CO_2-Mediated *ortho*-Lithiation of *N*-Alkylanilines and Its Use for the Construction of Polymerization Catalysts

Chun Ji Wu,[†] Sang Hoon Lee,[†] Seung Tack Yu,[†] Sung Jae Na,[†] Hoseop Yun,[‡] and Bun Yeoul Lee*,[†]

Department of Molecular Science and Technology, and Energy System Division, Ajou University, Suwon 443-749 Korea

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The *ortho*-lithiation of *N*-alkylanilines is accomplished by the treatment of ^{t}BuLi with the lithium carbamate compounds generated in situ from *N*-alkylanilines. The lithiated compounds attack the carbonyl-carbon on 2,3,4,5-tetramethylcyclopentenone, 1-indanone, or 9-fluorenone to yield tertiary alcohols, which are transformed to *N*-alkylanilines attaching a Me_4C_5, indenyl, or fluorenyl unit at an *ortho*-position. From the compounds, various *o*-phenylene-bridged (Me_4C_5, indenyl, or fluorenyl)/amido titanium complexes are prepared in one step. The Me_4C_5/ethylamido titanium complex exhibits a similar catalytic performance to the CGC [$Me_2Si(\eta^5$-$Me_4C_5)(N^tBu)$]$TiCl_2$ in ethylene/1-octene copolymerization in terms of activity, molecular weight of the obtained polymer, and 1-octene incorporation.

Introduction

Aryllithium is a powerful reagent in organic synthesis.[1] It can be prepared in two ways. The first one is through halo-lithium exchange reaction of haloarenes with commercially available butyllithium. A more atom-economical way of preparing aryllithium is through a process called directed *ortho*-lithiation, a regioselective *ortho*-deprotonation of heteroatom-substituted arenes.[2] The coordination of lithium ion on the heteroatom brings the reactive butyl carbanion into proximity for the directed deprotonation of the *ortho*-proton. The *ortho*-lithiations directed by functional groups such as $-F$,[3] $-OR$,[4] $-OC(O)NR_2$,[5] $-CH(OR)_2$,[6] $-CH_2NR_2$,[7] $-C(O)NR_2$,[8] $-CO_2Li$,[9] oxazolinyl,[10] imidazolyl,[11] imidazolinyl,[12] and benzimidazolyl[13] were achieved. However, those directed by an amino ($-NH_2$), *N*-alkylamino ($-N(H)R$), or *N*,*N*-dialkylamino ($-NRR'$) group have not been reported.

Recently, we disclosed a new method for *ortho*-lithiation of tetrahydroquinoline derivatives. The key to the success of this method is the transformation of a $-N(H)-$ group to the lithium carbamate group ($-N(COOLi)-$), which is able to act as an *ortho*-directing group (eq 1).[14] Almost two decades ago, Katritzky tried the lithiation reactions of tetrahydroquinoline, tetrahydroisoquinoline, indoline, and indole after the $-N(H)-$ group was transformed to the corresponding lithium carbamates. The main reaction, however, was α-lithiation and not *ortho*-lithiation through the treatment of ^{t}BuLi-KO^{t}Bu in THF at -78 to -50 °C.[15] The *ortho*-lithiation was only realized through the treatment of excess ^{t}BuLi (1.7 equiv) in THF using a substrate that does not contain any α-protons such as phenothiazine.[16] In the case of the lithium carbamate of 2-methylindol, the proton loss occurred regioselectively at the methyl position and not at

* Corresponding author. E-mail: bunyeoul@ajou.ac.kr.
† Department of Molecular Science and Technology.
‡ Energy System Division.

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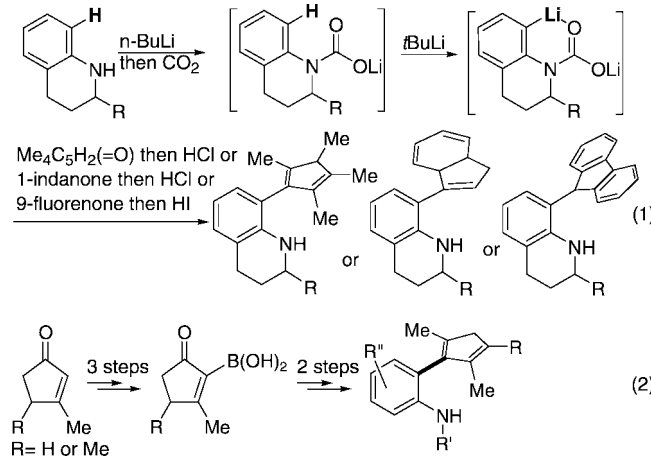
the *ortho*-position.[17] The lithium carbamate group has some advantages as an *ortho*-directing group. Aside from the fact that it is easily generated from the amino group (−NH−) through successive addition of ^{n}BuLi and CO_2 gas, it can also be easily deprotected to afford the original amino group (−NH−) through treatment of acidic water after the reaction. The −N(COOLi)− group may not be too basic to intervene in the reaction between the generated *ortho*-carbanion and an electrophile.

The new *ortho*-lithiation method of tetrahydroquinoline derivatives allowed for the facile construction of various tetrahydroquinoline-derived (tetramethylcyclopentadienyl, indenyl, or fluorenyl)/amido titanium complexes.[14] Some of these complexes show a better catalytic performance in ethylene/1-octene copolymerization than the well-known constrained-geometry catalyst (CGC) [$Me_2Si(\eta^5$-$Me_4C_5)(N^tBu)$]$TiCl_2$.[18] The design and preparation of new metal complexes are an issue in the field of homogeneous polymerization catalysts.[19,20] In this paper, we report an expansion of the new *ortho*-lithiation method to various *N*-alkylanilines and its utilization to construct various *ortho*-phenylene-bridged (tetramethylcyclopentadienyl, indenyl, or fluorenyl)/amido titanium complexes, which are screened as catalysts in ethylene/1-octene copolymerization. The syntheses of *ortho*-phenylene-bridged (Me_3C_5H or $Me_2C_5H_2$)/amido titanium or zirconium complexes were disclosed, but the synthetic route was rather lengthy (eq 2).[21] Furthermore, the variation on the π-ligand was limited only to dimethylcyclopentadienyl and trimethylcyclopentadienyl in the route. By developing the new *ortho*-lithiation method of *N*-alkylanilines, the number of steps to reach the similar ligand system is significantly reduced, and the π-ligand is expanded to tetramethylcyclopentadienyl, indenyl, and fluorenyl.

Results and Discussion

***ortho*-Lithiation of *N*-Alkylanilines.** The treatment of 1 equiv of ^{n}BuLi with a solution of *N*-ethylaniline in diethyl ether at −78 °C results in the deprotonation of the −NH− proton to afford a slurry of lithium amide. The addition of excess CO_2 gas to the slurry results in the immediate generation of a lithium carbamate. When ^{t}BuLi is treated with the resulting solution, after thoroughly removing excess CO_2 gas, in the absence of any additives, the *ortho*-lithiation yield is only 70%. A 70% intensity reduction of the *ortho*-proton is observed in the ^{1}H NMR spectrum of the D_2O-quenched product. The *ortho*-lithiation yield is improved to 86% by the addition of 1.1 equiv of THF as an additive (entry 2 in Table 1). The use of tetramethylethylenediamine (TMEDA) as an additive also results in a high yield, at 80% (entry 3). In the ^{1}H NMR spectra of the D_2O-quenched product, no intensity reduction is observed for the signal of the lateral N-CH_2 protons, indicating that the lithiation reaction is regiospecific. A complete *ortho*-lithiation is not accomplished either with a longer reaction time (8 h) or by adding more ^{t}BuLi (1.3 equiv). The failure to attain a complete *ortho*-lithiation may be ascribed to the incomplete formation of the lithium carbamate. If either the deprotonation reaction of −NH− proton or the next reaction with CO_2 is incomplete, some fraction of the added *N*-ethylaniline is present as a lithium amide in the stage of ^{t}BuLi treatment. The lithium amide group (−NLi(R)) is not able to act as an *ortho*-directing group, but it remains intact with the treatment of ^{t}BuLi to afford the reactant after the D_2O quenching.



N-Butylaniline, *N*-methylaniline, and *N*-neopentylaniline are also *ortho*-lithiated in high yields (>80%) by employing the same conditions and additive for the *ortho*-lithiation of *N*-ethylaniline. For these substrates, the lithiation is also regiospecific. The presence of methyl substituent at a *para*-position does not hamper the *ortho*-lithiation, and a high *ortho*-lithiation yield (84%) is also attained for *N*-ethyl-4-methylaniline (entry 7). In the ^{1}H NMR spectrum of the D_2O-quenched product, no intensity reduction of the benzylic-CH_3 signal is observed, which indicates that only the *ortho*-proton is regiospecifically deprotonated. However, placing the methyl substituent at an *ortho*-position completely blocks the *ortho*-lithiation (entry 8). In the case of *N*-isopropylaniline, the *ortho*-lithiation yield is rather low (62%, entry 10). The low yield is attributed to incomplete deprotonation of the −NH− proton by the action of ^{n}BuLi in diethyl ether at −78 °C for 2 h. The yield is improved to 81% when the isolated pure lithium amide is used as a starting material.

Syntheses of Titanium Complexes. A tetramethylcyclopentadiene unit is attached on an *ortho*-position of *N*-alkylanilines in a one-pot reaction using the *ortho*-lithiated compounds (Scheme 1). Thus, an in situ generated *ortho*-lithiated compound of *N*-ethylaniline attacks the carbonyl-carbon on 2,3,4,5-tetramethylcyclopentenone in the presence of $CeCl_3 \cdot 2LiCl$ in

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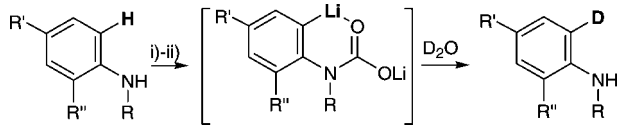
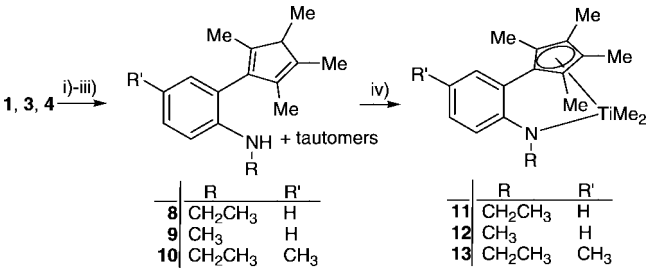
Table 1. CO_2-Mediated *ortho*-Lithiation Yields for *N*-Alkyl Anilines[a]



entry	compound	R	R′	R″	additive	yield (%)[b]
1	**1**	CH_2CH_3	H	H	not added	70
2	**1**	CH_2CH_3	H	H	THF	86
3	**1**	CH_2CH_3	H	H	TMEDA[c]	80
4	**2**	$CH_2(CH_2)_2CH_3$	H	H	THF	93
5	**2**	$CH_2(CH_2)_2CH_3$	H	H	TMEDA	91
6	**3**	CH_3	H	H	THF	83
7	**4**	CH_2CH_3	CH_3	H	THF	84
8	**5**	CH_2CH_3	H	CH_3	THF (or TMDEA)	0
9	**6**	$CH_2C(CH_3)_3$	H	H	THF	80
10	**7**	$CH(CH_3)_2$	H	H	THF	62 (81)[d]

[a] *ortho*-Lithiation conditions: (i) aniline (3.0 mmol) in diethyl ether (4.5 mL), ^{n}BuLi (1.0 equiv) then CO_2, −78 °C; (ii) additive (1.1 equiv) then ^{t}BuLi (1.1 equiv), −20 °C, 2 h. [b] Yield determined through an analysis of the ^{1}H NMR spectra of the D_2O-quenched products. [c] Tetramethylenediamine. [d] Yield in parentheses is the one from the pure lithium amide.

Scheme 1[a]



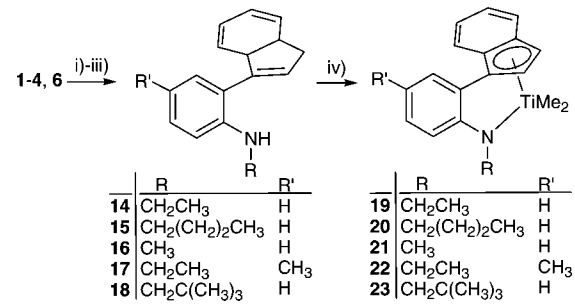
	R	R'
8	CH_2CH_3	H
9	CH_3	H
10	CH_2CH_3	CH_3
11	CH_2CH_3	H
12	CH_3	H
13	CH_2CH_3	CH_3

[a] Legend: (i) ^{n}BuLi (1.0 equiv) then CO_2; (ii) THF (1.1 equiv) then ^{t}BuLi (1.1 equiv); (iii) $Me_4C_5H_2$(=O) then aq HCl (2 N); (iv) MeLi (4.0 equiv) then $TiCl_4$·DME.

THF.[22] Through an aqueous HCl (2 N) workup, the elimination reaction of the resulting tertiary alcohol occurs to afford the tetramethylcyclopentadiene unit. Also, the lithium carbamate group is converted to the original *N*-ethylamino group during the acidic workup. A moderate overall yield from *N*-ethylaniline to the desired ligand (47%) is acceptable considering the yields reported for the reactions between other lithium compounds and 2,3,4,5-tetramethylcyclopentenone (40−50%).[23] Similar results are observed with the *ortho*-lithiated compound of *N*-methylaniline (**3**) and *N*-ethyl-4-methylaniline (**4**). However, the carbonyl attack of the *ortho*-lithiated compounds of *N*-butylaniline (**2**), *N*-neopentylaniline (**6**), and *N*-isopropylaniline (**7**) is unsuccessful. The yields for the formation of the desired ligands are very low (<10%). The steric bulkiness of the N-substituent may have hampered the carbonyl attack. The signals observed in the ^{1}H NMR spectra of the obtained ligands are broad. This is attributed to the facile 1,5-sigmatropic rearrangement frequently observed for the substituted cyclopentadiene compounds.[24]

The metalation is carried out efficiently in one step in good yields (65−86%) using the method introduced by Resconi

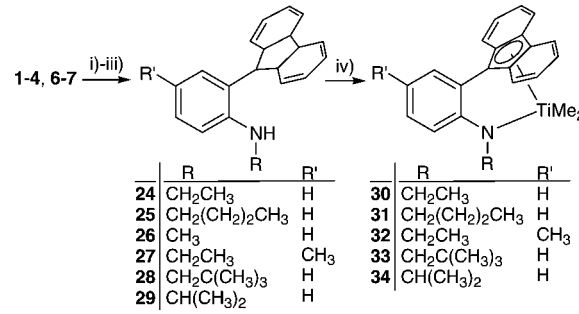
Scheme 2[a]



	R	R'
14	CH_2CH_3	H
15	$CH_2(CH_2)_2CH_3$	H
16	CH_3	H
17	CH_2CH_3	CH_3
18	$CH_2C(CH_3)_3$	H
19	CH_2CH_3	H
20	$CH_2(CH_2)_2CH_3$	H
21	CH_3	H
22	CH_2CH_3	CH_3
23	$CH_2C(CH_3)_3$	H

[a] Legend: (i) ^{n}BuLi (1.0 equiv) then CO_2; (ii) THF (1.1 equiv) then ^{t}BuLi (1.1 equiv); (iii) 1-indanone then aq HCl (6 N); (iv) MeLi (4.0 equiv) then $TiCl_4$·DME.

Scheme 3[a]



	R	R'
24	CH_2CH_3	H
25	$CH_2(CH_2)_2CH_3$	H
26	CH_3	H
27	CH_2CH_3	CH_3
28	$CH_2C(CH_3)_3$	H
29	$CH(CH_3)_2$	H
30	CH_2CH_3	H
31	$CH_2(CH_2)_2CH_3$	H
32	CH_2CH_3	CH_3
33	$CH_2C(CH_3)_3$	H
34	$CH(CH_3)_2$	H

[a] Legend: (i) ^{n}BuLi (1.0 equvi) then CO_2; (ii) THF (1.1 equiv) then ^{t}BuLi (1.1 equiv); (iii) 9-fluorenone then HI in acetic acid; (iv) MeLi (4.0 equiv) then $TiCl_4$·DME.

(Scheme 1).[25] Thus, compounds **8**−**10** are treated with 4 equiv of MeLi in diethyl ether, followed by the addition of $TiCl_4$·DME to give the desired compounds **11**−**13**. The ^{1}H and ^{13}C NMR spectra of **11**−**13** are very simple. In the ^{1}H NMR spectrum of **11**, the Ti-CH_3 signal is observed at 0.56 ppm, while the $C_5(CH_3)_4$ signals are observed at 1.58 and 2.03 ppm (C_6D_6). The NCH_2 signal is observed at 4.48 ppm as a quartet. The signal at 51 ppm in the ^{13}C NMR spectrum is assigned to the Ti-CH_3 signal.

The *ortho*-lithiated compounds of *N*-ethylaniline (**1**), *N*-methylaniline (**3**), and *N*-ethyl-4-methylaniline (**4**) also attack the carbonyl-carbon on 1-indanone in the presence of $CeCl_3$·2LiCl in THF (Scheme 2). The *ortho*-lithiated compounds of *N*-butylaniline (**2**) and *N*-neopentylaniline (**6**), which are not able to effectively attack the carbonyl on 2,3,4,5-tetramethylcyclopentenone, give the desired products in rather low yields (29% and 18%, respectively). However, the reaction using the *ortho*-lithiated compound of *N*-isopropylaniline is still unsuccessful. A more acidic condition, 6 N HCl instead of 2 N, is required for the elimination reaction of the resulting tertiary alcohol. A set of sharp signals, which is unambiguously assignable, is observed in the ^{1}H and ^{13}C NMR spectra of **14**−**18**.

The metalation is also carried out successfully using the method applied for the syntheses of the tetramethylcyclopentadienyl complexes **11**−**13**. Two separated Ti-CH_3 signals are observed at ∼0.0 and 0.82−0.91 ppm in the ^{1}H NMR spectra (C_6D_6). Two Ti-CH_3 carbon signals are observed at ∼58 and ∼55 ppm downfield shifted from the chemical shifts (50−51

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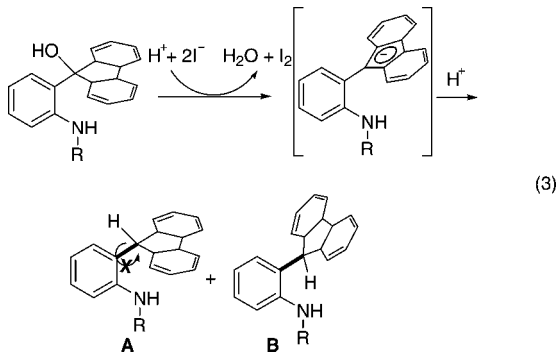
ppm) of the tetramethylcyclopentadienyl complexes. In the ^{1}H NMR spectrum of **23**, the N-CH_2 signal is not observed, presumably due to a broadening caused by a slow rotation around the N−CH_2^{t}Bu axis. The slow rotation may also have caused the very broad signal of the *ortho*-phenylene-proton at 6.1−6.3 ppm.

The 9-fluorenone is a good substrate for the nucleophilic attack, and all the *ortho*-lithiated compounds studied in this work give the desired tertiary alcohols in good yield (61−77%) even in the absence of $CeCl_3 \cdot 2LiCl$. The resulting tertiary alcohols are not susceptible to the acid-catalyzed elimination reaction. The hydroxyl group, however, should be removed by a reduction to obtain the desired fluorenyl ligands. Iodide anion acts as a reducing agent in acetic acid, and treating a solution of the resulting tertiary alcohol in acetic acid with HI affords the desired fluorenyl ligands along with generation of I_2 (eq 3).[26]

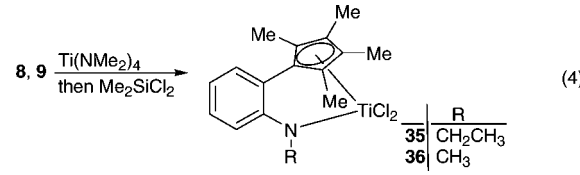


(3)

In the ^{1}H NMR spectra of **24**−**27**, two sets of very broad signals are observed in 0.74:0.26, 0.76:0.24, 0.68:0.32, and 0.71:0.29 ratios, respectively. In the ^{1}H NMR spectra of **28** and **29**, two sets of relatively sharp signals are observed in 0.94:0.06 and 0.82:0.18 ratios, respectively. The two sets of signals observed may be attributed to a rotational barrier around the (phenylene)-C−C(fluorenyl) axis. The methyl signals of *N*-alkyl in all compounds except **26** are observed abnormally upfield shifted at 0.3−0.5 ppm in the major set of signals, while the chemical shift of the corresponding −CH_3 signal is normal at ∼1.0 ppm in the minor set. The major set of signals might be assignable to structure **A** (eq 3), in which the ring current on the fluorenyl unit influences the chemical shift of the *N*-alkyl group, resulting in an upfield shift. The protonation of the fluorenyl anion, which is generated from the tertiary alcohol by electron transfers from iodide anions, may occur mainly from the side opposite the *N*-alky group, yielding predominantly the **A** isomer. The two isomers are not separable by a routine purification method of column chromatography on silica gel.

The metalations are also carried out successfully using the same method and conditions applied for the syntheses of tetramethylcyclopentadienyl and indenyl complexes. A set of sharp assignable signals is observed for the titanium complexes. For the methylamide ligand **26**, the metalation is unsuccessful. The Ti-CH_3 signals are observed at ∼0.1 and 59 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. The NCH_2 signal is broad at 4.0−4.3 ppm in ^{1}H NMR spectrum of neopentylamido complex **33** by a slow rotation around the N−CH_2^{t}Bu axis.

The tetramethylcyclopentadiene compounds **8** and **9** react with $Ti(NMe_2)_4$ to afford the desired chelated $(Me_2N)_2Ti$ complexes. The reaction rate, however, is too slow even at the boiling temperature of toluene that it takes two weeks or one month to convert all reactant to the desired product. Such reaction does not occur for the indenyl and flourenyl ligand systems **14**−**18** and **24**−**29**. The chelated $(Me_2N)_2Ti$ complexes are efficiently converted to the desired Cl_2Ti complexes through the treatment with Me_2SiCl_2 (eq 4).



(4)

X-ray Crystallographic Studies. Single crystals of fluorenyl/neopentylamido titanium complex **33** are obtained from a pentane solution at −30 °C, and the molecular structure is determined by X-ray crystallography (Figures 1). Selected bond distances and angles are summarized in Table 1 compared with those observed for Me_2Si-bridged analogue [Me_2Si-(fluorenyl)(N^{t}Bu)]$TiMe_2$.[27] A η^3-coordination of the fluorenyl is observed for the Me_2Si-bridged complex, which is inferred from the long Ti−C(peripheral) distances (2.575 and 2.573 Å). The corresponding Ti−C(peripheral) distances (2.469(3) and 2.466(3) Å) are relatively shorter in the *o*-phenylene-bridged analogue **33**, indicating that **33** adopts a η^5-coordination of the fluorenyl. The silicon atom is situated in a position that severely deviates from the cyclopentadienyl ring (angle of Si−C(bridgehead)−Flu(centroid), 154.26°) in [Me_2Si-(fluorenyl)(N^{t}Bu)]$TiMe_2$. However, the phenylene carbon (C(6)) connected with the cyclopentadienyl is not situated at such a highly strained position (angle of C(6)−C(7)−Flu(centroid), 173.25°). The Flu(centroid)−Ti−N angle observed for **33** is 108.15°, which is significantly smaller than that observed for the Me_2Si-bridged analogue (111.31°). The smaller angle implies that the reaction site is more opened from the steric blocking of the fluorenyl.

Single crystals of titanium complexes **35** and **36** are obtained from a solution in a mixture of toluene and pentane at −30 °C. The X-ray crystallographic studies confirm the structures, which are shown in Figures 2 and 3, while selected bond distances and angles are summarized in Table 2 compared with the CGC [$Me_2Si(\eta^5$-$Me_4C_5)$(N^{t}Bu)]$TiCl_2$. The Cp(centroid)−Ti−N angles (105.55° and 105.72° for **35** and **36**, respectively) are smaller than that observed for the CGC [$Me_2Si(\eta^5$-$Me_4C_5)$(N^{t}Bu)]$TiCl_2$ (107.6°).[28] The Cp(centroid)−Ti−N angle has been used as a

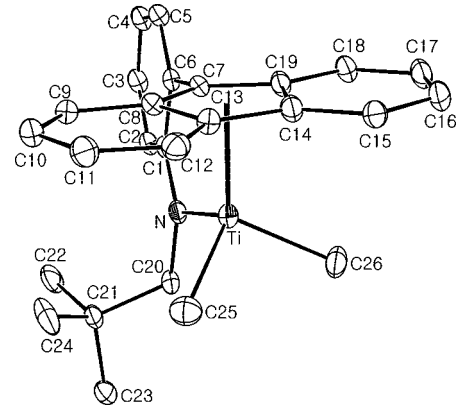


Figure 1. Thermal ellipsoid plot (30% probability level) of **33**.

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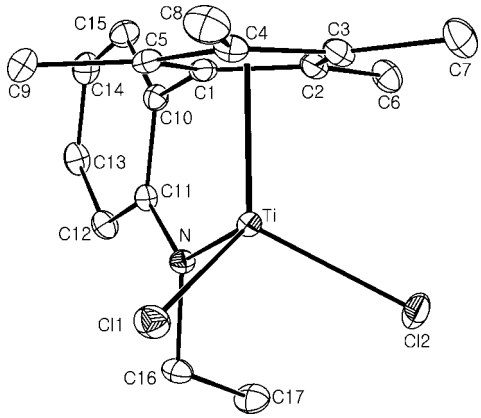

Figure 2. Thermal ellipsoid plot (30% probability level) of **35**.

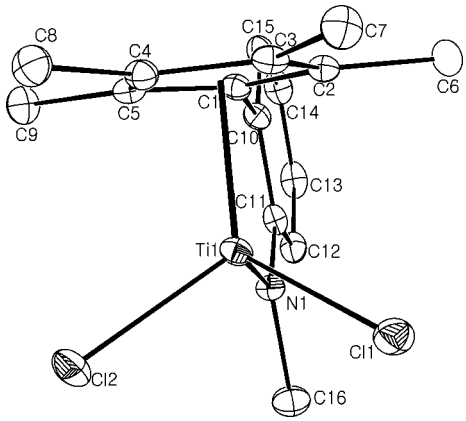

Figure 3. Thermal ellipsoid plot (30% probability level) of **36**.

Table 2. Selected Bond Distances (Å) and Angles (deg) in 33 and [Me_2Si(Fluorenyl)(N^{t}Bu)]TiMe_2

	33	[Me_2Si(fluorenyl)(N^{t}Bu)]TiMe_2[a]
Ti−N	1.943(3)	1.920(1)
Ti−C(7)	2.297(3)	2.251(2)
Ti−C(8)	2.398(3)	2.411(2)
Ti−C(19)	2.412(3)	2.414(2)
Ti−C(13)	2.469(3)	2.575
Ti−C(14)	2.466(3)	2.573
Ti−C(25)	2.102(4)	2.104(2)
Ti−C(26)	2.103(4)	2.108(2)
Ti−Flu(centroid)	2.076	2.120
Flu(centroid)−Ti−N(1)	108.15	111.31
C(6)−C(7)−Flu(centroid)	173.25	154.26[b]
C(7)−Flu(centroid)−Ti	83.87	79.20
C(25)−Ti−C(26)	100.0(2)	100.47(9)
C(1)−N−C(20)	121.0(3)	126.6(1)[c]
C(1)−N−Ti	123.3(2)	101.19(9)[d]
C(20)−N−Ti	114.6(2)	131.8(1)[e]

[a] Corresponding distances and angles, data from ref 27. [b] Si−C(bridgehead)−Flu(centroid). [c] Si−N−C(CH_3)$_3$. [d] Si−N−Ti. [e] (CH_3)$_3$C−N−Ti.

qualitative measure for "constrained geometry". The smaller the angle, the more pronounced the constrained geometry feature should be. The smaller angles observed for the *o*-phenylene-bridged complexes imply that the *o*-phenylene bridge framework provides a more constrained feature in the complexes than the Me_2Si bridge framework. The bridge atoms in the *o*-phenylene-bridged complexes are not situated in a severely strained position. The *ipso*-carbon (C(10)) on the *o*-phenylene is placed almost on the cyclopentadienyl plane (C(centroid)−C(bridgehead)−C(*ipso*) angle, 171.25° and 170.67° for **35** and **36**, respectively). The Ti−Cp(centroid) vector is situated almost perpendicularly to the cyclopentadienyl plane (Ti−Cp(centroid)−C(bridgehead) angle, 88.27° and 88.32° for **35** and **36**, respectively). On the contrary, the bridging silicon atoms in the Me_2Si-bridged CGCs are situated in a position that severely deviates from the cyclopentadienyl plane. The Cp(centroid)−C(bridgehead)−Si angles for $C_5R_4SiMe_2$(N^{t}Bu) titanium complexes are 150−154°. The Cp(centroid)−Ti distances are slightly shorter in **35** and **36** (2.002 and 2.003 Å, respectively) than the distance in the CGC (2.030 Å), while the Ti−N distances (1.9215(10) and 1.918(2) Å for **35** and **36**, respectively) are slightly longer than the distance in the CGC (1.907(4) Å). The Cl−Ti−Cl angle is wider in **35** and **36** (103.203(14)° and 104.45(4)°, respectively) than the angle observed in the CGC (102.97(7)°). The sum of the bond angles around the N atom is 360°, indicating π-donation of an electron pair on the N atom to the titanium through sp^2-hybridization.

The addition of 1 equiv of B(C_6F_5)$_3$ to a C_6D_6 solution of **11** provides a fairly clean, assignable ^{1}H NMR spectrum. Six singlet signals, one of which is broad, are observed at 0.8−1.8 ppm, which are assignable to four methyls attached on the cyclopentadienyl with one methyl attached on titanium and another on boron (eq 5). The broad one might be the methyl attached on boron. The two N-CH_2 protons are also observed separately as multiplets at 4.24 and 4.17 ppm. The layer diffusion of pentane to a toluene solution of the activated complex in a freezer (−30 °C) inside a glovebox gives two kinds of crystals. The major ones are red lumps, while the minor ones are yellow prisms, which are suitable for X-ray crystallography. The X-ray crystallographic studies of the minor crystals reveal an unexpected H_2O-reacted μ-oxo-bridged dinuclear complex. The atom attached on B(C_6F_5)$_3$ is assigned as oxygen, instead of CH_3, not only because the distance between B and the atom (1.503(2) Å) is shorter than the normally observed H_3C−B(C_6F_5)$_3$ distances (∼1.66 Å)[29] but also because the distance is close to the O−B(C_6F_5)$_3$ distances (∼1.52 Å) observed for other complexes.[30] The nitrogen atom is not an sp^2-hybride, but a nitrogen atom close to an sp^3-hybride (sum of bond angles around N, 339.87°). The Ti−N distance (2.2266(17) Å) is relatively long compared with those (1.9−2.0 Å) observed in amido titanium complexes. Thus, the nitrogen atom is assigned as a protonated neutral amine donor (eq 5). A similar protonation of an amido ligand was also observed during the formation of related μ-oxo-bridged dinuclear complexes.[31] The Ti−O(1)−Ti and B−O(2)−Ti angles (170.83(13)° and 175.32(13)°, respectively) are almost linear, indicating significant π-donation from both oxygens to the titanium center. On the basis of all these metrical features, we presume that the structure of the minor crystals is the zwitterionic one shown in eq 5, which is formed by the action of water impurity in solvents during recrystallization.

Polymerization Studies. The newly prepared complexes are screened for ethylene/1-octene copolymerization after activation with (Ph$_3$C)[B(C_6F_5)$_4$] and ^{i}Bu$_3$Al. The polymerization conditions and the results are summarized in Table 3. The indenyl complexes **19**−**23** and the fluorenyl complexes **30**−**34** show low activities (<10 × 10^6 g/molTi·h). The tetramethylcyclopentadienyl methylamido complex **12** also shows low activity, but the activity is significantly increased by changing the

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Table 3. Selected Bond Distances (Å) and Angles (deg) in 35, 36, and the CGC

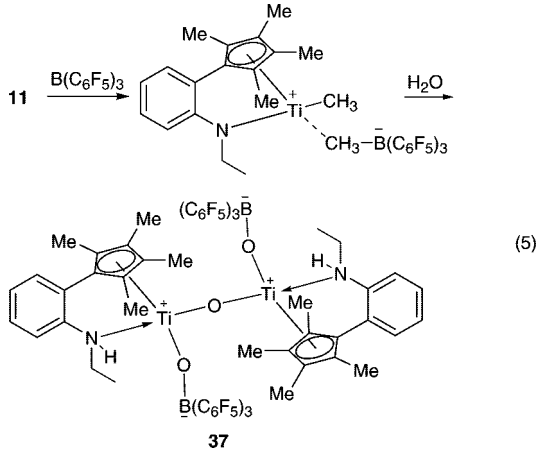
	35	36	CGC[a]
Ti−Cp(cent)	2.002	2.003	2.030
Ti−C(1) (bridgehead-C)	2.3045(11)	2.306(3)	
Ti−C(2)	2.3248(11)	2.340(3)	
Ti−C(5)	2.3324(11)	2.327(3)	
Ti−C(3) (peripheral-C)	2.3641(11)	2.363(3)	
Ti−C(4) (peripheral-C)	2.3726(12)	2.353(3)	
Ti−N	1.9215(10)	1.918(2)	1.907(4)
Ti−Cl(1)	2.2786(3)	2.2733(9)	2.2635(11)
Ti−Cl(2)	2.2779(3)	2.2725(10)	
Cp(cent)−Ti−N	105.55	105.72	107.6
Cl(1)−Ti−Cl(2)	103.203(14)	104.45(4)	102.97(7)
Cp(cent)−C(1)−C(10)	171.25	170.67	
C(1)−Cp(cent)−Ti	88.27	88.32	
Ti−N−C(11)	127.50(8)	127.27(19)	
Ti−N−C(16)	114.50(8)	115.2(2)	
C(11)−N−C(16)	117.99(10)	117.5(3)	
C(1)−C(10)−C(11)	113.60(10)	113.8(3)	
C(10)−C(11)−N	113.82(10)	114.0(3)	

[a] $[Me_2S(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$, data from ref 28.

Table 4. Ethylene/1-Octene Copolymerization Results[a]

entry	complex	time (min)	yield (g)	activity[b]	[Oct][c] (mol%)	M_w (× 10^{-3})	M_w/M_n
1	**11**	5	1.2	29	19	226	3.0
2	**12**	5	0.27	6.5	19	119	3.8
3	**13**	5	0.92	22	16	144	2.4
4	**19**	5	0.20	4.8	12	253	3.5
5	**20**	5	0.16	3.8	16	42	2.0
6	**21**	5	0.10	2.4	15	144	3.1
7	**22**	5	0.11	1.3	12	83	2.8
8	**23**	5	0.34	8.0	16	121	2.4
9	**30**	5	0.25	5.9	15	139	2.4
10	**31**	5	0.11	2.5	15	109	2.1
11	**32**	5	0.043	1.0	15	107	2.5
12	**33**	5	0.19	4.5	9	52	2.2
13	**34**	5	~0	~0			
14	**36**	5	0.40	9.5	17	129	3.4
15	**11**	2	0.62	37	21	145	2.6
16	**35**	2	0.74	45	17	115	2.8
17	CGC[d]	2	0.81	49	18	120	3.4

[a] Polymerization conditions: 30 mL of a toluene solution of 1-octene (0.30 M, 1.0 g), 0.50 μmol of Ti, 2.0 μmol of $[Ph_3C][B(C_6F_5)_4]$, 0.20 mmol of $Al(iBu)_3$, 60 psig of ethylene, initial temperature 70 °C. [b] Averaged activity in 2 or 3 runs in units of 10^6 g/molTi·h. [c] 1-Octene content in the copolymer determined by ^1H NMR. [d] $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$.



methyamido with an ethylamido ligand. Thus, the tetramethylcyclopentadienyl ethylamido complex **11** gives 1.2 g of polymer in 5.0 min (activity, 29 × 10^6 g/molTi·h; entry 1). Analysis of the ^1H NMR spectrum of the copolymer indicates 19 mol % 1-octene content, which corresponds to 58% consumption of the fed 1-octene. Because the drift of the 1-octene concentration is too high, the polymerization reaction is cut to 2 min to yield 0.62 g of copolymer (activity, 37 × 10^6 g/molTi·h; entry 15) with 21 mol % 1-octene content, which corresponds to 32% consumption of the fed 1-octene. Under the same reaction conditions, the CGC $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$ shows slightly higher activity (49 × 10^6 g/molTi·h) than **11**, while the 1-octene incorporation is slightly less (18 mol %). By changing the methyl ligands in **11** with chloro ligands, the activity is increased from 37 × 10^6 to 45 × 10^6 g/molTi·h, almost the same value observed for the CGC, while the 1-octene incorporation is reduced from 21 to 17 mol % (entry 15 versus entry 16). A similar trend is also observed for the tetramethylcyclopentadienyl methylamido complex by changing the methyl ligands with chloro ligands (entry 2 versus entry 14). A similar activity increase was also observed by changing the methyl ligands on Cp_2ZrMe_2 with chloro ligands.[32] The molecular weights of the polymers obtained with the highly active ethylamido complexes **11** and **35** are similar to that of the polymer obtained with the CGC (M_w, 120 000).

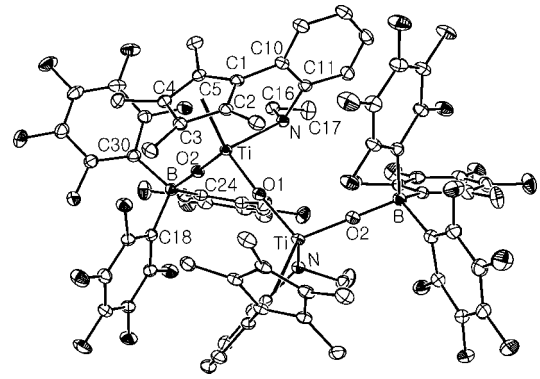


Figure 4. Thermal ellipsoid plot (30% probability level) of **37**. Selected bond distances (Å) and angles (deg): O(1)−Ti, 1.8559(4); O(2)−Ti, 1.7552(14); O(2)−B, 1.503(2); N−Ti, 2.2266(17); Cp(cent)−Ti, 2.077; Ti−O(1)−Ti, 170.83(12); B−O(2)−Ti, 175.32(13); C(11)−N−C(16), 111.47(16); C(11)−N−Ti(1), 114.91(12); C(16)−N−Ti(1), 113.49(12); Cp(cent)−Ti−N, 103.31.

Summary. The *ortho*-lithiation of *N*-alkylanilines is accomplished through the treatment of ^{t}BuLi with the lithium carbamate compounds generated in situ from the *N*-alkylanilines. The lithiated compounds are reacted with tetramethylcyclopentenone, 1-indanone, or 9-fluorenone to give tertiary alcohols, which are transformed to *N*-alkylanilines attaching a Me_4C_5, indenyl, or fluorenyl unit at an *ortho*-position. The operation can be carried out in one pot. From the compounds, various *o*-phenylene-bridged (Me_4C_5, indenyl, or fluorenyl)/amido titanium complexes are prepared in one step. The X-ray crystallographic studies reveal that the *o*-phenylene bridge provides more narrow Cp(centroid)−Ti−N angles than the Me_2Si bridge, while the elements constituting the chelate are not situated at a severely strained position. The Me_4C_5/ethylamido titanium complex exhibits a similar catalytic performance to the CGC $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$ in ethylene/1-octene copolymerization in terms of activity, molecular weight of obtained polymer, and 1-octene incorporation.

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques.

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Table 5. Crystallographic Parameters of 33, 35, 36, and 37[a]

	33	35	36	37
formula	$C_{26}H_{29}N_1Ti_1$	$C_{17}H_{21}Cl_2NTi$	$C_{16}H_{19}Cl_2$ NTi	$C_{80}H_{68}B_2F_{30}N_2O_3Ti_2$
fw	403.37	358.15	344.12	1792.78
size, mm^3	0.5 × 0.4 × 0.4	0.5 × 0.5 × 0.4	0.3 × 0.1 × 0.05	0.6 × 0.25 × 0.2
a, Å	15.263(2)	13.201	9.1152(5)	27.093
b, Å	9.5695(13)	14.920	13.6101(5)	11.969
c, Å	16.150(2)	17.373	13.2743(5)	24.561
α, deg	90	90	90	90
β, deg	113.963(4)	90	102.8805(14)	101.10
γ, deg	90	90	90	90
V, $Å^3$	2155.5(5)	1.390	1.424	7815.4
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	*Pcab*	$P2_1/c$	*C*2/*c*
D(calc), g cm^{-1}	1.206	1.390	1.424	1.524
Z	4	8	4	4
μ, mm^{-1}	0.408	0.805	0.855	0.326
no. of data collected	17 510	31 545	15 527	37 322
no. of unique data [*R*(int)]	4685 [0.1038]	3908 [0.0153]	3675 [0.0596]	8914 [0.0339]
no. of variables	369	274	257	627
R (%)	0.0714	0.0230	0.0395	0.0433
R_w (%)	0.1773	0.0626	0.0668	0.1266
goodness of fit	1.129	1.075	1.143	1.073

[a] Data collected at 233(2) K with Mo Kα radiation (λ(Kα) = 0.7107Å), $R(F) = \sum|F_o| - |F_c|/\sum|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

Diethyl ether, THF, and C_6D_6 were distilled from benzophenone ketyl. Toluene (anhydrous grade) and 1-octene used for the polymerization reactions were purchased from Aldrich and purified over Na/K alloy. Ethylene was purchased from Conley Gas (99.0%) and purified by contacting with molecular sieves and copper for one day under a pressure of 200 psig. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out at the Analytical Center, Kyunghee University. High-resolution mass spectra were obtained at Korea Basic Science Institute (Daegu, Korea). Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using a Waters model 150-C+ GPC, and the data were analyzed using a polystyrene analyzing curve.

Representative Procedure for the *ortho*-Lithiation. At −78 °C, ^{n}BuLi (1.2 mL, 3.0 mmol, 2.5 M solution in hexane) was added dropwise to a solution of *N*-ethylaniline (0.36 g, 3.0 mmol) in diethyl ether (4.5 mL). After the solution was stirred for 1 h at −78 °C, it was allowed to warm to room temperature. A white solid precipitated and butane gas was evolved. The gas was removed through a bubbler. The solution was cooled again to −78 °C, and the white solid disappeared immediately after CO_2 gas was added. After the solution was stirred for 40 min at −78 °C, the temperature was slowly raised to −20 °C while excess CO_2 gas was removed through the bubbler. Then, THF (0.24 g, 3.3 mmol) and ^{t}BuLi (1.9 mL, 3.3 mmol, 1.7 M solution in pentane) were successively added at −20 °C, and the solution was stirred for 2 h at −20 °C. The lithiated compound was quenched by addition of D_2O. The ^{1}H NMR spectrum of the organic phase shows a decrease of the intensity of the *ortho*-proton signal from 1.0 to 0.14, indicating an 86% *ortho*-lithiation yield.

Compound 8. To the *ortho*-lithiated compound of *N*-ethylaniline (0.960 g, 7.89 mmol) prepared using ^{n}BuLi (3.2 mL, 7.9 mmol, 2.5 M solution in hexane) and ^{t}BuLi (5.1 mL, 8.7 mmol, 1.7 M solution in pentane) was added 2,3,4,5-tetramethyl-2-cyclopentenone (0.927 g, 6.71 mmol) dissolved in THF containing $CeCl_3 \cdot 2LiCl$ (21 mL, 0.33 M). The solution was stirred for 1 h at −20 °C. After the solution was slowly warmed to room temperature for 1 h, water (20 mL) was added to generate a white gel, which was filtered over Celite. The filtrate was extracted using ethyl acetate (3 × 20 mL). Then, the organic phases were combined and transferred to a separatory funnel. After aqueous HCl (2 N, 45 mL) was added, the separatory funnel was shaken vigorously for 2 min. Aqueous saturated $NaHCO_3$ (70 mL) was carefully added to neutralize the water phase. The organic phase was collected and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). The product was obtained as a yellow oil (0.76 g, 47%). IR (neat): 3402 (N−H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.22 (td, J = 7.6,1.2 Hz, 1H, Ph-H), 7.05 (dd, J = 7.2, 1.2 Hz, 1H, Ph-H), 6.81 (td, J = 7.2, 0.8 Hz, 1H, Ph-H), 6.64 (t, J = 8.4 Hz, 1H, Ph-H), 3.72 (br, 1H, NH), 3.12−2.96 (m, 1H, Cp-CH), 2.96−2.79 (m, 2H, CH_2), 1.83 (s, 3H, Cp-CH_3), 1.79 (d, J = 2.0 Hz, 3H, Cp-CH_3), 1.78 (s, 3H, Cp-CH_3), 1.04−0.94 (m, 3H, Cp-CH_3), 0.92−0.88 (m, 3H, CH_3) ppm. HRMS (EI): *m*/*z* calcd for ($[M]^+$ $C_{17}H_{23}N$) 241.1830, found 241.1831.

Compound 9. The compound was synthesized using the same conditions and procedure as those for **8** from *N*-methylaniline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 40:1). A light yellow oil was obtained in 35% yield. IR (neat): 3410 (N−H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.26 (td, J = 7.6, 1.6 Hz, 1H, Ph-H), 7.06 (dd, J = 7.6, 1.6 Hz, 1H, Ph-H), 6.85 (td, J = 7.6, 1.2 Hz, 1H, Ph-H), 6.60 (d, J = 8.0 Hz, 1H, Ph-H), 3.72 (br, 1H, NH), 3.09−2.87 (m, 1H, Cp-CH), 2.48−2.32 (m, 3H, CH_3), 1.83 (s, 3H, Cp-CH_3), 1.78 (s, 3H, Cp-CH_3), 1.75 (d, J = 2.0 Hz, 3H, Cp-CH_3), 1.08−0.87 (m, 3H, Cp-CH_3) ppm. HRMS (EI): *m*/*z* calcd for ($[M]^+$ $C_{16}H_{21}N$) 227.1674, found 227.1671.

Compound 10. The compound was synthesized using the same conditions and procedure as those for **8** from *N*-ethyl-4-methylaniline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). A light yellow oil was obtained in 37% yield. IR (neat): 3406 (N−H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.07 (d, J = 8.0 Hz, 1H, Ph-H), 6.91 (s, 1H, Ph-H), 6.63 (d, J = 8.0 Hz, 1H, Ph-H), 3.68 (br, 1H, NH), 3.09−2.81 (m, 3H, Cp-CH and CH_2), 2.29 (s, 3H, *p*-CH_3), 1.84 (s, 3H, Cp-CH_3), 1.83 (d, J = 1.6 Hz, 3H, Cp-CH_3), 1.78 (s, 3H, Cp-CH_3), 1.08−1.01(m, 3H, Cp-CH_3), 0.95−0.82 (m, 3H, CH_2CH_3)-ppm. HRMS (EI): *m*/*z* calcd for ($[M]^+$ $C_{18}H_{25}N$) 255.1987, found 255.1991.

Complex 11. MeLi (4.45 g, 9.84 mmol, 2.21 mmol/g in diethyl ether) was added dropwise to a stirred solution of **8** (0.594 g, 2.46 mmol) in cold diethyl ether (−30 °C). The solution was stirred overnight at room temperature. The resulting solution was cooled to −30 °C, and $TiCl_4 \cdot DME$ (0.688 g, 2.46 mmol) was added in one portion. After the solution was stirred for 3 h at room temperature, solvent was removed under vacuum. Pentane was then added, and the solution was filtered over Celite. The removal of

the solvent gave a red solid (0.51 g, 65%), which was pure enough to be used for the polymerization. Analytically pure complex was obtained by recrystallization in pentane at −30 °C. ^{1}H NMR (C_6D_6): δ 7.18 (t, J = 7.6 Hz, 1H, Ph-H), 7.12 (d, J = 7.6 Hz, 1H, Ph-H), 6.88 (t, J = 7.6 Hz, 1H, Ph-H), 6.27 (d, J = 8.4 Hz, 1H, Ph-H), 4.48 (quartet, J = 6.8 Hz, 2H, NCH_2), 2.03 (s, 6H, Cp-CH_3), 1.58 (s, 6H, Cp-CH_3), 1.22 (t, J = 7.2 Hz, 3H, CH_3), 0.56 (s, 6H, Ti-CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 163.40, 136.08, 131.23, 129.27, 129.05, 128.96, 128.90, 128.70, 121.12, 119.82, 108.60, 50.89, 41.29, 14.14, 12.09, 12.03 ppm. Anal. Calc ($C_{19}H_{27}NTi$): C, 71.92; H, 8.58; N, 4.41. Found: C, 72.18; H, 8.21; N, 4.57.

Complex 12. The complex was synthesized using the same conditions and procedure as those for **11** from **9**. The product was obtained as a red solid in 86% yield. ^{1}H NMR (C_6D_6): δ 7.25 (td, J = 8.8, 0.8 Hz, 1H, Ph-H), 7.12 (dd, J = 7.2, 1.2 Hz, 1H, Ph-H), 6.92 (t, J = 7.6 Hz, 1H, Ph-H), 6.24 (d, J = 8.4 Hz, 1H, Ph-H), 3.73 (s, 3H, CH_3), 2.02 (s, 6H, Cp-CH_3), 1.57 (s, 6H, Cp-CH_3), 0.58 (s, 6H, $TiCH_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 165.27, 136.22, 131.22, 128.91, 128.87, 128.61, 121.12, 120.07, 108.09, 51.08, 35.46, 12.10, 12.03 ppm. Anal. Calc ($C_{18}H_{25}NTi$): C, 71.29; H, 8.31; N, 4.62. Found: C, 71.51; H, 8.59; N, 4.42.

Complex 13. The complex was synthesized using the same conditions and procedure as those for **11** from **10**. The product was obtained as a red solid in 85% yield. ^{1}H NMR (C_6D_6): δ 7.01 (dd, J = 8.8, 0.8 Hz, 1H, Ph-H), 6.98 (d, J = 1.2 Hz, 1H, Ph-H), 6.22 (d, J = 8.4 Hz, 1H, Ph-H), 4.52 (quartet, J = 6.8 Hz, 2H, CH_2), 2.26 (s, 3H, p-CH_3), 2.06 (s, 6H, Cp-CH_3), 1.63 (s, 6H, Cp-CH_3), 1.24 (t, J = 6.8 Hz, 3H, CH_3), 0.54 (s, 6H, $TiCH_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 161.10, 135.83, 131.19, 130.04, 129.69, 129.29, 129.20, 129.08, 128.78, 120.96, 108.32, 50.39, 41.44, 21.06, 14.22, 12.12, 12.10 ppm. Anal. Calc ($C_{20}H_{29}NTi$): C, 72.50; H, 8.82; N, 4.23. Found: C, 72.79; H, 8.59; N, 4.42.

Compound 14. To the *ortho*-lithiated compound of *N*-ethylaniline (1.02 g, 8.42 mmol) prepared using diethyl ether (11 mL), ^{n}BuLi (3.4 mL, 8.4 mmol, 2.5 M solution in hexane), THF (0.67 g, 9.3 mmol), and ^{t}BuLi (5.5 mL, 9.3 mmol, 1.7 M solution in pentane) was added 1-indanone (0.946 g, 7.16 mmol) dissolved in THF containing $CeCl_3 \cdot 2LiCl$ (22 mL, 0.33 M). The solution was stirred for 1 h at −20 °C. After the solution was slowly warmed to room temperature for 1 h, water (20 mL) was added to generate a white gel, which was filtered over Celite. The filtrate was extracted using ethyl acetate (3 × 20 mL). The organic phases were then combined and transferred to a separatory funnel. After aqueous HCl (6 N, 20 mL) was added, the separatory funnel was shaken vigorously for 2 min. Aqueous saturated NaOH (5 M, 25 mL) was carefully added to neutralize the water phase, then the organic phase was collected and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The product was obtained as a yellow oil (0.64 g, 38%). IR (neat): 3418 (N−H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.40−7.38 (m, 1H), 7.35 (dd, J = 7.6, 1.6 Hz, 1H), 7.32−7.27 (m, 2H), 7.18−7.13 (m, 2H), 6.85 (td, J = 7.2, 1.2 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H, Ph-H), 6.38 (t, J = 1.6 Hz, 1H, indenyl-H), 3.83 (br s, 1H, NH), 3.16 (d, J = 2.0 Hz, 2H, indenyl-CH_2), 2.85−2.76 (m, 2H, CH_2), 0.78 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 146.35, 144.68, 144.51, 143.70, 132.36, 130.27, 129.41, 126.57, 125.40, 124.24, 121.49, 121.40, 116.91, 110.70, 38.75, 38.56, 14.79 ppm. HRMS (EI): m/z calcd for ([M]$^+$ $C_{17}H_{17}N$) 235.1361, found 235.1364.

Compound 15. The compound was synthesized using the same conditions and procedure as those for **14** from *N*-butylaniline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). A yellow oil was obtained in 29% yield. IR (neat): 3421 (N−H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.40 (dd, J = 6.0, 1.6 Hz, 1H), 7.35 (dd, J = 8.0, 2.0 Hz, 1H), 7.33−7.28 (m, 2H), 7.19−7.11 (m, 2H), 6.84 (td, J = 7.2, 1.2 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.39 (t, J = 1.6 Hz, 1H, indenyl-H), 3.90 (br, 1H, NH), 3.18 (d, J = 1.6 Hz, 2H, indenyl-CH_2), 2.84 (t, J = 7.2 Hz, 2H, CH_2), 1.24−1.16 (m, 2H, CH_2), 1.14−1.02 (m, 2H, CH_2), 0.72 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 146.46, 144.68, 144.49, 143.78, 132.31, 130.26, 129.41, 126.55, 125.41, 124.23, 121.46, 116.81, 110.67, 43.86, 38.77, 31.79, 20.72, 14.18 ppm. HRMS (EI): m/z calcd for ([M]$^+$ $C_{19}H_{21}N$) 263.1674, found 263.1677.

Compound 16. The compound was synthesized using the same conditions and procedure as those for **14** from *N*-methylaniline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 40:1). A yellow oil was obtained in 37% yield. IR (neat): 3421 (N−H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.42−7.25 (m, 4H), 7.15 (t, J = 6.4 Hz, 2H), 6.84 (t, J = 7.2 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.33 (br, 1H, indenyl-H), 3.76 (br, 1H, NH), 3.18 (br, 2H, indenyl-CH_2), 2.32 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 147.23, 144.75, 144.44, 143.50, 132.39, 130.02, 129.42, 126.64, 125.38, 124.19, 121.36, 116.87, 110.07, 38.74, 30.52 ppm. HRMS (EI): m/z calcd for ([M]$^+$ $C_{16}H_{15}N$) 221.1204, found 221.1201.

Compound 17. The compound was synthesized using the same conditions and procedure as those for **14** from *N*-ethyl-4-methylaniline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 40:1). A yellow oil was obtained in 35% yield. IR (neat): 3411 (N−H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.44 (dd, J = 6.4, 2.0 Hz, 1H), 7.33 (dd, J = 6.8, 0.8 Hz, 1H), 7.20−7.10 (m, 4H), 6.67 (d, J = 8.0 Hz, 1H), 6.40 (t, J = 1.6 Hz, 1H, indenyl-H), 3.71 (br, 1H, NH), 3.20 (d, J = 2.4 Hz, 2H, indenyl-CH_2), 2.86 (quartet, J = 7.2 Hz, 2H, CH_2), 2.27 (s, 3H, p-CH_3), 0.82 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 144.80, 144.50, 144.28, 143.90, 132.22, 130.94, 129.84, 126.56, 125.50, 125.37, 124.22, 121.65, 121.41, 111.00, 38.91, 38.75, 20.82, 14.92 ppm. HRMS (EI): m/z calcd for ([M]$^+$ $C_{18}H_{19}N$) 249.1517, found 249.1516.

Compound 18. The compound was synthesized using the same conditions and procedure as those for **14** from *N*-neopentylaniline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). A yellow oil was obtained in 18% yield. IR (neat): 3431 (N−H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.41 (dd, J = 7.2, 1.6 Hz, 1H), 7.36 (dd, J = 7.6, 1.6 Hz, 1H), 7.33−7.27 (m, 2H), 7.18−7.08 (m, 2H), 6.85 (td, J = 7.2, 0.8 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.39 (t, J = 2.0 Hz, 1H, indenyl-H), 4.05 (br, 1H, NH), 3.18 (d, J = 1.6 Hz, 2H, indenyl-CH_2), 2.74 (d, J = 5.2 Hz, 2H, CH_2), 0.73 (s, 9H, $C(CH_3)_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 146.89, 144.55, 144.41, 143.78, 132.30, 130.18, 129.40, 126.54, 125.44, 124.20, 121.55, 121.52, 116.79, 110.72, 55.91, 38.74, 31.99, 27.82 ppm. HRMS (EI): m/z calcd for ([M]$^+$ $C_{20}H_{23}N$) 277.1830, found 277.1827.

Complex 19. The complex was synthesized using the same conditions and procedure as for **11** from **14**. The product was obtained as a red oil in 63% yield. The crude product was tolerably pure from the analysis of the ^{1}H and ^{13}C NMR spectra and was used for the polymerization without further purification. ^{1}H NMR (C_6D_6): δ 7.46 (d, J = 8.4 Hz, 1H), 7.26 (d, J = 7.2 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.88 (t, J = 6.8 Hz, 1H), 6.66 (t, J = 7.6 Hz, 1H), 6.63 (d, J = 2.8 Hz, 1H, indenyl-H), 6.26 (d, J = 8.0 Hz, 1H), 6.21 (d, J = 3.6 Hz, 1H, indenyl-H), 4.49−4.34 (m, 2H, NCH_2), 1.19 (t, J = 6.8 Hz, 3H, CH_3), 0.82 (s, 3H, $TiCH_3$), −0.07 (s, 3H, $TiCH_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 164.32, 134.70, 129.64, 129.16, 129.10, 128.73, 127.22, 125.72, 125.38, 125.36, 125.03, 123.05, 120.08, 108.49, 103.86, 58.55, 55.03, 41.66, 13.82 ppm.

Complex 20. The complex was synthesized using the same conditions and procedure as for **11** from **15**. The product was obtained as a red oil in 85% yield. The crude product was tolerably pure from the analysis of the ^{1}H and ^{13}C NMR spectra and was used for the polymerization without further purification. ^{1}H NMR

(C_6D_6): δ 7.47 (d, J = 8.4 Hz, 1H), 7.28 (dd, J = 7.2, 1.2 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.94−6.88 (m, 2H), 6.68 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 3.6 Hz, 1H, indenyl-H), 6.36 (d, J = 8.0 Hz, 1H), 6.23 (d, J = 3.6 Hz, 1H, indenyl-H), 4.39−4.12 (m, 2H, NCH_2), 1.84−1.72 (m, 1H, CH_2), 1.71−1.59 (m, 1H, CH_2), 1.38−1.27 (m, 2H, CH_2), 0.98−0.78 (m, 3H, CH_3), 0.86 (s, 3H, $TiCH_3$), −0.03 (s, 3H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 164.67, 134.68, 129.65, 129.12, 128.69, 127.25, 125.73, 125.41, 125.37, 125.04, 123.06, 120.10, 108.61, 104.04, 58.68, 55.11, 47.71, 30.86, 21.38, 14.34 ppm.

Complex 21. The complex was synthesized using the same conditions and procedure as for **11** from **16**. The product was obtained as a red oil in 43% yield. The crude product was tolerably pure from the analysis of the ^1H and ^{13}C NMR spectra and was used for the polymerization without further purification. ^1H NMR (C_6D_6): δ 7.45 (d, J = 8.4 Hz, 1H), 7.27 (dd, J = 7.6, 1.2 Hz, 1H), 7.26 (td, J = 6.8, 1.2 Hz, 1H), 6.98 (td, J = 7.6, 0.8 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.89 (dd, J = 8.4, 1.2 Hz, 1H), 6.65 (td, J = 8.0, 1.2 Hz, 1H), 6.60 (d, J = 3.2 Hz, 1H, indenyl-H), 6.22 (d, J = 8.8 Hz, 1H), 6.21 (d, J = 3.2 Hz, 1H, indenyl-H), 3.67 (s, 3H, CH_3), 0.82 (s, 3H, $TiCH_3$), −0.03 (s, 3H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 166.16, 134.87, 129.39, 129.27, 129.23, 129.05, 128.35, 127.17, 125.75, 125.38, 125.19, 123.12, 120.32, 108.08, 103.68, 58.80, 55.32, 35.81 ppm.

Complex 22. The complex was synthesized using the same conditions and procedure as for **14** from **17**. The product was obtained as a red solid in 53% yield. ^1H NMR (C_6D_6): δ 7.57 (d, J = 8.4 Hz, 1H), 7.25 (s, 1H, Ph-H), 7.14 (d, J = 6.8 Hz, 1H), 7.08 (t, J = 8.4 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.77 (t, J = 6.8 Hz, 1H), 6.74 (d, J = 3.2 Hz,1H, indenyl-H), 6.34 (d, J = 3.2 Hz, 1H, indenyl-H), 6.30 (d, J = 8.0 Hz, 1H), 4.53 (quartet, J = 6.8 Hz, 2H, NCH_2), 2.35 (s, 3H, p-CH_3), 1.30 (t, J = 6.8 Hz, 3H, CH_3), 0.91 (s, 3H, $TiCH_3$), 0.01 (s, 3H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 162.05, 134.67, 130.53, 129.40, 129.15, 129.03, 128.88, 127.20, 125.63, 125.38, 125.29, 125.02, 123.05, 108.18, 103.72, 57.91, 54.34, 41.80, 20.92, 13.89 ppm. Anal. Calc ($C_{20}H_{23}NTi$): C, 73.85; H, 7.13; N, 4.31. Found: C, 74.14; H, 6.75; N, 4.49.

Complex 23. The complex was synthesized using the same conditions and procedure as for **11** from **18**. The product was obtained as a red oil in 59% yield. The crude product was tolerably pure from the analysis of the ^1H and ^{13}C NMR spectra and was used for the polymerization without further purification. ^1H NMR (C_6D_6): δ 7.46 (d, J = 8.4 Hz, 1H), 7.24 (dd, J = 7.6, 0.8 Hz, 1H), 7.16 (td, J = 8.0, 2.0 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 6.97 (td, J = 7.6, 1.2 Hz, 1H), 6.82 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.68 (t, J = 7.6 Hz, 1H), 6.48 (d, J = 8.0 Hz, 1H), 6.21 (br, 1H), 4.98−3.82 (m, 2H, NCH_2), 0.98 (s, 9H, $C(CH_3)_3$), 0.89 (s, 3H, $TiCH_3$), 0.03 (s, 3H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 164.36, 132.79, 129.47, 128.34, 127.33, 127.08, 125.48, 125.35, 123.43, 119.81, 116.03, 110.03, 61.09, 58.98, 57.20, 36.80, 30.82 ppm.

Compound 24. To the *ortho*-lithiated compound of *N*-ethylaniline (0.934 g, 7.71 mmol) prepared using diethyl ether (10 mL), ^{n}BuLi (3.1 mL, 7.7 mmol, 2.5 M solution in hexane), THF (0.61 g, 8.5 mmol), and ^{t}BuLi (5.0 mL, 8.5 mmol, 1.7 M solution in pentane) was added 9-fluorenone (1.18 g, 6.55 mmol) dissolved in THF (8 mL) at −20 °C. After the solution was stirred for 1 h at −20 °C, it was slowly warmed to room temperature for another hour. After water (20 mL) was added, the mixture was transferred to a separatory funnel containing ethyl acetate (20 mL). The organic phase was collected, and the aqueous phase was extracted with additional ethyl acetate (3 × 20 mL). The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). A yellow solid was obtained (1.52 g, 77%). The solid was dissolved in glacial acetic acid (90 mL), and HI (5.86 g, 24.9 mmol, 55 wt %) was added. After the solution was refluxed for 2 h, it was cooled to room temperature. Aqueous $Na_2S_2O_3$ solution was added to reduce the generated I_2. Then, the solution was extracted with diethyl ether (3 × 60 mL). The collected organic phase was washed with aqueous KOH solution (1 N) and dried over anhydrous $MgSO_4$. This was followed by the removal of the solvent using a rotary evaporator to give a residue, which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). A yellow solid was obtained (0.85 g, 59%). In the ^1H NMR spectrum, two sets of broad signals were observed in a 0.74:0.26 ratio. Observation of the two sets of signals is attributed to a rotational barrier around (phenylene)C−C(fluorenyl). Mp: 83−85 °C. IR (neat): 3427 (N−H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.64 (d, J = 7.2 Hz, 2H, fluorenyl-H), 7.42−7.36 (br, 0.52 H, fluorenyl-H), 7.32 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1.48H, fluorenyl-H), 7.21 (t, J = 7.2 Hz, 2H, fluorenyl-H), 7.04 (d, J = 6.8 Hz, 2H, fluorenyl-H), 7.03 (t, J = 7.6 Hz, 0.74H, Ph-H), 6.89 (t, J = 7.2 Hz, 0.74H, Ph-H), 6.74−6.67 (br, 0.26H, Ph-H), 6.65−6.58 (br, 0.26H, Ph-H), 6.52−6.44 (br, 0.26H), 6.41 (d, J = 7.6 Hz, 0.74 Hz, Ph-H), 4.88 (br s, 0.26H, fluorenyl-CH), 4.81 (s, 0.74H, fluorenyl-CH), 3.80 (br s, 0.26H, NH), 2.90 (br, 0.52H, CH_2), 2.44 (br, 0.74H, NH), 2.40−2.22 (m, 1.48H, CH_2), 1.02 (br, 0.78H, CH_3), 0.32 (t, J = 6.4 Hz, 2.22H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.17, 146.72, 146.38, 141.58, 140.62, 133.25, 129.01, 127.86, 127.70, 126.11, 125.41, 123.84, 120.05, 118.10, 116.72, 111.75, 55.37, 48.29, 39.04, 38.09, 15.22, 14.17 ppm. Anal. Calc ($C_{21}H_{19}N$): C, 88.38; H, 6.71; N, 4.91. Found: C, 88.12; H, 6.98; N, 5.02.

Compound 25. The compound was synthesized using the same conditions and procedure as those for **24** from *N*-butylaniline. The intermediate tertiary alcohol was isolated in 76% yield by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The yield for the second reduction step was 86%. Two sets of broad signals were observed in a 0.76:0.24 ratio in the ^1H NMR spectrum. Mp: 86−88 °C. IR (neat): 3424 (N−H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.65 (d, J = 7.6 Hz, 2H, fluorenyl-H), 7.42−7.36 (m, 0.48H, fluorenyl-H), 7.33 (d, J = 6.8 Hz, 1.52H), 7.25 (d, J = 7.2 Hz, 1H, Ph-H), 7.22 (t, J = 7.2 Hz, 1H, Ph-H), 7.21(t, J = 7.2 Hz, 2H, fluorenyl-H), 7.04 (t, J = 7.2 Hz, 2H, fluorenyl-H), 6.89 (t, J = 7.2 Hz, 0.76H, Ph-H), 6.78−6.71 (br, 0.24H, Ph-H), 6.66−6.59 (br, 0.24H, Ph-H), 6.43 (d, J = 8.0 Hz, 0.76 Hz, Ph-H), 4.88 (s, 0.24H, fluorenyl-CH), 4.81 (s, 0.76H, fluorenyl-CH), 3.82 (br, 0.24H, NH), 3.06(br, 0.48H, CH_2), 2.52 (br s, 0.76H, NH), 2.38 (quartet, J = 5.6 Hz, 1.52H, CH_2), 1.42 (br, 0.48H, CH_2), 1.24 (br, 0.48H, CH_2), 0.89 (br, 0.72H, CH_3), 0.80−0.71 (m, 1.52H, CH_2), 0.62−0.49 (m, 3.8H, CH_2 and CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.66, 146.42, 140.61, 133.28, 129.03, 127.86, 127.67, 125.41, 123.65, 120.02, 116.50, 111.35, 55.44, 42.79, 31.15, 19.90, 14.04 ppm. Anal. Calc ($C_{23}H_{23}N$): C, 88.13; H, 7.40; N, 4.47. Found: C, 88.51; H, 7.19; N, 4.78.

Compound 26. The compound was synthesized using the same conditions and procedure as for **24** from *N*-methylaniline. The intermediate tertiary alcohol was isolated in 76% yield by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The yield for the second reduction step was 86%. Two sets of broad signals were observed in a 0.62:0.38 ratio in the ^1H NMR spectrum. Mp: 118−120 °C. IR (neat): 3414 (N−H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.65 (d, J = 7.6 Hz, 2H, fluorenyl-H), 7.38−7.34 (br, 0.76H, fluorenyl-H), 7.32 (d, J = 6.0 Hz, 1.24H), 7.23 (d, J = 7.2 Hz, 1H, Ph-H), 7.21 (t, J = 7.2 Hz, 2H, fluorenyl-H), 7.05 (d, J = 7.2 Hz, 2H, fluorenyl-H), 7.02 (br, 0.62H, Ph-H), 6.90 (t, J = 7.2 Hz, 0.62H, Ph-H), 6.67 (br, 0.38H, Ph-H), 6.59 (br, 0.38H, Ph-H), 6.52−6.42 (br, 0.38 Hz, Ph-H), 6.36 (d, J = 7.2 Hz, 0.62H,

Ph-H), 4.79 (s, 1H, fluorenyl-CH), 3.71 (br, 0.38H, NH), 2.62 (br, 0.62H, NH), 2.54 (s, 1.14H, CH_3), 1.84 (s, 1.86H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.17, 147.45, 146.23, 140.44, 134.26, 133.32, 129.09, 127.86, 127.56, 125.61, 125.29, 124.38, 123.63, 120.20, 118.16, 116.76, 110.99, 55.43, 48.24, 31.14, 30.16 ppm. Anal. Calc ($C_{20}H_{17}N$): C, 88.52; H, 6.31; N, 5.16. Found: C, 88.22; H, 6.65; N, 4.78.

Compound 27. The compound was synthesized using the same conditions and procedure as those for **24** from *N*-ethyl-4-methylaniline. The intermediate tertiary alcohol was isolated in 61% yield by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The yield for the second reduction step was 75%. Two sets of broad signals were observed in a 0.71:0.29 ratio in the ^1H NMR spectrum. Mp: 124−126 °C. IR (neat): 3421 (N−H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.77 (d, J = 7.6 Hz, 2H, fluorenyl-H), 7.54 (br, 0.58H, fluorenyl-H), 7.40 (d, J = 7.2 Hz, 1.42H, fluorenyl-H), 7.34 (t, J = 7.2 Hz, 2H, fluorenyl-H), 7.28 (s, 0.71H, Ph-H), 7.19 (d, J = 7.6 Hz, 0.71H, Ph-H), 7.18 (t, J = 7.6 Hz, 2H, fluorenyl-H), 7.08 (br, 0.29H, Ph-H), 6.82 (br d, J = 7.2 Hz, 0.29H, Ph-H), 6.64 (br, 0.29H, Ph-H), 6.51 (d, J = 7.6 Hz, 0.71H, Ph-H), 5.08 (s, 0.29H, fluorenyl-CH), 4.95 (s, 0.71H, fluorenyl-CH), 3.80 (br, 0.29H, NH), 3.14 (br, 0.58H, CH_2), 2.52−2.34(m, 4.26H, CH_2 and *P*-CH_3 and NH), 1.94 (s, 0.87H, *p*-CH_3), 1.17 (br, 0.87H, CH_3), 0.46 (t, J = 6.4 Hz, 2.13H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.63, 144.69, 140.70, 134.02, 129.39, 128.74, 127.85, 127.67, 127.06, 125.59, 125.41, 125.27, 124.07, 120.07, 112.17, 55.44, 48.39, 39.46, 38.46, 20.94, 20.56, 15.35, 14.28 ppm. Anal. Calc ($C_{22}H_{21}N$): C, 88.25; H, 7.07; N, 4.68. Found: C, 88.65; H, 6.69; N, 4.81.

Compound 28. The compound was synthesized using the same conditions and procedure as those for **24** from *N*-neopentylaniline. The intermediate tertiary alcohol was isolated in 68% yield by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The yield for the second reduction step was 72%. Two sets of broad signals were observed in 0.94:0.06 ratio in the ^1H NMR spectrum. Mp: 134−135 °C. IR (neat): 3427 (N−H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.65 (d, J = 8.0 Hz, 2H, fluorenyl-H), 7.34 (dd, J = 7.6, 1.6 Hz, 1H, Ph-H), 7.27 (td, J = 7.6, 1.6 Hz, 1H, Ph-H), 7.25−7.18 (m, 4H, fluorenyl-H), 7.05 (td, J = 7.6, 0.8 Hz, 2H, fluorenyl-H), 6.90 (td, J = 7.2, 1.2 Hz, 1H, Ph-H), 6.45 (d, J = 8.0 Hz, 1 Hz, Ph-H), 5.12 (s, 0.06H, fluorenyl-CH), 4.81 (s, 0.94H, fluorenyl-CH), 4.14 (br, 0.06H, NH), 2.88 (br, 0.12H, CH_2), 2.58 (br, 0.94H, NH), 2.27 (d, J = 5.6 Hz, 1.88H, CH_2), 0.92 (s, 0.54H, $C(CH_3)_3$), 0.34 (s, 8.46H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.70, 146.46, 140.62, 133.39, 129.06, 127.88, 127.71, 125.35, 123.65, 120.23, 116.46, 111.04, 55.54, 55.36, 30.85, 27.29 ppm. Anal. Calc ($C_{24}H_{25}N$): C, 88.03; H, 7.70; N, 4.28. Found: C, 87.92; H, 7.32; N, 4.61.

Compound 29. The compound was synthesized using the same conditions and procedure as those for **24** from *N*-isopropylaniline. The intermediate tertiary alcohol was isolated in 61% yield by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The yield for the second reduction step was 72%. Two sets of broad signals were observed in a 0.82:0.18 ratio in the ^1H NMR spectrum. Mp: 81−82 °C. IR (neat): 3427 (N−H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.63 (d, J = 7.2 Hz, 2H, fluorenyl-H), 7.40−7.32 (br, 0.36H, fluorenyl-H), 7.32 (d, J = 7.2 Hz, 1H, Ph-H), 7.26−7.16 (m, 3.64H, fluorenyl-H), 7.05 (d, J = 7.2 Hz, 2H, fluorenyl-H), 7.04 (t, J = 7.2 Hz, 0.82H, Ph-H), 6.86 (t, J = 7.6 Hz, 0.82H, Ph-H), 6.73 (br, 0.18H, Ph-H), 6.60 (br, 0.18H, Ph-H), 6.48 (br, 0.18H, Ph-H), 6.45 (d, J = 8.0 Hz, 0.82 Hz, Ph-H), 4.94 (s, 0.18H, fluorenyl-CH), 4.79 (s, 0.82H, fluorenyl-CH), 3.83 (br, 0.18 H, NH), 3.57 (br, 0.18 H, CH), 2.99 (septet, J = 6.4 Hz, 0.82H, CH), 2.40 (d, J = 7.2 Hz, 0.82H, NH), 1.09 (br, 1.08 H, $CH(CH_3)_2$), 0.43 (d, J = 6.0 Hz, 4.92H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.49, 145.88, 140.68, 133.47, 128.92, 127.69, 125.54, 124.15, 119.97, 116.46, 112.57, 55.39, 43.76, 22.45 ppm. Anal. Calc ($C_{22}H_{21}N$): C, 88.25; H, 7.07; N, 4.68. Found: C, 87.92; H, 7.32; N, 4.61.

Complex 30. The complex was synthesized using the same conditions and procedure as those for **11** from **24**. A red solid was obtained in 65% yield. ^1H NMR (C_6D_6): δ 7.91 (dd, J = 8.4, 1.2 Hz, 2H, fluorenyl-H), 7.37 (dd, J = 7.6, 1.6 Hz, 1H, Ph-H), 7.30 (td, J = 7.2, 1.2 Hz, 1H, Ph-H), 7.08−7.03(m, 4H, fluorenyl-H), 6.95 (td, J = 7.6, 0.8 Hz, 1H, ph-H), 6.86 (td, J = 7.6, 0.8 Hz, 2H, fluorenyl-H), 6.29 (d, J = 8.0 Hz, 1H, ph-H), 4.12 (quartet, J = 7.2 Hz, 2H, NCH_2), 1.12 (t, J = 7.2 Hz, 3H, CH_3), 0.08 (s, 6H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 163.29, 136.78, 131.47, 129.37, 127.87, 127.40, 126.13, 123.87, 123.31, 120.02, 118.82, 107.82, 59.35, 40.62, 13.71 ppm. Anal. Calc ($C_{23}H_{23}NTi$): C, 76.46; H, 6.42; N, 3.88. Found: C, 76.81; H, 6.13; N, 3.99.

Complex 31. The complex was synthesized using the same conditions and procedure as those for **11** from **25**. A red solid was obtained in 60% yield. ^1H NMR (C_6D_6): δ 7.91 (dd, J = 8.4, 1.2 Hz, 2H, fluorenyl-H), 7.39 (dd, J = 6.8, 1.6 Hz, 1H, Ph-H), 7.33 (td, J = 8.0, 1.6 Hz, 1H, Ph-H), 7.12−7.04 (m, 4H, fluorenyl-H), 6.96 (td, J = 7.6, 1.2 Hz, 1H, Ph-H), 6.89 (td, J = 6.4, 0.8 Hz, 2H, fluorenyl-H), 6.39 (d, J = 8.0 Hz, Ph-H), 4.18 (t, J = 8.0 Hz, 2H, NCH_2), 1.72−1.60 (m, 2H, CH_2), 1.32−1.19 (m, 2H, CH_2), 0.84 (t, J = 7.2 Hz, 3H, CH_3), 0.11 (s, 6H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 163.57, 136.70, 131.47, 129.39, 127.88, 127.30, 126.16, 123.90, 123.31, 120.04, 118.82, 110.81, 107.90, 59.55, 46.61, 30.81, 21.31, 14.37 ppm. Anal. Calc ($C_{25}H_{27}NTi$): C, 77.12; H, 6.99; N, 3.60. Found: C, 77.02; H, 7.21; N, 3.86.

Complex 32. The complex was synthesized using the same conditions and procedure as those for **11** from **27**. A red solid was obtained in 60% yield. ^1H NMR (C_6D_6): δ 7.93 (dd, J = 9.6, 0.8 Hz, 2H, fluorenyl-H), 7.18 (d, J = 2.0 Hz,1H, Ph-H), 7.13−7.06 (m, 5H), 6.88 (td, J = 6.4, 0.8 Hz, 2H, fluorenyl-H), 6.23 (d, J = 8.0 Hz, 1H, Ph-H), 4.14 (quartet, J = 6.8 Hz, 2H, NCH_2), 2.31 (s, 3H, *p*-CH_3), 1.15 (t, J = 6.8 Hz, 3H, CH3), 0.08 (s, 6H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.01, 136.76, 132.38, 129.73, 129.09, 127.79, 127.51, 126.13, 123.78, 123.28, 118.77, 110.78, 107.50, 58.74, 40.78, 20.98, 13.77 ppm. Anal. Calc ($C_{24}H_{25}NTi$): C, 76.80; H, 6.71; N, 3.73. Found: C, 77.02; H, 6.45; N, 3.99.

Complex 33. The complex was synthesized using the same conditions and procedure as those for **11** from **28**. A red solid was obtained in 54% yield. ^1H NMR (C_6D_6): δ 7.87 (dt, J = 8.4, 0.8 Hz, 2H, fluorenyl-H), 7.36 (dd, J = 7.2, 1.6 Hz, 1H, Ph-H), 7.25 (td, J = 7.2, 1.6 Hz, 1H, Ph-H), 7.15 (d, J = 8.8 Hz, 2H, fluorenyl-H), 7.10 (td, J = 7.2, 1.2 Hz, 2H, fluorenyl-H), 6.91 (td, J = 7.6, 1.2 Hz, 2H, fluorenyl-H), 6.89 (td, J = 7.2, 1.2 Hz, 1H, Ph-H), 6.53 (d, J = 8.0 Hz, 1H, Ph-H), 4.14 (br, 2H, NCH_2), 0.93 (s, 9H, C(CH3)3), 0.14 (s, 6H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 163.18, 134.69, 131.38, 128.62, 127.69, 125.81, 125.69, 124.07, 119.85, 110.48, 109.44, 61.63, 58.66, 56.24, 36.90, 30.70 ppm. Anal. Calc ($C_{26}H_{29}NTi$): C, 77.41; H, 7.25; N, 3.47. Found: C, 77.25; H, 7.48; N, 3.29.

Complex 34. The complex was synthesized using the same conditions and procedure as those for **11** from **29**. A red solid was obtained in 54% yield. ^1H NMR (C_6D_6): δ 7.93 (dd, J = 8.4 Hz, 2H, fluorenyl-H), 7.36 (dd, J = 7.2, 1.6 Hz, 1H, Ph-H), 7.25 (td, J = 8.8, 1.6 Hz, 1H, Ph-H), 7.11(td, J = 8.0, 1.2 Hz, 2H, fluorenyl-H), 7.02 (d, J = 8.4, 2H, fluorenyl-H), 6.93 (td, J = 7.2, 0.8 Hz, 1H, Ph-H), 6.88 (td, J = 7.6, 1.2 Hz, 2H, fluorenyl-H), 6.61 (d, J = 8.0 Hz, 1H, Ph-H), 5.39 (br, 1H, NCH), 1.42 (d, J = 6.4 Hz, 6H, $CH(CH_3)_2$), −0.02 (s, 6H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.94, 136.37, 131.86, 129.27, 128.75, 128.51, 127.79, 125.98, 124.00, 123.34, 119.82, 110.05, 56.19, 45.40, 19.68 ppm. Anal.

Calc ($C_{24}H_{25}NTi$): C, 76.80; H, 6.71; N, 3.73. Found: C, 77.11; H, 6.82; N, 3.37.

Complex 35. Compound **8** (0.182 g, 0.754 mmol) and $Ti(NMe_2)_4$ (0.169 g, 0.754 mmol) were dissolved in toluene (2.0 mL), and the flask was sealed. The solution was heated for one month at 110 °C. Removal of solvent gave a red solid. NMR data for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 7.36−7.26 (m, 1H, Ph-H), 7.25 (dd, J = 7.2, 1.6 Hz, 1H, Ph-H), 6.92 (t, J = 7.2 Hz, 1H, Ph-H), 6.45 (d, J = 7.6 Hz, 1H, Ph-H), 3.94 (quartet, J = 7.2 Hz, 2H, NCH_2), 2.97 (s, 12H, $N(CH_3)_2$), 1.92 (s, 6H, Cp-CH_3), 1.77 (s, 6H, Cp-CH_3), 1.02 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 165.70, 134.95, 129.14, 128.71, 125.41, 119.25, 117.74, 107.96, 48.60, 45.05, 44.21, 15.55, 11.82, 11.19 ppm. To the flask containing the bis(dimethylamido)titanium complex were added toluene (2 mL) and Me_2SiCl_2 (0.292 g, 2.26 mmol) successively at room temperature. After the solution was stirred for 4 h at room temperature, the solvent was removed by vacuum. An analytically pure red solid was isolated by trituration in pentane at room temperature (0.157 g, 58% from **8**). ^{1}H NMR (C_6D_6): δ 7.15−7.07 (m, 2H, Ph-H), 6.97 (t, J = 7.6 Hz, 1H, Ph-H), 6.06 (d, J = 8.0 Hz, 1H, Ph-H), 4.28 (quartet, J = 6.8 Hz, 2H, CH_2), 2.04 (s, 6H, Cp-CH_3), 1.70 (s, 6H, Cp-CH_3), 1.11 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 165.47, 143.42, 141.63, 131.61, 129.59, 129.13, 128.77, 123.07, 108.96, 44.93, 13.19, 13.02, 11.73 ppm. Anal. Calc ($C_{17}H_{21}Cl_2NTi$): C, 57.01; H, 5.91; N, 3.91. Found: C, 57.26; H, 5.69; N, 3.99.

Complex 36. The complex was synthesized using the same conditions and procedures as those for **35** from **9**. Overall yield from **9** was 66%. NMR data for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 7.25 (td, J = 7.2, 1.2 Hz, 1H, Ph-H), 7.15 (dd, J = 7.2, 1.6 Hz, 1H, Ph-H), 6.87 (td, J = 7.2, 1.2 Hz, 1H, Ph-H), 6.35 (d, J = 8.4 Hz, 1H, Ph-H), 3.38 (s, 3H, NCH_3), 2.98 (s, 12H, $N(CH_3)_2$), 1.89 (s, 6H, Cp-CH_3), 1.75 (s, 6H, Cp-CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 167.89, 137.79, 129.16, 128.93, 126.27, 119.58, 118.35, 108.18, 48.60, 44.58, 39.00, 12.06, 11.59 ppm. The analytical data for **36**: ^{1}H NMR (C_6D_6): δ 7.16 (td, J = 7.2, 1.2 Hz, 1H, Ph-H), 7.09 (dd, J = 7.6, 1.6 Hz, 1H, Ph-H), 6.99 (td, J = 7.2, 0.8 Hz, 1H, Ph-H), 6.00 (d, J = 8.0 Hz, 1H, Ph-H), 3.61 (s, 3H, NCH_3), 2.04 (s, 6H, Cp-CH_3), 1.70 (s, 6H, Cp-CH_3) ppm, ^{13}C{^{1}H} NMR (C_6D_6): δ 167.21, 143.57, 141.79, 131.12, 129.62, 129.25, 128.46, 123.31, 108.48, 39.53, 13.16, 13.03 ppm. (0.183 g, overall 66%). Anal. Calc ($C_{16}H_{19}Cl_2NTi$): C, 55.85; H, 5.57; N, 4.07. Found: C, 55.59; H, 5.69; N, 3.99.

Ethylene/1-Octene Copolymerization. In a glovebox, 30 mL of a toluene solution of 1-octene (1.0 g, 0.30 M) was added to a dried 60 mL glass reactor. The reactor was assembled and brought out from the glovebox. The reactor was then heated to 70 °C using a mantle. After an activated catalyst, which was prepared by mixing the complex (0.50 μmol), $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ (2.0 μmol), and (^{t}Bu)$_3$Al (0.20 mmol) for 5 min, was added via a syringe, ethylene gas (60 psig) was fed immediately. In the case of highly active catalysts, the mantle was removed immediately after the injection of the activated catalyst to remove the generated heat. After polymerization was conducted for 5 (or 2) min, the ethylene gas was vented. Acetone was added to the reactor to give white precipitates, which were collected by filtration, and then they were dried under vacuum at 60 °C. The 1-octene contents were calculated by analysis of the ^{1}H NMR spectra of the copolymers. In the ^{1}H NMR spectra, the methyl (CH_3) signals (0.93−1.02 ppm) are well isolated from the methine (CH) and methylene (CH_2) signals (1.30−1.50 ppm), and the 1-octene contents can be calculated from the integration values of the two regions.[14,21a,b] The integration values measured on the NMR instrument were rather sensitively changeable depending on the conditions of the shimming, signal phase, or integration phase. However, cutting with scissors and weighing the two signals after printing the spectrum on a paper in the 0.5−2.0 ppm region gave consistently invariable values. The copolymer (5 mg) was dissolved in C_6D_6, and the ^{1}H NMR spectra were recorded at 80 °C.

X-ray Crystallography. Crystals of **33**, **35**, **36**, and **37** coated with grease (Apiezon N) were mounted onto a thin glass fiber with epoxy glue and placed in a cold nitrogen stream at 150(2) K on Rigaku single-crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97) and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table 4.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of a copolymer and cif files for **33**, **35**, **36**, and **37**. This material is available free of charge via the Internet at http://pubs.acs.org.

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