MAO clearly show that the low molecular weight components are comprised of two overlapping bands, consistent with two types of chain transfer mechanism. As was the case for the **1**/MAO catalyst system, reducing the precatalyst loading for **2**−**5**/MAO to 2.5 μmol gave a change in molecular weight distributions. Unlike the **1**/MAO system, however, the aryl imido systems formed polymer with only a well-defined high molecular weight component (Table 3, entries 8, 10, 12, 14) with PDIs in the range 2.8−5.9. In each of the systems **1**−**5**/MAO, the molecular weight of the polymer formed with a 2.5 μmol precatalyst loading was significantly higher than that obtained at the 10 μmol level. The increased molecular weights at higher dilution (of both the imido precatalyst and MAO cocatalyst) may tentatively be attributed to reduced chain transfer to aluminum.

The polyethylenes produced by the **1**−**5**/MAO catalyst systems contrast with those formed with MAO-activated TACN and TPM systems **I-R** and **II-R**.[29,32,33] In these cases the highly active systems produced only unimodal polyethylene with molecular weights 300 000−2 250 000 g mol^{-1} and polydispersities generally in the range 2.4−4.8. The origins of the differing behavior are not clear at this time, and it is not appropriate to speculate further.

Monomeric or Dimeric Precatalysts/Active Species? Previous reports have shown that imido-bridged binuclear titanium complexes can act as ethylene polymerization precatalysts.[30,31] The ready formation of $Cp^*_2Ti_2(\mu\text{-N-2-Br-4-}C_6H_3Me)_2Cl_2$ (**7**) and related dimers in the literature prompted us to determine under what conditions the monomeric compounds Cp*Ti(NR)-Cl(py) (**1**−**5**) might be induced to form dimeric analogues. It has been reported before that compound **1** does not lose pyridine on heating under dynamic vacuum.[54] However, MAO contains numerous Lewis acidic sites that would be expected to abstract pyridine from Cp*Ti(NR)Cl(py), which could subsequently form the corresponding $Cp^*_2Ti_2(\mu\text{-NR})_2Cl_2$ as the “true” catalyst precursors. The Lewis acid BAr^F_3 ($Ar^F = C_6F_5$)[64] has previously been used as an effective pyridine-abstracting agent to form low-coordinate titanium imido compounds[65] and so was employed as a model Lewis acid in studies of **1** and **2**.

Addition of BAr^F_3 (1 equiv) to an NMR tube sample of **1** in C_6D_6 formed the adduct py·BAr^F_3[65] and a new compound whose ^{t}Bu and Cp* resonances were shifted from those of **1**. It is not clear if this compound is the binuclear species $Cp^*_2Ti_2(\mu\text{-N-}^tBu)_2Cl_2$ or monomeric Cp*Ti(N^{t}Bu)Cl, analogous to the previously described[42] [Ti(TACN)(N^{t}Bu)Cl]$^+$ (which also readily

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[63] Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1992.

[64] Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1.

[65] Blake, A. J.; Collier, P. E.; Gade, L. H.; Mountford, P.; Lloyd, J.; Pugh, S. M.; Schubart, M.; Skinner, M. E. G.; Trösch, J. M. *Inorg. Chem.* **2001**, *40*, 870.

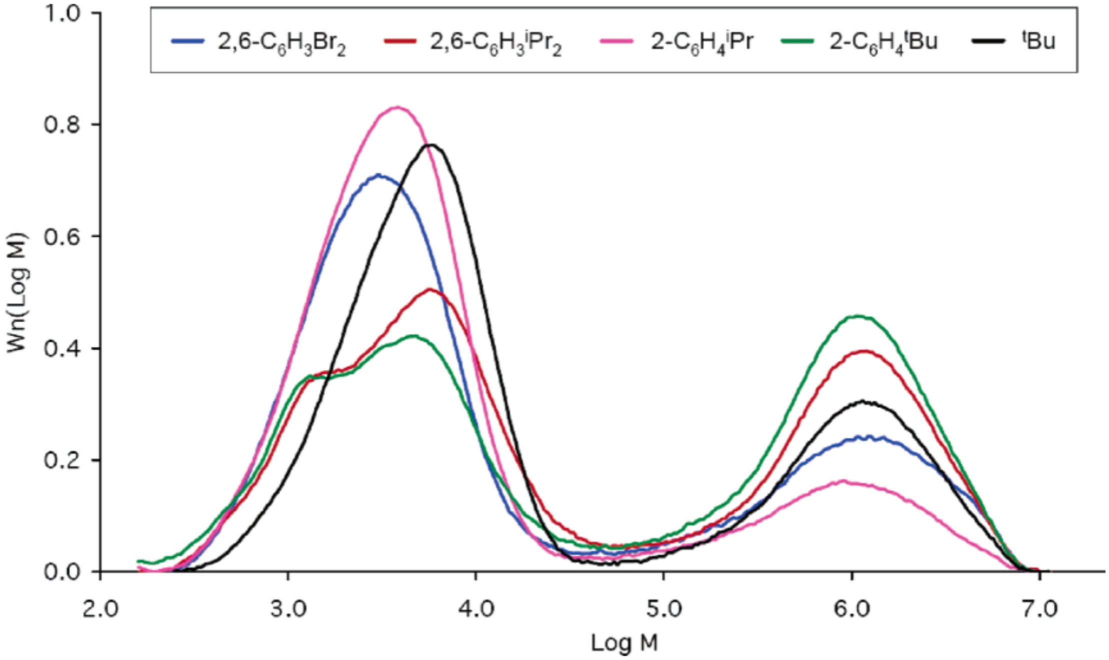
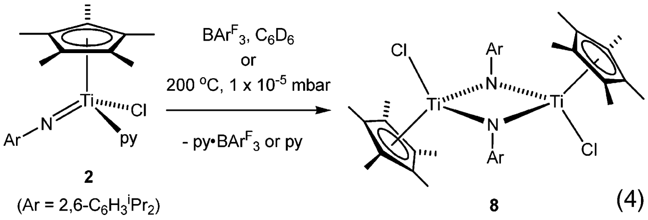


Figure 4. Molecular weight distributions determined by GPC for the polyethylenes produced by MAO-activated Cp*Ti(N^{t}Bu)Cl(py) (**1**) and Cp*Ti(NAr)Cl(py) (Ar = 2,6-$C_6H_3{}^iPr_2$ (**2**), 2,6-$C_6H_3Br_2$ (**3**), 2-$C_6H_4{}^tBu$ (**4**), and 2-$C_6H_4{}^iPr$ (**5**)) at 10 μmol precatalyst loadings.

forms a crystallographically characterized pyridine adduct). Attempts to isolate "Cp*Ti(N^{t}Bu)Cl" on a preparative scale were unsuccessful, as was the case for [Ti(TACN)(N^{t}Bu)Cl]$^+$.



(4)

The corresponding reaction of **2** (as a representative aryl imido compound) with BAr^F_3 was carried out in C_6D_6. The adduct py·BAr^F_3 was again formed, along with a sparingly soluble brown powder (**8**). Attempts to obtain pure samples of **8** from the preparative scale reaction of **2** with BAr^F_3 were unsuccessful, but heating a sample of **2** at 200 °C under 1 × 10^{-5} mbar dynamic vacuum for 2 h gave **8** in 92% yield (eq 4). Attempts to obtain a pyridine-free derivative of **1** by this method (i.e., "Cp*Ti(N^{t}Bu)Cl") gave a complex mixture of products by NMR spectroscopy.

Although **8** has low solubility in C_6D_6, it dissolves adequately in CD_2Cl_2. The ^{1}H and ^{13}C NMR spectra showed resonances for a single Cp* and 2,6-$C_6H_3{}^iPr_2$ environment and none for pyridine. The EI mass spectrum showed a molecular ion centered at $m/z = 786$ with the correct isotope distribution for a dimeric species $Cp^*_2Ti_2(\mu\text{-N-2,6-}C_6H_3{}^iPr_2)_2Cl_2$. The relatively low solubility of **8** is consistent with it possessing a symmetrical, dimeric structure. The structure proposed for **8** (see eq 4) has molecular C_{2h} symmetry with mutually *trans* Cp* ligands. In accord with this, the chemically equivalent isopropyl substituents give rise to a single methine resonance (septet, integral 2 H with respect to that for each Cp*) but two methyl resonances (doublets, each of relative integral 6 H). Alternative structures with mutually *cis* Cp* groups and/or bridging chloride ligands would be inconsistent with these data. The proposed structure is also analogous to those determined crystallographically for $Cp_2Ti_2(\mu\text{-NPh})_2Cl_2$[51] and $Cp^*_2Ti_2(\mu\text{-N-2,4,6-}C_6H_2Me_3)_2Me_2$.[60] A similar structure was postulated for the phenyl imido-bridged dication $[Ti_2(TACN)_2(\mu\text{-NPh})_2Cl_2]^{2+}$, which could be isolated as its $[BAr^F_4]^-$ salt (unlike the *tert*-butyl imido species [Ti(TACN)(N^{t}Bu)Cl]$^+$).[66]

The ethylene polymerization capabilities of Cp*Ti(N-2,6-$C_6H_3{}^iPr_2$)Cl(py) (**2**) and $Cp^*_2Ti_2(\mu\text{-N-2,6-}C_6H_3{}^iPr_2)_2Cl_2$ (**8**) were evaluated at 10 μmol precatalyst loading (based on Ti centers) with an Al:Ti ratio of 1,500:1. The results given in Table 3 (entries 15 and 16) show that under otherwise identical experimental conditions the productivities of **2**/MAO and **8**/MAO are very similar.[67] The polymer molecular weights and their distributions are also highly analogous, therefore indicating that **2**/MAO and **8**/MAO both ultimately give rise to the same catalyst system, each producing ca. 45 polymer chains (low molecular weight fraction) per titanium center present.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Protio- and deutero-solvents were predried over activated 4 Å molecular sieves and were refluxed over the appropriate drying agent, distilled, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of DEPT-135, DEPT-90, and two-dimensional ^{1}H−^{1}H and ^{13}C−^{1}H NMR experiments. ^{1}H and ^{13}C spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{19}F spectra were referenced externally to

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[66] Bolton, P. D.; Adams, N.; Clot, E.; Cowley, A. R.; Wilson, P. J.; Schröder, M.; Mountford, P. *Organometallics* **2006**, *25*, 5549.

[67] It should be noted that the MAO used in entries 15 and 16 was a more aged sample (but from the same batch) than that used in entries 1−14 (and in particular entry 7). An even more pronounced beneficial effect of aging of MAO on catalyst performance has been noted by Jordan and coworkers: Murtuza, S.; Casagrande, O. L.; Jordan, R. F. *Organometallics* **2002**, *21*, 1882.

$CFCl_3$. Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls between KBr or NaCl plates and were recorded on Perkin-Elmer 1600 and 1710 series FTIR spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry. Elemental analyses were carried out by the Elemental Analysis Service of the Inorganic Chemistry Laboratory, University of Oxford, or at London Metropolitan University. GPC analyses were carried out by Rapra Technology Ltd. in 1,2,4-trichlorobenzene solvent at 160 °C relative to polystyrene calibrants and using the appropriate Mark Houwink parameters for polyethylene.

Literature Preparations. The compounds $Ti(N^tBu)Cl_2(py)_3$ and $Cp^*Ti(N^tBu)Cl(py)$ (**1**) were prepared according to published methods.[54,55] MAO was kindly provided by Albermarle. LiCp* was prepared by treating Cp*H[68] with *n*-butyllithium in cold hexanes. All other compounds and reagents were purchased from commercial chemical suppliers and used without further purification, with the exception of the variety of substituted anilines, which were dried over calcium hydride and degassed prior to use.

$Cp^*Ti(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl(py)$ (2). A solution of $Cp^*Ti(N^tBu)Cl(py)$ (**1**, 1.00 g, 2.71 mmol) in C_6H_6 (30 mL) was made up and transferred to a thick walled ampule. To this was added $H_2N\text{-}2,6\text{-}C_6H_3{}^iPr_2$ (0.511 mL, 2.71 mmol) under an N_2 atmosphere in a dry box. The reaction mixture was stirred, degassed via freeze pump thawing, and then heated at 80 °C for 4 days. The color of the solution was observed to deepen from cherry red to dark brown. The volatiles were then removed under reduced pressure, furnishing a brown solid. This was subsequently dissolved in the minimum amount of CH_2Cl_2/pentane and stored at −80 °C for one week. A quantity of dark brown powder precipitated, from which the supernatant was removed by filtration. Yield: 0.74 g (63%). ^1H NMR (CD_2Cl_2, 499.9 MHz, 293 K): 8.71 (d, $^3J = 5.0$ Hz, 2 H, *o*-NC_5H_5), 7.95 (t, $^3J = 7.6$ Hz, 1 H, *p*-NC_5H_5), 7.55 (app t, app $^3J = 4.8$ Hz, 2 H, *m*-NC_5H_5), 6.87 (d, $^3J = 7.5$ Hz, 2 H, 3-$C_6H_3{}^iPr_2$), 6.68 (t, $^3J = 7.5$ Hz, 1 H, 4-$C_6H_3{}^iPr_2$), 3.51 (app sept, app $^3J = 6.8$ Hz, 2 H, C*H*Me_2), 1.90 (s, 15 H, C_5Me_5), 1.21 (d, $^3J = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.08 (d, $^3J = 6.8$ Hz, 6 H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz, 293 K): 155.0 (1-$C_6H_3{}^iPr_2$), 150.7 (*o*-NC_5H_5), 143.8 (2-$C_6H_3{}^iPr_2$), 140.0 (*p*-NC_5H_5), 125.6 (*m*-NC_5H_5), 122.3 (*C*$_5Me_5$), 122.1 (3-$C_6H_3{}^iPr_2$), 120.6 (4-$C_6H_3{}^iPr_2$), 28.0 (*C*HMe_2), 24.6 (CH*Me*$_2$), 24.4 (CH*Me*$_2$), 11.8 (C_5*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 1605 (s), 1327 (m), 1273 (s), 1216 (w), 1099 (br, s), 1015 (br, s), 963 (m), 800 (br, s), 757 (s), 697 (s), 641 (m), 460 (w), 441 (m). FIMS: *m/z* 393.0 $[M - py]^+$ (70%), 135.1 $[C_5Me_5]^+$ (5%), 79.0 $[NC_5H_5]^+$ (5%). Anal. Found (calcd for $C_{27}H_{37}ClN_2Ti$): C 68.7 (68.6), H 7.8 (7.9), N 5.8 (5.9).

$Cp^*Ti(N\text{-}2,6\text{-}C_6H_3Br_2)Cl(py)$ (3). Prepared by analogy to **2**. Yield: 0.46 g (31%). ^1H NMR (C_6D_6, 499.9 MHz, 293 K): 8.87 (d, $^3J = 5.1$ Hz, 2 H, *o*-NC_5H_5), 7.27 (d, $^3J = 8.1$ Hz, 2 H, 3-$C_6H_3Br_2$), 6.46 (t, $^3J = 6.3$ Hz, 1 H, *p*-NC_5H_5), 6.35 (app t, app $^3J = 6.3$ Hz, 2 H, *m*-NC_5H_5), 5.99 (t, $^3J = 8.1$ Hz, 1 H, 4-$C_6H_3Br_2$), 1.95 (s, 15 H, C_5*Me*$_5$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 293 K): 154.0 (1-$C_6H_3Br_2$), 151.6 (*o*-NC_5H_5), 138.7 (*p*-NC_5H_5), 131.8 (3-$C_6H_3Br_2$), 124.1 (*m*-NC_5H_5), 123.5 (*C*$_5Me_5$), 120.8 (4-$C_6H_3Br_2$), 119.4 (2-$C_6H_3Br_2$), 12.2 (C_5*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 1605 (s), 1260 (s), 1218 (w), 1071 (br, s), 953 (s), 800 (br, s), 753 (s), 722 (s), 694 (s), 645 (w), 559 (w), 459 (w). FIMS: *m/z* 334.7 $[M - py - C_5Me_5]^+$ (100%), 251.1 $[H_2N\text{-}2,6\text{-}C_6H_3Br_2]^+$ (20%), 135.1 $[C_5Me_5]^+$ (5%), 79.1 $[NC_5H_5]^+$ (15%). Anal. Found (calcd for $C_{21}H_{23}Br_2ClN_2Ti$): C 45.9 (46.2), H 4.4 (4.2), N 4.9 (5.1).

$Cp^*Ti(N\text{-}2\text{-}C_6H_4{}^tBu)Cl(py)$ (4). Prepared by analogy to **2**. Yield: 0.38 g (31%). ^1H NMR (C_6D_6, 499.9 MHz, 293 K): 8.39 (d, $^3J = 4.6$ Hz, 2 H, *o*-NC_5H_5), 7.32 (dd, $^3J = 7.8$ Hz, $^4J = 1.3$ Hz, 1 H, 3-$C_6H_4{}^tBu$), 7.26 (dd, $^3J = 7.8$ Hz, $^4J = 2.1$ Hz, 1 H, 6-$C_6H_4{}^tBu$), 7.30 (app td, app $^3J = 7.8$ Hz, $^4J = 1.3$ Hz, 1 H, 5-$C_6H_4{}^tBu$), 6.89 (ddd, $^3J = 7.8$, 7.8 Hz, $^4J = 2.1$ Hz, 1 H, 4-$C_6H_4{}^tBu$), 6.60 (br app s, 1 H, *p*-NC_5H_5), 6.23 (br app s, 1 H, *m*-NC_5H_5), 1.94 (s, 15 H, C_5*Me*$_5$), 1.75 (s, 9 H, C*Me*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 293K): 159.1 (1-$C_6H_4{}^tBu$), 150.1 (*o*-NC_5H_5), 142.0 (2-$C_6H_4{}^tBu$), 139.3 (*p*-NC_5H_5), 130.4 (3-$C_6H_4{}^tBu$), 126.4 (6-$C_6H_4{}^tBu$), 125.8 (5-$C_6H_4{}^tBu$), 124.2 (*m*-NC_5H_5), 121.4 (*C*$_5Me_5$), 121.2 (4-$C_6H_4{}^tBu$), 35.9 (*C*Me_3), 30.4 (C*Me*$_3$), 11.8 (C_5*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 1608 (w), 1305 (s), 1263 (m), 1100 (br, s), 1018 (br, s), 961 (m), 799 (s), 747 (m), 699 (m), 464 (w). FIMS: *m/z* 364.9 $[M - py]^+$ (75%). Anal. Found (calcd for $C_{25}H_{33}ClN_2Ti$): C 67.4 (67.5), H 7.6 (7.5), N 6.2 (6.3).

$Cp^*Ti(N\text{-}2\text{-}C_6H_4{}^iPr)Cl(py)$ (5). Prepared by analogy to **2**. Yield: 0.61 g (52%). ^1H NMR (C_6D_6, 299.8 MHz, 293 K): 8.45 (br s, 2 H, *o*-NC_5H_5), 7.21−7.11 (overlapping m, 3 H, 3-, 5-, and 6-$C_6H_4{}^iPr$), 6.89 (app t, app $^3J = 7.3$ Hz, 1 H, 4-$C_6H_4{}^iPr$), 6.73 (br app s, 1 H, *p*-NC_5H_5), 6.40 (br app s, 2 H, *m*-NC_5H_5), 4.20 (sep, $^3J = 6.8$ Hz, 1 H, C*H*Me_2), 1.92 (s, 15 H, C_5*Me*$_5$), 1.35 (d, $^3J = 7.1$ Hz, 6 H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293K): 158.0 (1-$C_6H_4{}^iPr$), 150.4 (*o*-NC_5H_5), 143.7 (2-$C_6H_4{}^iPr$), 137.7 (*p*-NC_5H_5), 125.6, 125.4 and 125.2 (3-, 5-, and 6-$C_6H_4{}^iPr$), 124.0 (*m*-NC_5H_5), 121.4 (C_5Me_5), 121.3 (4-$C_6H_4{}^iPr$), 28.1 (*C*HMe_2), 23.9 (CH*Me*$_2$), 11.8 (C_5*Me*$_5$). IR (KBr plates, Nujol mull, cm^{-1}): 1605 (w), 1311 (s), 1261 (s), 1086 (br, s), 1026 (br, s), 971 (m), 800 (s), 691 (m), 448 (m). FIMS: *m/z* 387.1 $[M - {}^iPr]^+$ (1%), 79.0 $[NC_5H_5]^+$ (100%). Anal. Found (calcd for $C_{24}H_{31}ClN_2Ti$): C 64.7 (66.9), H 7.1 (7.3), N 6.3 (6.5). A satisfactory %C analysis could not be obtained.

$Ti(N\text{-}2\text{-}C_6H_4CF_3)Cl_2(py)_3$ (6). To a stirred solution of $Ti(N^tBu)Cl_2(py)_3$ (1.00 g, 2.34 mmol) in CH_2Cl_2 (25 mL) was added $H_2N\text{-}2\text{-}C_6H_4CF_3$ (0.291 mL, 2.34 mmol). The reaction mixture was transferred to a thick walled Rotaflow ampule, degassed via freeze pump thawing, and heated at 40 °C for 16 h. The solution was then filtered and concentrated under reduced pressure until saturated. Hexane (30 mL) was added until the microcrystalline product precipitated out of solution. The supernatant was then filtered away and the yellow-brown solid washed with hexane (1 × 20 mL). Yield: 0.81 g (67%). ^1H NMR ($CDCl_3$, 299.9 MHz, 293 K): 9.07 (d, $^3J = 5.6$ Hz, 4 H, *o*-NC_5H_5 *cis* to imide), 8.65 (br s, 2 H, *o*-NC_5H_5 *trans* to imide), 7.77 (t, $^3J = 7.3$ Hz, 2 H, *p*-NC_5H_5 *cis*), 7.62 (br s, 1 H, *p*-NC_5H_5 *trans*), 7.32 (app t, app $^3J = 6.5$ Hz, 4 H, *m*-NC_5H_5 *cis*), 7.29−7.11 (overlapping m, 5 H, 3-, 4-, and 6-$C_6H_4CF_3$ and *p*-NC_5H_5 *trans*), 6.73 (t, $^3J = 7.6$ Hz, 1 H, 5-$C_6H_4CF_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz, 293 K): 155.4 (1-$C_6H_4CF_3$), 151.5 (*o*-NC_5H_5 *cis*), 150.3 (br, *o*-NC_5H_5 *trans*), 138.8 (*p*-NC_5H_5 *cis*), 136.7 (*p*-NC_5H_5 *trans*), 131.7 (4-$C_6H_4CF_3$), 130.1 (6-$C_6H_4CF_3$), 124.8 (q, $^3J_{C-F} = 5.4$ Hz, 3-$C_6H_4CF_3$), 124.2 (*m*-NC_5H_5 *cis*), 123.7 (*m*-NC_5H_5 *trans*), 123.7 (q, $^2J_{C-F} = 272.9$ Hz, 2-$C_6H_4CF_3$), 121.0 (5-$C_6H_4CF_3$). $^{13}C\{^{19}F\}$ NMR data ($CDCl_3$, 75.4 MHz, 293 K): 360.0 (C_6H_4*C*F_3), other resonances observed between 156 and 120 ppm. ^{19}F NMR ($CDCl_3$, 282.1 MHz, 293 K): −61.2 (CF_3). IR (KBr plates, Nujol mull, cm^{-1}): 1606 (w), 1331 (m), 1304 (w), 1260 (s), 1094 (br, s), 1015 (br, s), 799 (s), 150 (w), 690 (m). FIMS: *m/z* 161.1 $[H_2N\text{-}2\text{-}C_6H_4CF_3]^+$ (10%), 79.0 $[NC_5H_5]^+$ (100%). Anal. Found (calcd for $C_{22}H_{19}Cl_2F_3N_4Ti$): C 51.0 (51.3), H 3.8 (3.7), N 10.8 (10.9).

$Cp^*_2Ti_2(\mu\text{-}N\text{-}2\text{-}Br\text{-}4\text{-}C_6H_3Me)_2Cl_2$ (7). A solution of $Ti(\eta\text{-}C_5Me_5)(N^tBu)Cl(py)$ (**1**, 1.00 g, 2.71 mmol) in C_6H_6 (30 mL) was made up and transferred to a thick walled ampule. To this was added a solution of $H_2N\text{-}2\text{-}Br\text{-}4\text{-}C_6H_3Me$ (0.336 mL, 2.71 mmol) in C_6H_6 (15 mL). The reaction mixture was stirred, degassed via freeze pump thawing, and heated at 80 °C for 4 days. The color of the solution deepened from cherry red to deep red-brown. The volatiles were then removed under reduced pressure, yielding an impure brown solid. This was subsequently dissolved in the minimum amount of CH_2Cl_2/hexane and stored at −80 °C for one week. A quantity of red-brown powder was precipitated, from which

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[68] Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 119.

Table 4. X-ray Data Collection and Processing Parameters for Cp*Ti(NAr)Cl(py) (Ar = 2,6-$C_6H_3{}^iPr_2$ (2), 2,6-$C_6H_3Br_2$ (3), 2-$C_6H_4{}^tBu$ (4), and 2-$C_6H_4{}^iPr$ (5)) and Ti(N-2-$C_6H_4CF_3$)Cl_2(py)$_3$ (6)

		2	3	4	5	6
formula		$C_{27}H_{37}ClN_2Ti$	$C_{21}H_{23}Br_2ClN_2Ti$	$C_{25}H_{33}ClN_2Ti$	$C_{24}H_{31}ClN_2Ti$	$C_{22}H_{19}Cl_2F_3N_4Ti$
fw		472.96	546.59	444.90	430.88	515.22
cryst syst		orthorhombic	triclinic	triclinic	triclinic	monoclinic
space group		*Pbca*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å		17.7428(2)	8.6809(2)	8.4499(2)	8.3636(2)	12.4719(4)
b/Å		13.2892(2)	9.7070(3)	11.7126(2)	11.5408(3)	19.5247(8)
c/Å		21.3972(3)	13.8311(5)	13.6175(3)	12.7908(4)	9.6046(3)
α/deg		90	97.8878(12)	70.3832(9)	75.1960(9)	90
β/deg		90	90.4074(12)	81.1385(9)	82.9984(10)	93.795(2)
γ/deg		90	111.1461(14)	70.9648(10)	74.2354(12)	90
V/Å^3		5045.19(12)	1074.70(6)	1198.58(4)	1146.89(5)	2333.69(14)
Z		8	2	2	2	2
μ/mm^{-1}		0.462	4.249	0.481	0.501	0.637
total no. of reflns		11 476	18 043	17 408	19 884	9008
R indices R_1, $R_w{}^a$	R_1 =	0.0359	0.0331	0.0349	0.0368	0.0311
$[I > 3\sigma(I)]$	R_w =	0.0410	0.0387	0.0405	0.0391	0.0324

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sqrt{\{\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2)\}}$.

the supernatant was removed by filtration. The above recrystallization process was then repeated to obtain clean product. Yield: 0.19 g (17%). ^{1}H NMR (C_6D_6, 499.9 MHz, 293 K) isomer **7A**: 7.62 (d, ^3J = 8.3 Hz, 2 H, 6-C_6H_3BrMe), 7.28 (d, ^4J = 1.2 Hz, 2 H, 3-C_6H_3BrMe), 6.72 (dd, ^4J = 2.2, 8.2 Hz, 2 H, 5-C_6H_3BrMe), 1.88 (s, 6 H, C_6H_3Br{C*H*$_3$}), 1.85 (s, 15 H, C_5*Me*$_5$), 1.82 (s, 15 H, C_5*Me*$_5$); isomer **7B**: 8.16 (d, ^3J = 8.3 Hz, 2 H, 6-C_6H_3BrMe), 7.33 (d, ^4J = 1.2 Hz, 2 H, 3-C_6H_3BrMe), 6.81 (dd, ^4J = 1.5, 8.3 Hz, 2 H, 5-C_6H_3BrMe), 1.89 (s, 6 H, C_6H_3Br{C*H*$_3$}), 1.86 (s, 30 H, C_5*Me*$_5$). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 293 K) isomer A: 153.0 (1-C_6H_3BrMe), 135.4 (2-C_6H_3BrMe *ipso* to bromo), 134.4 (3-C_6H_3-BrMe), 129.9 (*C*$_5$Me$_5$), 127.6 (*C*$_5$Me$_5$), 127.4 (5-C_6H_3BrMe), 125.7 (6-C_6H_3BrMe), 118.4 (4-C_6H_3BrMe), 20.1 (C_6H_3Br{*C*H$_3$}), 12.1 (C_5*Me*$_5$), 12.0 (C_5*Me*$_5$); isomer B: 133.7 (3-C_6H_3BrMe), 127.9 (5-C_6H_3BrMe), 125.5 (6-C_6H_3BrMe), 128.8 (*C*$_5$Me$_5$), 20.1 (C_6H_3Br-{*C*H$_3$}), 12.0 (C_5*Me*$_5$). Resonances for three aromatic quaternary carbons not resolved. IR (KBr plates, Nujol mull, cm^{-1}): 2895 (s), 2281 (w), 1599 (m), 1504 (w), 1270 (s), 1230 (w), 1110 (w), 1069 (w), 1010 (m), 962 (w), 797 (w), 755 (s), 715 (s), 696 (s), 520 (w), 482 (w). Anal. Found (calcd for $C_{34}H_{42}Br_2Cl_2N_2Ti_2$): C 50.2 (50.7), H 5.1 (5.3), N 3.5 (3.5).

Cp*$_2$Ti$_2$(μ-N-2,6-$C_6H_3{}^iPr_2$)$_2$Cl$_2$ (8). A sublimation tube was loaded with Cp*Ti(N-2,6-$C_6H_3{}^iPr_2$)Cl(py) (**2**, 1.00 g, 2.11 mmol) and heated at 200 °C under dynamic vacuum (1×10^{-5} mbar) for 2 h to yield **8** as a brown powder. Yield: 0.77 g (92%). ^{1}H NMR (CD_2Cl_2, 499.9 MHz, 293 K): 6.92 (d, ^3J = 7.6 Hz, 4 H, 3-C_6H_3-$^iPr_2$), 6.76 (t, ^3J = 7.6 Hz, 2 H, 4-$C_6H_3{}^iPr_2$), 3.19 (sept, ^3J = 6.8 Hz, 4 H, C*H*Me$_2$), 2.05 (s, 30 H, C_5Me_5), 1.27 (d, ^3J = 6.8 Hz, 12 H, CH*Me*$_2$), 1.10 (d, ^3J = 6.8 Hz, 12 H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, 293 K): 144.3 (2-$C_6H_3{}^iPr_2$), 125.5 (*C*$_5$Me$_5$), 122.5 (3-$C_6H_3{}^iPr_2$), 121.6 (4-$C_6H_3{}^iPr_2$), 28.1 (*C*HMe$_2$), 25.4 (CH*Me*$_2$), 23.8 (CH*Me*$_2$), 12.2 (C_5*Me*$_5$), the 1-$C_6H_3{}^iPr_2$ resonance was not resolved. IR (NaCl plates, Nujol mull, cm^{-1}): 1325 (s), 1277 (s), 1100 (m), 1024 (w), 969 (w), 795 (m), 742 (s), 729 (s), 699 (m). EIMS: m/z = 786.0 [M]$^+$ (50%), 743.1 [M − ^{i}Pr]$^+$ (10%), 652.1 [M − C_5Me_5]$^+$ (10%), 393.0 [Ti(η-C_5Me_5)(N-2,6-$C_6H_3{}^iPr_2$)Cl]$^+$ (100%). Anal. Found (calcd for $C_{44}H_{64}Cl_2N_2Ti_2$): C 63.4 (67.1), H 8.4 (8.2), N 3.2 (3.6). A satisfactory %C analysis could not be obtained.

Typical Procedure for Ambient Temperature Ethylene Polymerization Studies. To a sealable metal reactor containing a glass insert was added the appropriate amount of MAO (Albermarle, 10% in toluene) made up to 200 mL with toluene. The solution was stirred at 250 rpm for 5 min, and then the precatalyst (20, 10, or 2.5 μmol) in toluene (50 mL) was added to the reactor and the mixture stirred for a further 30 min. The reaction vessel was placed under dynamic vacuum for 10 s, the stirring was increased to 750 rpm, and a dynamic pressure of ethylene (6 bar) was admitted. After 60 min, the reactor was isolated and the pressure was released. Methanol (5 mL) was added to the mixture, followed by water (50 mL) with stirring. The mixture was acidified to pH = 1 using a solution of 10% HCl(aq) in MeOH and stirred overnight. The precipitated polymers were filtered, washed with water (total volume ca. 1000 mL), and dried to constant weight at room temperature.

Crystal Structure Determinations of Cp*Ti(NAr)Cl(py) (Ar = 2,6-$C_6H_3{}^iPr_2$ (2), 2,6-$C_6H_3Br_2$ (3), 2-$C_6H_4{}^tBu$ (4), and 2-$C_6H_4{}^iPr$ (5)) and Ti(N-2-$C_6H_4CF_3$)Cl_2(py)$_3$ (6). Crystal data collection and processing parameters are given in Table 4. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to an Enraf-Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystems low-temperature device.[69] Data were collected at low temperature using Mo Kα radiation; equivalent reflections were merged, and the images were processed with the DENZO and SCALEPACK programs.[70] Corrections for Lorentz−polarization effects and absorption were performed, and the structures were solved by direct methods using SIR92.[71] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were placed geometrically. Crystallographic calculations were performed using SIR92[71] and CRYSTALS.[72]

For **2** the thermal parameters of the pyridyl C atoms were unusually large, suggesting that this group has a pronounced librational motion about an axis perpendicular to the plane of the ring. For **4** the large thermal parameters of the Cp* and to some extent the pyridyl ligands suggest that the librational motion of these groups is also facile.

Molecules of **6** (refined in the space group $C2/c$) lie across crystallographic 2-fold axes on which Ti(1), N(1), N(2), and C(10) are situated. This necessarily results in disorder of the 2-$C_6H_4CF_3$ group, as this cannot possess internal 2-fold symmetry. Nonetheless, all non-H atoms of **6** were satisfactorily refined anisotropically. An attempt was also made to refine the structure in the space group Cc, in which the 2-fold axis that causes the disorder is not present. However, the disorder of the $C_6H_4CF_3$ group was still clearly apparent in Fourier maps, and attempts to refine the structure failed to converge, confirming the original assignment of symmetry

Details of the structure solution and refinements are given in the Supporting Information (CIF data). A full listing of atomic coordinates, bond lengths and angles, and displacement parameters

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for all the structures has been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of Cp*Ti(NAr)Cl(py) (Ar = 2,6-$C_6H_3{}^iPr_2$ (**2**), 2,6-$C_6H_3Br_2$ (**3**), 2-$C_6H_4{}^tBu$ (**4**), and 2-$C_6H_4{}^iPr$ (**5**)) and Ti(N-2-$C_6H_4CF_3$)Cl_2(py)$_3$ (**6**). This information is available free of charge via the Internet at http://pubs.acs.org.

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