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Syntheses, Characterization, and Ethylene Polymerization of Titanium Complexes with Double-Duty Tridentate [ONN] Ligands

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Supporting Information

ABSTRACT: A series of titanium complexes containing the tridentate [ONN] ligands **La**−**Lf** were synthesized and characterized. The ligands **Lb** (8-quinolinolato-CH_2NHAr; Ar = 2,6-diisopropylphenyl) has been prepared by the reduction of the corresponding imino-quinolinol compound **La** (8-quinolinolato-CH=NAr; Ar = 2,6-diisopropylphenyl) with $LiAlH_4$ in high yield. Ligands **Lc**−**Lf** were synthesized by a procedure similar to that used to prepare ligand **Lb**. Reaction of $TiCl_4$ with imino-quinolinol ligand **La** affords the six-coordinate trichloride titanium complex **1**. The selective synthesis of tri- and dichlorotitanium complexes containing ligand **Lb** was achieved by changing the base for deprotonation. When it is deprotonated by NaH, ligand **Lb** can be used as a tridentate monoanionic ligand to synthesize trichlorotitanium complex **2**. While deprotonated by ^{n}BuLi, it can be used as a tridentate dianionic ligand to synthesize dichlorotitanium complex **3**. Other dichlorotitanium complexes **4**−**7** were synthesized by a procedure similar to that used to prepare complex **3**. All complexes have been characterized by ^{1}H NMR spectra and elemental analysis. The molecular structures of ligand **Lb** and complex **1** have been characterized by single-crystal X-ray diffraction analyses. XANES and EXAFS spectroscopy performed on the representative complexes **2** and **3** reveals the different coordination geometries. When they are activated by excess methylaluminoxane (MAO), all of the titanium complexes can be used as catalysts for ethylene polymerization and exhibit moderate to good activities. It was found that the catalytic behaviors of the title complexes were highly affected by the coordination entironment of the metal center and the effect of substituent groups on ligands.

INTRODUCTION

The search for new olefin polymerization catalysts based on transition-metal complexes is a field of major interest, involving many academic and industrial research groups. Ever since the discovery of Ziegler−Natta catalysis,[1] non-metallocene catalysts,[2] which include early-,[3] middle-,[4] and late-transition-metal[5] and lanthanide[6] species incorporating noncyclopentadiene-based ligands, have attracted great attention. Non-metallocene group IV metal complexes containing various types of ligands are among the typical examples.[7−10] Fujita et al.[9] developed an FI catalyst family based on bis(salicylaldiminato) ligands. This type of catalyst can be used to produce polyethylene or syndiotactic polypropylene with high molecular weight and narrow molecular weight distribution, and the catalytic behavior is highly affected by the substituent on both the phenoxy and the imino groups. Kol et al.[10] reported [ONO] and [ONNO] ligand systems and found that their [ONNO] zirconium complexes were highly active in 1-hexene polymerization.

We noticed that most of the non-metallocene group IV precatalysts described above were dihalide (or dialkyl or monohalide monoalkyl) complexes. In comparison, only a few of the trihalide (or trialkyl) nonmetallocene precursors were found to be active for olefin polymerization.[11] Commercially, it is of further interest if these catalysts can be procured in as few steps as possible and from "non-toxic" starting materials.[12] Recently, we have reported half-sandwich zirconium complexes with tridentate imino-quinolinol ligands which exhibited high activities for ethylene polymerization.[13] Herein, it is a natural extension of this type of imino-quinolinol ligand to synthesize a trichloride nonmetallocene titanium catalyst. Furthermore, the selective synthesis of tri- and dichlorotitanium species containing tridentate [ONN] ligands, protonated from the imino-quinolinol ligand, was achieved by changing the base. These title complexes, activated with methylaluminoxane (MAO), show moderate to high activities for ethylene polymerization. We report the syntheses, characterization, and polymerization behavior of the title complexes in detail.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis of ligands **La** and **Lb** is outlined in Scheme 1. The tridentate monoanionic [O^-NN] ligand **La** was prepared according to our previously reported method.[13] Ligand **Lb** was obtained easily in high yield by reduction of ligand **La** with excess $LiAlH_4$ in cool diethyl ether.

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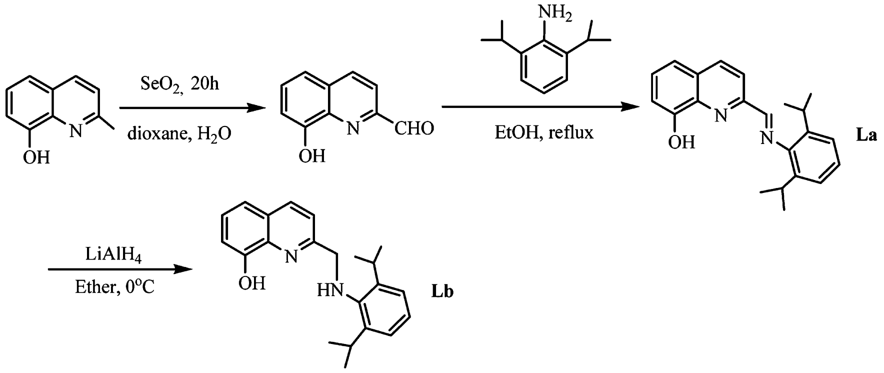
Scheme 1. Synthetic Route to Ligands La and Lb



Ligands **La** and **Lb** were characterized by elemental analysis, IR, and ^{1}H NMR. The chemical shift of the CH═N proton in ligand **La** is 8.37 ppm. The signal disappeared in the ^{1}H NMR spectrum of compound **Lb**, while new signals appeared and were identified as CH$_2$ (4.4 ppm) protons, indicating that the CH═N (imine) has been transformed to CH$_2$NH (amine). In the IR spectrum of ligand **Lb**, a strong and sharp peak at 3351 cm^{-1} can be ascribed to the stretching vibration of N−H, indicating the existence of secondary amine. The structure of **Lb** was further confirmed by single-crystal X-ray diffraction analysis (Figure 1). In **Lb**, the C(10)−N(2) bond length is 1.471(3) Å, which is typical of a carbon−nitrogen single bond. The three donor atoms ONN are not coplanar.

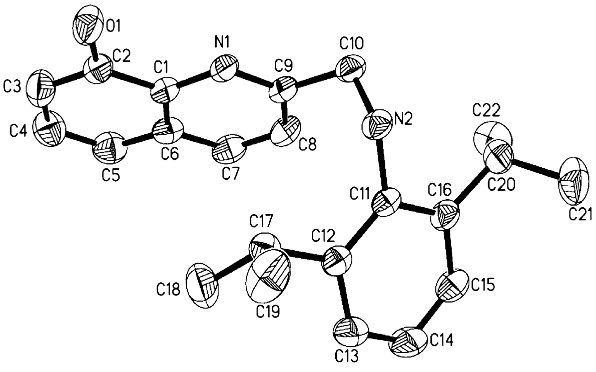


Figure 1. Molecular structure of **Lb** with thermal ellipsoids drawn at the 30% level. Selected bond lengths (Å) and angles (deg): C(2)−O(1), 1.354(3); C(10)−N(2), 1.471(3); C(1)−N(1), 1.370(3); C(9)−N(1), 1.319(3); C(1)−C(2), 1.415(3); C(9)−C(10)−N(2), 114.6(2); C(10)−N(2)−C(11), 116.14(19).

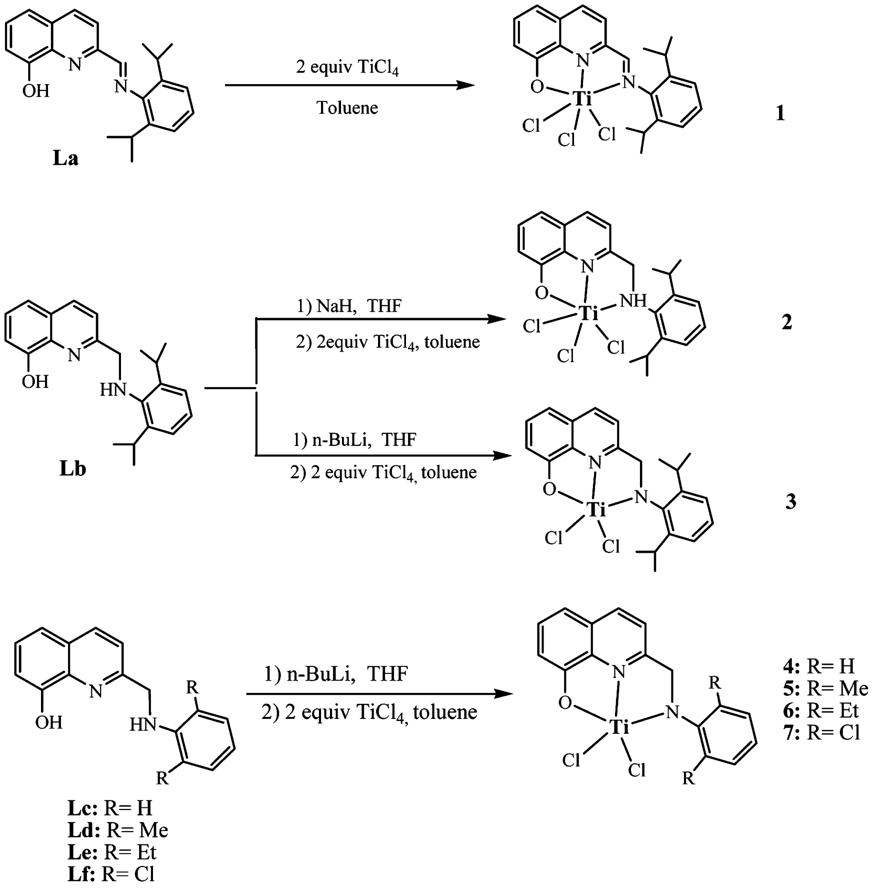
The synthesis of complexes **1**−**3** is outlined in Scheme 2. Without any base ligand **La** could react with TiCl$_4$ to give the desired trichloride complex **1** in the presence of excess of TiCl$_4$ (2 equiv) at −78 °C in toluene in high yield. We first attempted to synthesized complex **2** by a procedure similar to that used to prepare complex **1**. The reaction of ligand **Lb** with excess TiCl$_4$ without any base in toluene solution was carried out; however, the reaction seemed to be more complicated than expected, and the desired product was isolated in low yield. After continuous screening of proper reaction conditions, we found a better way to synthesize complex **2**. On deprotonation of ligand **Lb** with excess sodium hydride (NaH) in tetrahydrofuran (THF), the resultant sodium compounds reacted further with 2 equiv of TiCl$_4$ in toluene. Red crystals of the pure trichloride titanium complex **2** were isolated in good yield (83%). It is worth noting that deprotonation of ligand **Lb** using 2 equiv of ^{n}BuLi instead of NaH led to the five-coordinated dichlorotitanium complex **3** in toluene solution.

Complexes **1**−**7** were fully characterized by IR, ^{1}H NMR, and elemental analyses (see the Experimental Section). The signal of the CH═N proton in the ^{1}H NMR spectrum of complex **1** is downfield approximately 0.12 ppm from that of the free ligand, indicating the obvious coordination of the imino nitrogen atom to the metal center. In the IR spectrum of complex **2**, a strong and sharp peak at 3283 cm^{-1} can be ascribed to the stretching vibration of N−H, indicating the existence of secondary amine, but there are no stretching vibration signals of N−H in the IR spectra of complexes **3**−**7**. This phenomenon indicated that the proton of the secondary amine cannot be deprotonated by NaH. When using ^{n}BuLi instead of NaH, the proton of the secondary amine can be deprotonated. Hence, we were pleased to find that ligand **Lb** is a double-duty ligand. When it is deprotonated by NaH, ligand **Lb** can be used as a tridentate monoanionic ligand. However, when it is deprotonated by ^{n}BuLi, it can be used as a tridentate dianionic ligand. The solid-state structure of complex **1** was further determined by single-crystal X-ray diffraction. The crystal of complex **1** was obtained by slow diffusion of hexane into its CH$_2$Cl$_2$ solution. Selected structural parameters, along with those for related titanium complex **1**, are collected in the Supporting Information.

The molecular structure of complex **1** is shown in Figure 2 as a titanium trichloride complex with one imino-quinolinol ligand. The geometry at the titanium center can be described as a slightly distorted octahedral structure in which the five atoms Ti(1), N(1), N(2), O(1), and Cl(2) are nearly coplanar. The two atoms Cl(1) and Cl(3) are in a trans configuration (Cl(1)−Ti(1)−Cl(3) = 168.44(4)°).

X-ray absorption spectroscopy (XAS) was used to investigate the local structure of Ti atoms in complexes **2** and **3**. Figure 3 compares the XANES (X-ray absorption near edge structure) of **2** and **3**. There is no apparent difference, which proves that the Ti atom has a similar coordination environment in the two complexes. Further Fourier transforms of EXAFS (extended X-ray absorption fine structure) data are compared in Figure 4. The significant differences appear in the main peak at 1.9 Å, which corresponds to the backscatter of Ti−Cl and Ti−N. In order to explain the difference, the fitting of the Ti K-edge EXAFS spectra (Table 1) of **2** and **3** was performed using a three-shell model, which consists of Ti−O, Ti−N, and Ti−Cl. With the help of EXAFS analysis, the solid-state structures of **2** and **3** were confirmed to be six-coordinate as [1O,2N,3Cl] and five-coordinate as [1O,2N,2Cl], respectively.

Scheme 2. Synthesis of Titanium Complexes 1−7



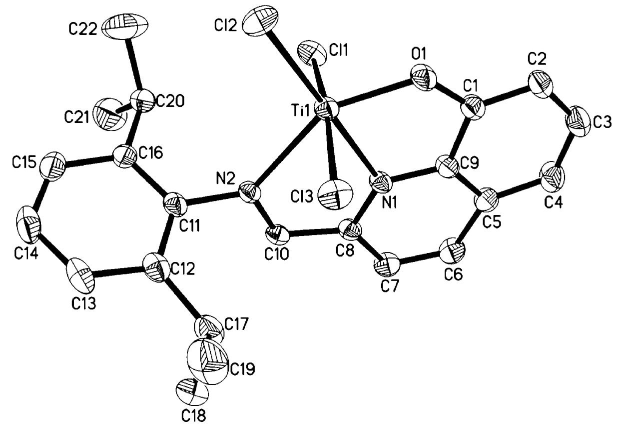


Figure 2. Molecular structure of complex 1 with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)−N(1), 2.126(3); Ti(1)−N(2), 2.305(2); Ti(1)−O(1), 1.862(2); Ti(1)−Cl(1), 2.2900(12); Ti(1)−Cl(2), 2.2510(11); Ti(1)−Cl(3), 2.3218(12); C(10)−N(2), 1.281(4); Cl(1)−Ti(1)−Cl(2), 94.22(5); Cl(2)−Ti(1)−Cl(3), 93.45(4); Cl(1)−Ti(1)−Cl(3), 168.44(4); Cl(2)−Ti(1)−N(1), 177.09(8).

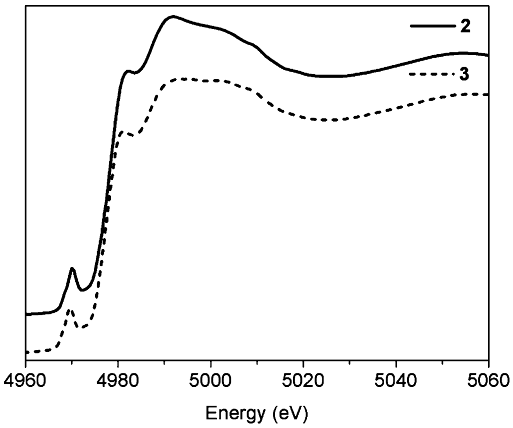


Figure 3. Ti K-edge XANES spectra of complexes 2 and 3.

Ethylene Polymerization. Upon activation with methylaluminoxane (MAO), complexes 1−7 were found to be active for ethylene polymerization. The polymerization results are summarized in Tables 2 and 3. The active catalysts were generated in situ in toluene by addition of methylaluminoxane (MAO) to the precursors in toluene. In the title catalytic systems, the red mixture turned transparent yellow immediately as MAO was charged, indicating the active species had better solubility in toluene. In the 1/MAO and 3/MAO systems, respectively, according to observations at different Al/Ti ratios (entries 1−3 and 15−17 in Table 2), the maximum activities were shown at an Al/Ti molar ratio of 2000. However, the maximum activity was shown at an Al/Ti molar ratio of 1000 in the 2/MAO system. Most worthy of note is the fact that the activity of 2/MAO did not change very much when the cocatalyst/catalyst ratio decreased from 2000 to 250 (entries 6−11, Table 2). Such a phenomenon suggested that its activity could be maintained at a high level even at low Al/Ti ratios. In addition, the obtained polyethylene exhibits lower M_v values

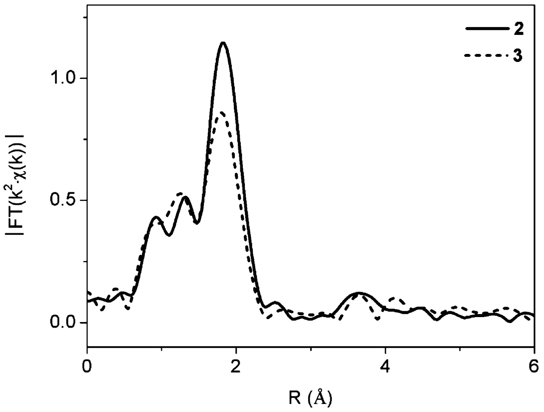


Figure 4. Fourier transform of the k2 weighted EXAFS oscillations of complexes **2** and **3**.

Table 1. Fit Parameters of Ti EXAFS Spectra for Complexes 2 and 3

shell	N[a]	R[b]	σ^2 (10^{-3} Å^2)[c]	ΔE_0 (eV)[d]
		Complex **2**		
Ti−O	0.6 ± 0.1	1.84 ± 0.02	6.9 ± 3.0	5.9 ± 4.0
Ti−N	1.7 ± 0.4	2.28 ± 0.02	2.0 ± 1.3	9.3 ± 1.1
Ti−Cl	2.2 ± 0.5	2.31 ± 0.01	5.5 ± 0.8	5.1 ± 1.2
		Complex **3**		
Ti−O	0.7 ± 0.1	1.83 ± 0.01	1.8 ± 0.4	7.5 ± 1.0
Ti−N	1.6 ± 0.2	2.12 ± 0.02	3.8 ± 2.4	5.2 ± 1.1
Ti−Cl	1.4 ± 0.4	2.36 ± 0.01	10.2 ± 2.1	9.1 ± 2.1

[a] Coordination number. [b] Distance between absorber and backscatter atoms. [c] Debye−Waller factor. [d] Inner potential correction.

Table 2. Results of Ethylene Polymerization Initiated by Titanium Catalysts 1−3/MAO[a]

entry	precat.	t/min	Al/Ti ratio	temp/°C	activity[b]	$M_{\rm v}$[c] × 10^{-4}
1	**1**	10	1000	20	140	38
2	**1**	10	2000	20	230	33
3	**1**	10	3000	20	180	27
4	**1**	10	2000	50	290	28
5	**1**	10	2000	80	350	22
6	**2**	10	2000	20	2300	38
7	**2**	10	1500	20	3600	41
8	**2**	10	1000	20	4110	44
9	**2**	10	500	20	3720	47
10	**2**	10	250	20	2700	60
11	**2**	10	1000	50	3450	40
12	**2**	10	1000	80	1530	33
13	**2**	30	1000	20	3500	49
14	**2**	60	1000	20	2010	56
15	**3**	10	1000	50	6220	55
16	**3**	10	2000	50	9530	52
17	**3**	10	2500	50	4130	49
18	**3**	10	2000	20	6680	58
19	**3**	10	2000	80	4880	37

[a] Conditions: 2 μmol of catalyst, toluene (total volume 50 mL), 10 atm of ethylene. [b] Activity in kg of PE (mol of Ti)$^{-1}$ h^{-1}. [c] $M_{\rm v}$ measured by the Ubbelohde calibrated viscosimeter technique.

when the ratio of Al/Ti is increased, because the chain transfer increases with high Al concentration.[14]

Table 3. Results of Ethylene Polymerization Initiated by Titanium Catalysts 3−7/MAO[a]

entry	precat.	amt of PE (g)	activity[b]	$M_{\rm v}$[c] × 10^{-4}
1	**3**	3.17	9530	52
2	**4**	1.08	3240	21
3	**5**	1.81	5430	38
4	**6**	2.40	7210	44
5	**7**	0.29	870	23

[a] Conditions: 2 μmol of catalyst, toluene (total volume 50 mL), 50 °C, 10 atm of ethylene, 10 min, Al/Ti ratio 2000. [b] Activity in kg of PE (mol of Ti)$^{-1}$ h^{-1}. [c] $M_{\rm v}$ measured by the Ubbelohde calibrated viscosimeter technique.

As presented in Table 2, the temperature tolerances of title complexes **1**−**3** for performing ethylene polymerizations were good. The **1**/MAO system showed the highest activity around 80 °C, and the **2**/MAO system showed the highest activity at room temperature. The better thermal stability of complex **1** suggested that the ligand with imino-quinolinol backbone in the catalyst plays an important role in stabilizing the active species at high temperature. In addition, the **3**/MAO system showed the highest activity around 50 °C, which is similar to the case for classical FI catalysts. The molecular weights of polyethylene obtained decrease with elevating reaction temperature due to a faster chain transfer and termination at higher temperature.

To determine the effect of reaction time on the activity and molecular weight ($M_{\rm v}$) of the resulting polymers, the ethylene polymerization using the **2**/MAO catalytic system was conducted over different time periods, namely, 10, 30, and 60 min (entries 8, 13, and 14, Table 2); the highest activity (4.11×10^6 g of PE (mol of Ti)$^{-1}$ h^{-1}) was obtained in a period of 10 min. Complex **3** showed the highest activity (about 9.53×10^6 g of PE (mol of Ti)$^{-1}$ h^{-1}). Moreover, complex **1** was found to be less active by 1 order of magnitude than titanium complexes **2** and **3**, which contain a more flexible ligand. Dichloride titanium complex **3** presented higher activity than trichloride titanium complex **2**. According to the literature,[11d] one of the reasons is probably that the space of the central metal in the trichloride complex is more open than in the similar dichloride species because the chlorine atom is small, influencing the chain-transfer process of polymerization. From the electronic effect of an ancillary ligand, dianionic ligand **Lb** coordinates more strongly to a titanium metal center than the similar monoanion ligand **Lb** in a tridentate fashion. Therefore, **Lb**, as a dianionic ligand, can stabilize Ti$^{\rm IV}$ species better. This is probably one of the reasons complex **3** has better performance than complex **2** in ethylene polymerizaiton.

Using the optimized conditions for the **3**/MAO system (10 atm of ethylene, 50 °C, and Al/Ti ratio 2000), the precatalysts **3**−**7** have been examined to understand the substituent effects of the ligands. The results are collected in Table 3.

The activity data in Table 3 indicates that the R group on the ligand has a significant effect on catalytic activity and $M_{\rm v}$ value for resultant polymer. There are observable effects of the ligands' environment, and the activities of complexes decrease in the order **3** (R = ^{i}Pr) > **6** (R = Et) > **5** (R = Me) > **4** (R = H) > **7** (R = Cl). In terms of steric influence, the bulky ^{i}Pr group enhances the activity of its precatalyst, because the active species are better protected in the polymerization process.[14b] The Cl-substituted derivatives showed the lowest activities (entry 5 in Table 3). These results clearly demonstrate that the bulky and donating substituents on the ligands in the ortho position seem to be important for high catalytic activity.

■ CONCLUSIONS

New types of double-duty tridentate [ONN] ligands were easily prepared in one step on the basis of the corresponding imino-quinolinol ligands. On deprotonation by NaH, ligands **Lb**−**Lf** can be used as tridentate monoanionic ligands to synthesize trichlorotitanium complexes. However, when they are deprotonated by ^{n}BuLi, they can be used as tridentate dianionic ligands to synthesize dichlorotitanium complexes. The molecular structures of the double-duty tridentate [ONN] ligand **Lb** and complex **1** have been characterized by single-crystal X-ray diffraction analysis. The local atomic environments and charge states of Ti in compounds **2** and **3** were investigated by X-ray absorption spectroscopy. On activation by excess methylaluminoxane (MAO), titanium complexes **1**−**7** can be used as catalysts for ethylene polymerization and exhibited different catalytic behaviors. Titanium complexes **2** and **3**, bearing the secondary amine ligand **Lb**, are more active than titanium complex **1**, bearing imine ligand **La**. In addition, bulky and donating substituents on analogous secondary amine ligands (**Lb**−**Lf**) enhance the activity of their precatalysts.

■ EXPERIMENTAL SECTION

General Data. All manipulations of air- and/or water-sensitive compounds were carried out under dry argon using standard Schlenk techniques. Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium-benzophenone. Dichloromethane was distilled from calcium hydride. Commercial reagents, namely $TiCl_4$, methylaluminoxane (MAO, 1.46 M in toluene), $LiAlH_4$, NaH, ^{n}BuLi, 2-methylquinolin-8-ol, SeO_2, and 2,6-substituted benzenamine, were purchased from Acros Co. 8-Hydroxyquinoline-2-carbaldehyde was prepared according to the literature procedure.[15]

IR spectra were measured on a Nicolet Avatar-360 spectrophotometer. NMR measurements were obtained on a Bruker AC 400 spectrometer in $CDCl_3$ solution. The NMR spectra of all the compounds and complexes were recorded at ambient temperature. Elemental analyses for C, N, and H were carried out on an Elementar III Vario EI analyzer.

Preparation of Ligands. *Ligand **La**.* A mixture of 8-hydroxyquinoline-2-carbaldehyde (0.6 g, 3.5 mmol) and 30 mL of ethanol was heated to 80 °C, and then a solution of (2,6-diisopropylphenyl)amine (0.62 g, 3.5 mmol) in 30 mL of ethanol was added dropwise. The reaction mixture was refluxed for 6 h and cooled to room temperature. Purification by column chromatography used 1/3 dichloromethane/petroleum ether (1% triethylamine). The product was obtained as yellow crystals in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.47 (d, 1H, quin), 8.40 (d, 1H, quin), 8.37 (s, 1H, N═CH), 8.22 (br, 1H, OH), 7.77 (t, 1H, quin), 7.45 (d, 1H, quin), 7.23 (d, 1H, quin), 7.16 (d, 2H, Ar H), 7.08 (d, 1H, Ar H), 3.49 (sept, 2H, iPr), 1.21(d, 6H, iPr), 1.15 (d, 6H, iPr). IR (KBr): $\nu_{C=N}$ 1637 cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43. Found: C, 79.50; H, 7.31; N, 8.47.

*Ligand **Lb**.* To a suspension of $LiAlH_4$ (0.38 g, 10.0 mmol) in ether (20 mL) was slowly added a solution of ligand **La** (2.5 mmol) in ethyl ether (30 mL). After the mixture was stirred for 2 h at room temperature, water (6.5 mL) and aqueous HCl (20%; 10 mL) were added sequentially at 0 °C. The organic phase was separated and washed with water (15 mL × 3). The organic layers were dried with anhydrous $NaSO_4$. The solvent was removed under vacuum, and the pure product **Lb** was obtained as a light yellow powder in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.40 (d, 1H, quin), 8.14 (br, 1H, OH), 7.46 (t, 1H, quin), 7.44 (d, 1H, quin), 7.20 (d, 1H, quin), 7.14 (d, 1H, quin), 7.12 (d, 2H, Ar H), 7.03 (d, 1H, Ar H), 6.80 (t, 1H, Ar H), 4.40 (s, 2H, CH_2NH), 3.40 (sept, 1H, iPr), 2.93 (sept, 1H, iPr), 1.28 (dd, 12H, iPr). IR (KBr): ν_{N-H} 3417 cm^{-1}. Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.00; H, 7.84; N, 8.38. Found: C, 78.94; H, 7.83; N, 8.36.

*Ligand **Lc**.* A procedure analogous to that used to prepare **Lb** was used, but starting from an R-substituted imino-quinolinol ligand (R = H) (620 mg, 2.5 mmol). Yield: 82.5%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.42 (d, 1H, quin), 8.24 (d, 1H, quin), 8.19 (br, 1H, OH), 7.48 (t, 1H, quin), 7.45 (d, 1H, quin), 7.23 (d, 1H, quin), 7.11−7.07 (m, 4H, Ar H), 7.04 (d, 1H, Ar H), 4.32 (d, 2H, CH_2NH). IR (KBr): ν_{N-H} 3420 cm^{-1}. Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 78.76; H, 5.69; N, 11.15.

*Ligand **Ld**.* A procedure analogous to that used to prepare **Lb** was used, but starting from an R-substituted imino-quinolinol ligand (R = Me) (690 mg, 2.5 mmol). Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.42 (d, 1H, quin), 8.28 (d, 1H, quin), 8.18 (br, 1H, OH), 7.56 (t, 1H, quin), 7.41 (d, 1H, quin), 7.23 (d, 1H, quin), 7.11 (d, 2H, Ar H), 7.02 (d, 1H, Ar H), 4.36 (d, 2H, CH_2NH), 2.22 (s, 6H, $2CH_3$). IR (KBr): ν_{N-H} 3427 cm^{-1}. Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.69; H, 6.50; N, 10.03.

*Ligand **Le**.* A procedure analogous to that used to prepare **Lb** was used, but starting from an R-substituted imino-quinolinol ligand (R = Et) (760 mg, 2.5 mmol). Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.44 (d, 1H, quin), 8.27 (d, 1H, quin), 8.14 (br, 1H, OH), 7.59 (t, 1H, quin), 7.48 (d, 1H, quin), 7.33 (d, 1H, quin), 7.21 (d, 2H, Ar H), 7.08 (d, 1H, Ar H), 4.32 (d, 2H, CH_2NH), 2.58 (m, 4H, $2CH_2$), 1.27 (t, 6H, $2CH_3$). IR (KBr): ν_{N-H} 3415 cm^{-1}. Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.44; H, 7.23; N, 9.14.

*Ligand **Lf**.* A procedure analogous to that used to prepare **Lb** was used, but starting from an R-substituted imino-quinolinol ligand (R = Cl) (792 mg, 2.5 mmol). Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.44 (d, 1H, quin), 8.30 (d, 1H, quin), 8.17 (br, 1H, OH), 7.55 (t, 1H, quin), 7.41 (t, 3H, Ar H), 7.25 (d, 1H, quin), 7.06 (d, 1H, quin), 4.45 (d, 2H, CH_2NH). IR (KBr): ν_{N-H} 3434 cm^{-1}. Anal. Calcd for $C_{16}H_{12}Cl_2N_2O$: C, 60.21; H, 3.79; N, 8.78. Found: C, 60.19; H, 3.81; N, 8.73.

Preparation of Complexes. *Complex **1**.* To a stirred solution of **La** (83 mg, 0.25 mmol) in 20 mL of toluene was added $TiCl_4$ (0.25 mL, 0.5 mmol) at −78 °C. The yellow solution immediately changed to a red suspension, and HCl gas was evolved. The mixture was warmed to room temperature by itself, and stirring was maintained for 6 h at room temperature. The red product **1** was obtained by filtration and washed twice with 10 mL of toluene and dried in vacuo (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.68 (d, 1H, quin), 8.49 (s, 1H, HC═N), 8.05 (d, 1H, quin), 7.91 (d, 1H, quin), 7.72 (d, 1H, quin), 7.41 (d, 1H, quin), 7.35 (d, 2H, Ar H), 7.05 (d, 1H, Ar H), 3.74 (sept, 2H, iPr), 2.35 (s, 12H, iPr). IR (KBr): $\nu_{C=N}$ 1610 cm^{-1}. Anal. Calcd for $C_{22}H_{23}Cl_3N_2OTi$: C, 54.41; H, 4.77; N, 5.77. Found: C, 54.44; H, 4.79; N, 5.75.

*Complex **2**.* To a slurry of NaH (24 mg, 1.0 mmol) in THF (10 mL) was added a solution of ligand **Lb** (83.5 mg, 0.25 mmol) in THF (10 mL) at 0 °C. The resulting yellow suspension was warmed to room temperature and stirred for 1 h. After the solvent of the filtrate was removed under vacuum, 30 mL of toluene was added to the residue, followed by a toluene solution of $TiCl_4$ (2 M, 0.25 mL, 0.5 mmol). The yellow solution immediately changed to a red suspension. The mixture was warmed to room temperature by itself, and stirring was maintained for 6 h at room temperature. The red product **2** was obtained by filtration and washed twice with 10 mL of toluene and dried in vacuo (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.70 (d, 1H, quin), 8.63 (s, 1H, NH), 8.08 (d, 1H, quin), 7.69−7.59 (m, 2H, quin), 7.44 (d, 1H, quin), 7.37 (d, 1H, Ar H), 7.29 (d, 1H, Ar H), 7.19 (d, 1H, Ar H), 3.7 (d, 2H, CH_2), 3.14 (sept, 1H, iPr), 2.97 (sept, 1H, iPr), 1.35 (d, 6H, iPr), 1.22 (d, 6H, iPr). IR (KBr): ν_{N-H} 3283 cm^{-1}. Anal. Calcd for $C_{22}H_{25}Cl_3N_2OTi$: C, 54.18; H, 5.17; N, 5.74. Found: C, 54.22; H, 5.19; N, 5.72.

*Complex **3**.* ^{n}BuLi (1.6 M, 0.32 mL, 0.5 mmol) was added through a syringe to a solution of **Lb** (83.5 mg, 0.25 mmol) in THF (20 mL) cooled to 0 °C. The resulting dark red solution was stirred at room temperature for 1 h. After the solvent was removed under vacuum, 30 mL of toluene was added to the residue, followed by a toluene solution of $TiCl_4$ (2 M, 0.25 mL, 0.5 mmol) at −78 °C. The solution immediately changed to a red suspension. The mixture was warmed to room temperature, and stirring was maintained for 6 h at room temperature. The red product **3** was obtained by filtration and washed twice with 10 mL of toluene and dried in vacuo (88% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.55 (d, 1H, quin), 7.61 (d, 1H, quin), 7.53 (d, 1H, quin), 7.36 (d, 1H, quin), 7.30 (d, 1H, quin), 7.22−7.15 (m, 2H, Ar H), 6.8 (d, 1H, Ar H), 3.63 (s, 2H, CH_2), 3.07 (sept, 2H, iPr), 1.28 (d, 6H, iPr), 1.16 (d, 6H, iPr). Anal. Calcd for $C_{22}H_{24}Cl_2N_2OTi$: C, 58.56; H, 5.36; N, 6.21. Found: C, 58.60; H, 5.39; N, 6.19.

*Complex **4**.* Using the same procedure for the synthesis of **3**, complex **4** was obtained as a red solid in 80% yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.45 (d, 1H, quin) δ 7.82 (d, 1H, quin), 7.74 (t, 1H, quin), 7.40 (d, 1H, quin), 7.28 (d, 1H, quin), 7.22−7.16 (m, 4H, Ar H), 7.13 (d, 1H, Ar H), 3.81 (s, 2H, CH_2). Anal. Calcd for $C_{16}H_{12}Cl_2N_2OTi$: C, 52.36; H, 3.30; N, 7.63. Found: C, 52.31; H, 3.33; N, 7.58.

*Complex **5**.* Using the same procedure for the synthesis of **3**, complex **5** was obtained as a red solid in 84% yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.54 (d, 1H, quin), 7.89 (d, 1H, quin), 7.67 (t, 1H, quin), 7.42 (d, 1H, quin), 7.25−7.17 (m, 3H, Ar H), 7.11 (d, 1H, quin), 3.79 (s, 2H, CH_2), 2.47 (s, 6H, $2CH_3$). Anal. Calcd for $C_{18}H_{16}Cl_2N_2OTi$: C, 54.72; H, 4.08; N, 7.09. Found: C, 54.76; H, 4.08; N, 7.11.

*Complex **6**.* Using the same procedure for the synthesis of **3**, complex **6** was obtained as a red solid in 79% yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.50 (d, 1H, quin), 7.84 (d, 1H, quin), 7.67 (t, 1H, quin), 7.46 (d, 1H, quin), 7.24−7.17 (m, 3H, Ar H), 7.05 (d, 1H, quin), 3.68 (s, 2H, CH_2), 3.25−3.10 (m, 2H, CH_2), 3.05−3.00 (m, 2H, CH_2), 1.59 (t, 3H, CH_3), 1.12 (t, 3H, CH_3). Anal. Calcd for $C_{20}H_{20}Cl_2N_2OTi$: C, 56.77; H, 4.76; N, 6.62. Found: C, 56.71; H, 4.78; N, 6.62.

*Complex **7**.* Using the same procedure for the synthesis of **3**, complex **7** was obtained as a orange-red solid in 65% yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.59 (d, 1H, quin), 8.44 (d, 1H, quin), 7.71 (t, 1H, quin), 7.63 (t, 3H, Ar H), 7.31 (d, 1H, quin), 7.16 (d, 1H, quin), 3.40 (s, 2H, CH_2). Anal. Calcd for $C_{16}H_{10}Cl_4N_2OTi$: C, 44.08; H, 2.31; N, 6.43. Found: C, 44.01; H, 2.32; N, 6.41.

Single-Crystal X-ray Structure Determination of Ligand Lb and Complex 1. Ligand **Lb** showed no signs of decomposition during X-ray data collection, which was carried out at room temperature. For complex **1**, a single crystal suitable for X-ray analysis was sealed in a glass capillary, and the intensity data of the single crystal were collected on a CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All data were collected at room temperature using the ω-scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program.[16] All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. Crystallographic data are summarized in the Supporting Information part.

XAFS Data Collection. The X-ray absorption data at the Ti K-edge of the sample were measured in the fluorescence mode with a Lytle fluorescence detector on beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, People's Republic of China. The station was operated with a double crystal monochromator, Si(111), detuned to 40% intensity to minimize the presence of higher harmonics. All measurements were done in transmission or fluorescence mode using ion chambers filled with a mixture of He and N_2 to have an X-ray absorbance of 20% in the first and 80% in the second chamber. Data processing and analysis were performed using the program ATHENA.[17] All fits to the EXAFS data were performed using the program ARTEMIS.[17]

General Procedure for Ethylene Polymerization at High Pressure. A 100 mL autoclave was charged with 50 mL of toluene under argon. MAO (10 wt % in toluene) was added. A solution of the precatalyst in toluene was added. After three exchanges of ethylene gas, the ethylene pressure was raised to the specified value and maintained for a certain time. The polymerization was terminated by addition of ethanol and dilute HCl (3%). The solid polyethylene was filtered, washed with ethanol, and dried at 80 °C under vacuum.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, figures, and a table giving crystallographic data, ORTEP diagrams, and details of the crystal structure determinations of **Lb** and **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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