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Dinuclear Titanium(IV) Complexes Bearing Phenoxide-Tethered N-Heterocyclic Carbene Ligands with *cisoid* Conformation through Control of Hydrolysis

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Keywords: Titanium / Carbene ligands / Phenoxides

In situ generated N-heterocyclic carbene salt derivative $Na_2(L)$ of 1,3-bis(4,6-di-*tert*-butyl-2-hydroxybenzyl)imidazolium bromide, $[H_3(L)]Br$, reacted with 1 equiv. of $TiBr_4$ at –78 °C to give a titanium complex of the composition $[(L)TiBr_2(thf)]$ (**1**), while the reaction in a 2:1 ratio under the same conditions afforded bisligand titanium complex $[(L)_2Ti]$ (**2**). Two oxygen-bridged titanium dimers, $\{[(L)TiBr]_2(\mu\text{-}O)\}$ (**4**) and $\{[(L)Ti(\mu\text{-}O)]_2\}$ (**5**), were obtained by control of hydrolysis of **1** and $[(L)Ti(CH_2Ph)_2]$ (**3**) in tetrahydrofuran and diethyl ether. The molecular structures of **2**, **4**, and **5** have been confirmed by X-ray single-crystal analysis. The phenoxide-functionalized NHC ligand adopts *transoid* conformation in mononuclear complex **2** but rare *cisoid* conformation in dinuclear complexes **4** and **5**.

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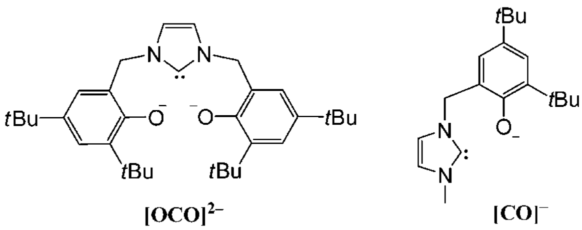
Introduction

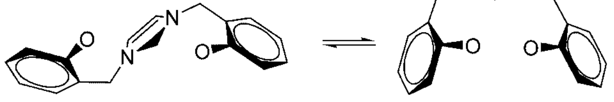
N-Heterocyclic carbene (NHC) ligands are heterocycles that bind as soft, two-electron donors through the NCN carbon atom, and are now used widely as strongly basic phosphane analogs, to support transition-metal complexes.[1] The overwhelming majority of NHCs are functionalized (with respect to the N and N′ substituents) by incorporating neutral donor or anionic groups such as pyridyl, phosphane, NHC, amide, alkoxide, and cyclopentadienyl.[1–14] In contrast, the diversity of NHC ligands found in high-oxidation-state transition-metal chemistry and homogeneous catalysis is conspicuously absent in early transition-metal NHC systems because of the ease of dissociation of the NHC ligand from the electron-deficient metal center, which makes it difficult to study the chemistry of NHCs in early transition metals and f-elements.[2–8]

In recent years, we have been investigating the use of aryl oxides linked to the NHC donor by a C_1 alkyl chain to generate asymmetric, heterobidentate and symmetric, heterotridentate ligands (Scheme 1) through which we can explore the NHC binding to *s*-block and early transition metal cations.[8] Earlier we reported the application of the bisphenoxy-substituted NHC ligand $(L)^{2-}$ – $[H_3(L)]Br$ = 1,3-bis(4,6-di-*tert*-butyl-2-hydroxybenzyl)imidazolium bromide) – and its corresponding aryloxy–NHC IVB metal complexes $[(L)MX_2]$ (M = Ti, Zr; X = Cl, CH_2Ph).[8a,8c] Among these complexes, the dichloride titanium complex has been proven to be a highly active procatalyst (up to 10^5 g PE mol^{-1} Ti h^{-1}) for polymerization of ethylene under methylaluminoxane (MAO) activation.[8c] The X-ray crystallography analysis of these Ti and Zr compounds revealed that only *transoid* conformation ligands were observed (Scheme 2). Herein, we wish to describe the synthesis and structural characterization of the first dinuclear titanium complexes supported by phenoxide-tethered N-heterocyclic carbene ligands, the tridentate chelate bianionic $(L)^{2-}$ with *cisoid* conformation (Scheme 3).



[OCO]$^{2-}$ **[CO]$^{-}$**

Scheme 1.



***transoid* conformation** ***cisoid* conformation**

Scheme 2.

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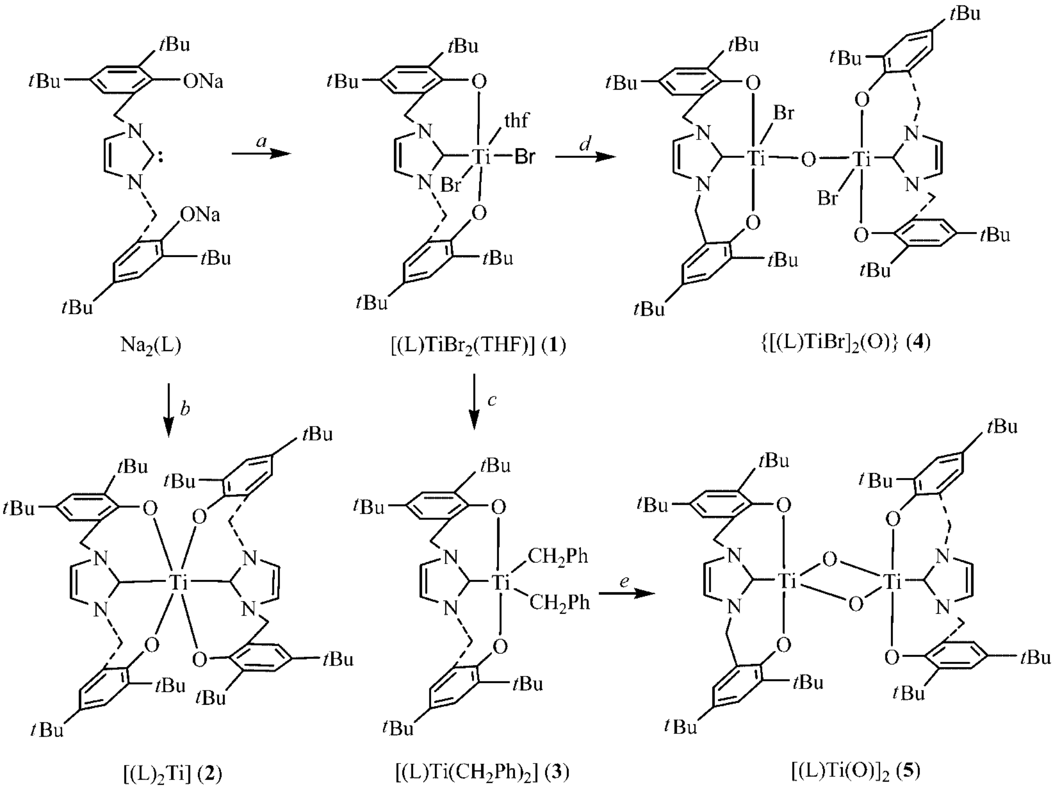

Scheme 3. Synthesis of titanium complexes **1**–**5**. Reaction conditions: *a*: $TiBr_4$/THF, –78 °C to room temp. *b*: $0.5\,TiBr_4$/THF, –78 °C to room temp. *c*: $2\,PhCH_2MgCl/Et_2O$, –78 °C to room temp. (d) H_2O/THF, room temp. (e) H_2O/Et_2O, room temp.

Results and Discussion

The bromide titanium complex [(L)$TiBr_2$(THF)] (**1**) is easily prepared in 76% yield by the in situ reaction at low temperature of 3 equiv. of $NaN(SiMe_3)_2$ with [H_3(L)]Br, followed by addition to $TiBr_4$ in 1:1 ratio in THF. The temperature-dependent NMR spectroscopic features of **1** are similar to those of the reported [(L)$TiCl_2$(THF)].[8c] $TiBr_4$, a more expensive reagent than $TiCl_4$, was also chosen to study the influence of different halide ions on the solid-state structures of titanium complexes. Unfortunately the poor quality of the orange-red crystals of **1** prevented us from carrying out X-ray analysis to determine its molecular structure.

Attempts to prepare the titanium complex [$(L)_2$Ti] (**2**), a NHC phenoxide titanium derivative analogous to [$(L)_2$Zr],[8a] were successful by the reaction of $TiCl_4(THF)_2$ or $TiBr_4$ with 2.0 equiv. of in situ generated Na_2(L) in THF. The structure of **2** was determined crystallographically (Figure 1). The selected bond lengths and angles of **2** are listed in Table 1, which includes the data of zirconium complex [$(L)_2$Zr][8a] for comparison. The titanium center shows a slightly distorted octahedral geometry and features two meridionally coordinated tridentate $(L)^{2-}$ ligands, each with mutually *trans* NHC donors [C8–Ti–C25, 179.9(2)°; O1–Ti–O2, 177.3(1)°; O3–Ti–O4, 176.6(1)°]. The molecule has approximate C_2 symmetry and the ligands adopt a *transoid* conformation. The Ti–C(carbene) [2.2053(4) and 2.196(4) Å] and Ti–O(phenoxide) distances [average 1.909 Å] are comparable to the corresponding distances found in [(L)$TiCl_2$(THF)].[8c]

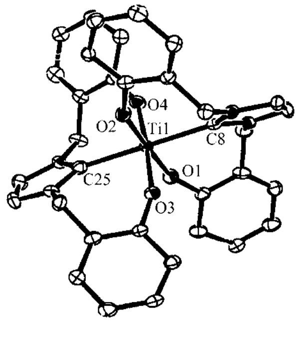

Figure 1. The molecular structure of **2**. All *t*Bu groups, solvent molecules, and hydrogen atoms are omitted for clarity.

The NMR spectroscopic data of **2** in [D_1]chloroform are consistent with the solid-state structure, and signals for only a single D_2 symmetric bis(phenoxide)–NHC ligand environment are seen, although the slight broadening of signals assigned to the N–CH_2 protons at δ = 3.88 and 6.42 ppm indicates some fluxional process at room temperature. The *tert*-butyl groups appear as two singlets at δ = 1.11 and 1.42 ppm, and the NHC ring protons are observed as a singlet at δ = 6.18 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the NHC carbon is observed at δ = 182.4 ppm.

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Table 1. Selected bond lengths [Å] and bong angles [°] of **2** and $[(L)_2Zr]$.[8a]

Bond lengths	$[(L)_2Zr]$	**2**	Bond angles	$[(L)_2Zr]$	**2**
M–C8(carbene)	2.385(30)	2.205(4)	C8–M–C25	160.23(10)	179.9(2)
M–C25(carbene)	2.381(3)	2.196(4)	O1–M–O2	161.85(8)	177.3(1)
M–O1	2.028(1)	1.910(3)	O3–M–O4	161.00(8)	176.6(1)
M–O2	2.041(2)	1.914(3)	C8–M–O1	84.57(9)	89.2(1)
M–O3	2.018(2)	1.912(3)	C8–M–O2	80.05(9)	88.3(1)
M–O4	2.035(2)	1.898(3)	C25–M–O3	83.79(9)	88.3(1)
			C25–M–O4	79.82(9)	88.5(2)

Complex $[(L)Ti(Ch_2Ph)_2]$ (**3**) has been prepared from $[(L)TiCl_2(thf)]$ by salt metathesis in toluene at room temperature and characterized by X-ray analysis, but a lower yield (30%) was obtained with this method.[8a] We modified this method by changing the reaction solvent and temperature. Reaction of **1** with 2 equiv. of $PhCH_2MgCl$ in Et_2O at –78 °C (Scheme 1) affords an orange microcrystalline solid of alkyl derivatives **3** in high yield (>88%) after washing with hexamethyldisiloxane (HMDSO), in which they are insoluble. As we previously reported, these derivatives are air- and moisture-sensitive and soluble in common organic solvents, including benzene, toluene, and dimethyl ether.

Hydrolysis of **1** with 0.5 equiv. of water in THF affords a dinuclear titanium complex $\{[(L)TiBr]_2(\mu\text{-}O)\}$ (**4**) with the release of 1 equiv. of hydrogen bromide (Scheme 1). The proton resonances of $N–CH_2–Ar$ appeared at δ = 4.27 and 6.00 ppm as two broad signals and $^{13}C\{^1H\}$ NMR spectra revealed the coordinated carbene carbon signal at δ = 185.0 ppm.

The X-ray single-crystal analysis of needle crystals of **4** showed that the titanium center binds to the carbene–phenoxide ligand, a bromide, and a bridged oxygen atom to form a pseudo-trigonal-bipyramidal geometry in the solid state (see Figures 2 and 4a). The aryloxy–NHC ligands are bound in a meridional fashion; the phenoxide donors occupy axial positions and two tops are occupied by bromide and carbene carbon. The most notable feature of this structure is that each carbene–phenoxide ligand coordinated to titanium favors *cisoid* conformation, but not *transoid* conformation. Bond lengths Ti–Br [2.5759(7) Å] and Ti–O(phenoxide) [1.822(3)–1.810(5) Å] (Table 2) are longer than those in monomeric aryl oxide complexes $[Ti(OC_6H_3Ph_2)_2Br_2]$ [2.3719(4) Å; 1.746(2) Å][15] and [Ti(ebmp)Br_2] [ebmp = $(3\text{-}t\text{Bu-5-Me-2-O-}C_6H_2CH_2)_2$] [2.372(2), 2.363(2) Å; 1.754(4), 1.747(4) Å].[16]

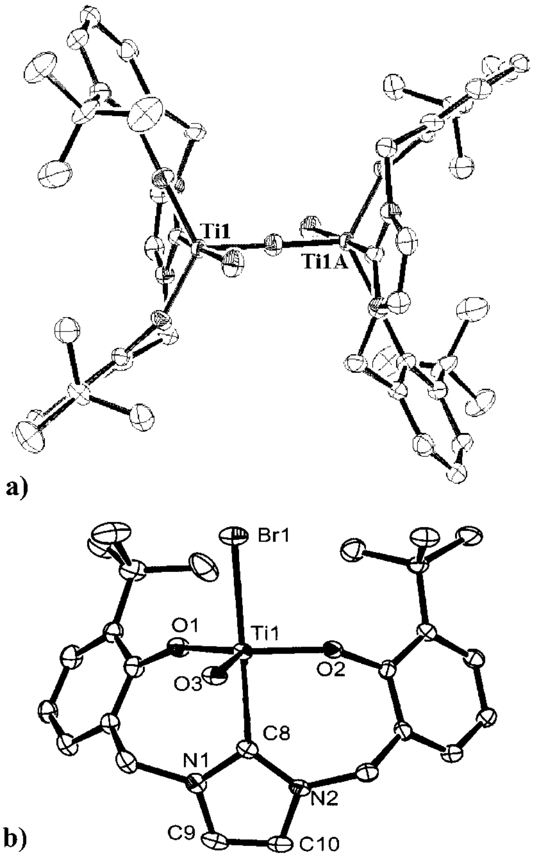


Figure 2. The molecular structure of **4**. All *t*Bu groups, solvent molecules, and hydrogen atoms are omitted for clarity. (a) The side view of the whole molecule; (b) one of the two symmetrically related Ti units.

Alkyl titanium complex **3** reacts with 1.0 equiv. of H_2O in Et_2O to afford $\{[(L)Ti]_2(\mu\text{-}O)_2\}$ (**5**) as a light yellow solid in almost quantitative yield. Its ^1H NMR spectrum exhibits resonances at 3.98 and 6.06 ppm attributable to the $N–CH_2–Ar$ protons of the carbene–phenoxide ligand.

Light yellow single crystals of **5** suitable for X-ray diffraction were obtained by recrystallization from hexane/THF at –20 °C. X-ray analysis of **5** revealed the dinuclear

Table 2. Selected bond lengths [Å] and angles [°] of **4** and **5**.

Bond lengths	**4**	**5**	Bond angles	**4**	**5**
Ti1–C8	2.208(5)	2.250(5)	C8–Ti1–O3A		177.0(2)
Ti1–O1	1.822(4)	1.862(3)	C8–Ti1–Br	176.4(1)	
Ti1–O2	1.841(3)	1.868(4)	C8–Ti1–O1	87.0(2)	86.7(1)
Ti1–O3	1.8074(8)	1.760(3)	C8–Ti1–O2	87.0(2)	87.4(2)
Ti1–O3(2)		1.970(2)	O1–Ti1–O2	125.4(2)	131.7(1)
Ti1–Br	2.5700(9)		O1–Ti1–O3	115.9(1)	113.4(2)
Ti1···Ti1A		2.7804(8)	O2–Ti1–O3	117.5(1)	114.8(1)

titanium structure to be linked by two μ-oxygen atoms; the geometry around the titanium atom is distorted trigonal-bipyramidal (Figures 3 and 4b). Each aryloxy–NHC ligand coordinated to titanium favors *cisoid* conformation, as titanium complex **4** does. The coordinated dianionic [Ti(μ-O)$_2$-Ti] core strongly compresses the carbene–phenoxide ligand to *cisoid* conformation. The titanium–carbene distance [2.249(5) Å] is obviously longer than those in other titanium complexes bearing a *transoid* conformation ligand because of the presence of two bridged O^{2-} groups that strongly bind to the titanium centers. A similarly short Ti···Ti distance of 2.704(8) Å has been observed in other titanium compounds where the dianionic groups such as oxo, imido, or alkylidene bridge the d^0 metals. Examples include [{$C_5H_2(SiMe_3)_3$}ClTi(μ-O)$_2$TiCl {$C_5H_2(SiMe_3)_3$}] 2.7071(4) Å,[17] [(2,6-$Me_2C_6H_3$)$_2$Ti(μ-N*t*Bu)$_2$Ti($OC_6H_3Me_2$-2,6)$_2$] 2.7909(7) Å,[18] [(cb)$_2$ClTi(μ-$CHSiMe_3$)$_2$Ti(cb)$_2$] (Hcb = carbazole) 2.9504(8) Å,[19] and [(Cy_2N)$_2$ClTi(μ-CH_2)$_2$-Ti(NCy_2)$_2$] 2.934(2) Å.[20]

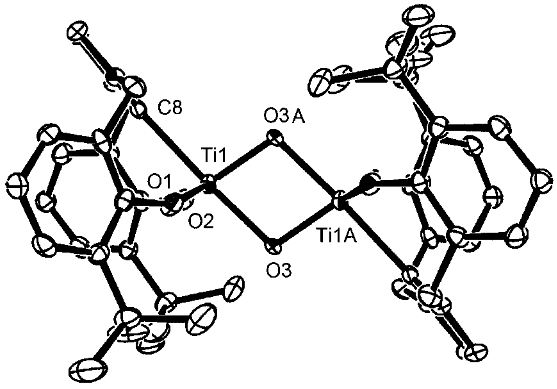
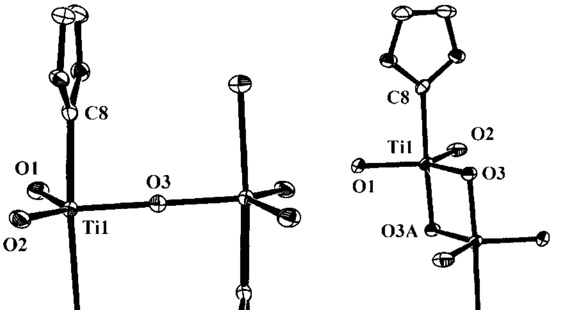


Figure 3. The molecular structure of **5**. All *t*Bu groups, solvent molecules, and hydrogen atoms are omitted for clarity.



(a) (b)

Figure 4. The coordinate sphere of dinuclear titanium complexes **4** (a) and **5** (b) with trigonal-bipyramidal geometry around the metal centers.

Compounds **1**, **4**, and **5** were found to catalyze the polymerization of ethylene at ambient temperature to give polyethylene with MAO as cocatalyst (Table 3). Compared with **1** and previously reported [(L)TiCl$_2$(thf)],[8a] which reveal high activity up to 10^5 g PE mol^{-1} Ti h^{-1}, the dinuclear complexes **4** and **5** show very low activities for polymerization of ethylene. The catalytic activity in the polymerization of ethylene decreases in the order of **1** > **4** > **5**. We are not convinced there is any relationship between conformation (*cisoid* or *transoid*) of the auxiliary carbene ligand and activity in polymerization reactions, because the ground-state conformation of the procatalysts is largely irrelevant to what happens following the addition of a MAO cocatalyst. We tried but failed to obtain information from theory calculation to support this idea. A possible reason for this is that the oxo compounds **4** and **5** are less reactive than **1** following MAO activation.

Table 3. Results of polymerization of ethylene.[a]

Complex	*T* [°C]	Polymer [g]	Activity[b]
[(L)TiCl$_2$(thf)][c]	30	–	290
1	25–35	2.3	164
4	25–35	0.5	39
5	25–35	0.3	21

[a] Polymerization conditions: 2 μmol of titanium, activated by MAO (Al/Ti = 1000), 1 h, 250 mL of toluene, 7 bar. [b] kg PE mol^{-1} Ni h^{-1} bar^{-1}. [c] See ref.[8a], 1 L of toluene, 0.5 h, 9 bar.

Conclusions

In summary, the present work demonstrated that two unique dinuclear titanium phenoxide-tethered N-heterocyclic carbene compounds, **4** and **5**, could be synthesized by control of the hydrolysis of **1** and **2** with the right amount of water. The phenoxide-functionalized NHC ligand adopts *transoid* conformation in mononuclear complexes but rare *cisoid* conformation in dinuclear complexes. This synthetic strategy may be applied to the preparation of other early transition-metal complexes. We are currently working on the synthesis of multinuclear macrocyclic metal compounds with a similar phenoxide-functionalized carbene ligand.

Experimental Section

General Considerations: All manipulations were carried out under dry oxygen-free argon using standard Schlenk techniques. Solvents were dried by refluxing with appropriate drying agents (sodium/benzophenone for toluene, diethyl ether, THF, and hexane; CaH_2 for dichloromethane) and distilled under argon prior to use. $CDCl_3$ and C_6D_6 were distilled from CaH_2 or K and degassed by three freeze–pump–thaw cycles prior to use. The chemicals $TiBr_4$, NaN($SiMe_3$)$_2$ (1.1 M in THF), and $C_6H_5CH_2MgCl$ (1.0 M in diethyl ether) were obtained commercially and used as received. Ligand [H_3(L)]Br and complexes [(L)TiCl$_2$(thf)] and [(L)Ti(CH_2Ph)$_2$] were prepared according to the literature.[8] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a JEOL Lambda-500 spectrometer. Chemical shifts are reported in parts per million. Elemental analyses were measured using Yanaco MT-6 and MSU-32 microanalyzers.

Synthesis of [(L)TiBr$_2$(THF)] (1): Complex **1** was prepared using $TiBr_4$ instead of $TiCl_4(THF)_2$ according to a similar way of preparing [(L)TiCl$_2$(THF)].[8a] A 200-mL round-bottomed flask was charged with $[H_3L]Br$ (1.930 g, 3.3 mmol). THF (50 mL) was added and the mixture was cooled to –78 °C. A solution of 3.0 equiv. $NaN(SiMe_3)_2$ (9.9 mmol) in THF (1.0 M, 9.9 mL) was added drop by drop using a syringe. The reaction mixture was kept at –78 °C and stirred for another 30 min to afford the suspended solution of sodium salt of the ligand $Na_2[L]$. The obtained sodium salt was slowly transferred to a suspension of $TiBr_4$ (1.237 g, 3.3 mmol) in THF (50 mL) at –78 °C by cannula. The dark red solution was slowly warmed to room temperature and stirred for another 12 h. The metathesis reaction was evident by the formation of NaBr; all volatile compounds were removed under vacuum, and the crude product was extracted with toluene (50 mL) and filtered through a layer of Celite to remove NaBr. The extracts were concentrated to 10 mL and hexane (30 mL) was added. Filtration followed by drying in vacuo gave an orange-red solid, **1** (0.958 g). The mother liquid was cooled to –30 °C overnight to yield a second crop of **1** (1.023 g). Yield 75.8%. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.27 (s, 18 H, CH_3 of *t*Bu), 1.52 (s, 18 H, CH_3 of *t*Bu), 1.85 (m, 2 H, CH_2 of THF), 3.76 (m, 2 H, CH_2 of THF), 4.5–6.0 (br. m, 4 H, Ar–CH_2–N), 6.93 (br. s, 2 H, Ar-H), 7.10 (br. s, 2 H, N–CH=), 7.27 (br. s, 2 H, Ar-H) ppm. $^{13}C\{^1H\}$ NMR (127 MHz, $CDCl_3$): δ = 24.8 (CH_2 of THF), 31.0 (CH_3 of *t*Bu), 34.2, 35.10 (CMe_3), 52.2 (N–CH_2–Ar), 67.5 (O–CH_2 of THF), 119.4 (CH of imidazol), 123.7, 124.3, 124.9, 128.6, 137.8, 145.3, 164.8 (NCN) ppm. $C_{37}H_{54}Br_2N_2O_3Ti$ (782.51): calcd. C 56.79, H 6.96, N 3.58; found C 56.84, H 7.04, N 3.61.

Synthesis of $[(L)_2Ti]$ (2): $TiBr_4$ (0.187 g, 0.50 mmol) in THF (20 mL) was slowly added by channel transfer to a suspended solution of sodium salt $Na_2(L)$ obtained from the reaction of $[H_3(L)]$-Br (0.587 g, 1.0 mmol) with $NaN(SiMe_3)_2$ (3.3 mL, 1.1 M in THF) at –78 °C. The mixture was warmed to room temperature and stirred for another 12 h. The residue was evaporated to dryness and extracted with hexane/toluene (30 mL/20 mL), and the salt was removed by centrifugation. The light yellow solution was concentrated to dryness, washed with HMDSO and dried in vacuo to give a yellow solid of **2** in 73% yield. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.11 (s, 36 H, CH_3 of *t*Bu), 1.42 (s, 36 H, CH_3 of *t*Bu), 3.88 (d, 4 H, CH_2), 6.18 (s, 4 H, CH), 6.41 (d, 4 H, CH_2), 6.96 (s, 4 H, ArH), 7.46 (s, 4 H, Ar-H) ppm. $^{13}C\{^1H\}$ NMR (127 MHz, $CDCl_3$): δ = 30.4, 31.8 (CH_3 of *t*Bu), 34.1, 34.9 (CMe_3), 53.7 (CH_2), 119.5 (CH of imidazol), 123.1, 123.7, 124.4, 136.2, 138.0, 161.8, 182.4 (NCN) ppm. $C_{66}H_{94}N_4O_4Ti$ (1055.34): calcd. C 75.11, H 8.98, N 5.31; found C 75.05, H 8.92, N 5.47.

Synthesis of $[(L)Ti(CH_2Ph)_2]$ (3): Complex **3** was prepared from $[(L)TiBr_2(thf)]$ (**1**) instead of $[(L)TiCl_2(thf)]$ using a modified method. Benzylmagnesium chloride (1.4 mL, 1.0 M in diethyl ether, 1.4 mmol) was added dropwise to a precooled suspension of **1** (0.536 g, 0.69 mmol) in Et_2O (30 mL) at –78 °C. The mixture was slowly warmed to 0 °C and stirred for another 4 h at 0 °C. The solvent was removed under vacuum, and CH_2Cl_2 (20 mL) was added to the solid residue. The suspension was centrifuged to remove the formed salt and the upper clear solution was evacuated to dryness. The orange-red crude product was washed with HMDSO (5 mL) and dried in vacuo, yielding an orange solid, **3** (0.439 g). Yield 88%. $C_{47}H_{60}N_2O_2Ti$ (732.86): calcd. C 77.03, H 8.25, N 3.82; found C 76.87, H 8.33, N 3.91.

Synthesis of $\{[(L)TiBr]_2(\mu\text{-}O)\}$ (4): Water (1.0 M in Et_2O) (193 µL, 0.193 mmol) was added dropwise to a THF solution (20 mL) of **1** (0.300 g, 0.386 mmol) with an ice–water bath. The mixture was stirred overnight at room temperature and was evaporated to dryness. The crude mixture was recrystallized from THF/hexane to give red plate microcrystals (0.206 g). Yield 84%. ^1H NMR (500 MHz, C_6D_6): δ = 0.88 (t, CH_3 of hexane), 1.24 (m, CH_2 of hexane), 1.28 (s, 18 H, CH_3 of *t*Bu), 1.41 (m, OCH_2CH_2 of THF), 1.75 (s, 18 H, CH_3 of *t*Bu), 3.57 (m, OCH_2CH_2 of THF), 4.27 (br. s, 2 H, N–CH_2–Ar), 6.00 (br. s, 1 H, N–CH_2–Ar), 6.93 (br. s, 2 H, N–CH=), 7.17 (s, overlapped by 7.15 of C_6D_6), 7.49 (d, *J* = 6.4 Hz, 2 H, H-Ar) ppm. $^{13}C\{^1H\}$ NMR (127 MHz, C_6D_6): δ = 14.3 (CH_3 of hexane), 23.0 (CH_2 of hexane), 25.8 (OCH_2CH_2 of THF), 31.4, 32.7 (CH_3 of *t*Bu), 31.9 (CH_2 of hexane), 34.5, 35.8 (CMe_3), 53.2 (N–CH_2–Ar), 67.8 (OCH_2CH_2 of THF), 119.2 (CH of imidazol), 124.8, 124.9, 125.6, 127.9, 128.1, 128.3, 138.4, 143.5 (arom.), 164.0 (Ti–O–C), 185.0 (NCN) ppm. $C_{66}H_{94}Br_2N_4O_5Ti_2$ (1279.02): calcd. C 61.98, H 7.41, N 4.38; found C 61.41, H 7.12, N 3.89.

Synthesis of $\{[(L)Ti(\mu\text{-}O)]_2\}$ (5): H_2O (1 M Et_2O) (0.35 mL, 0.35 mmol) was added dropwise to a THF solution (20 mL) of **3** (0.350 mmol) with an ice–water bath. The mixture was stirred over-

Table 4. Summary of data collection and structure refinement details for **2**, **4**, and **5**.

	$2\cdot5C_6H_6$	$4\cdot C_4H_8O\cdot C_6H_{12}$	$5\cdot C_4H_8O$
Empirical formula	$C_{99}H_{125}N_4O_4Ti$	$C_{40}H_{61}BrN_2O_4Ti$	$C_{37}H_{54}N_2O_4Ti$
F_w	1483.00	761.74	638.74
T [K]	123	123	123
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	12.608(6)	10.387(6)	9.523(4)
b [Å]	14.217(6)	13.419(7)	13.419(6)
c [Å]	24.70(1)	15.916(8)	15.086(7)
α [°]	90.831(7)	69.00(3)	76.60(2)
β [°]	97.75(1)	74.25(3)	77.53(2)
γ [°]	94.51(1)	76.89(3)	75.40(2)
V [Å^3]	4371(3)	1972.5(18)	1789.1(13)
Z	2	2	2
$D_{calcd.}$ [g cm^{-3}]	1.127	1.282	1.186
μ(Mo-K_α) [mm^{-1}]	1.503	12.733	2.78
Measured reflections	70112	31334	28788
Unique reflections	19241	8684	7857
R_1/wR_2[a]	0.098/0.286	0.075/0.217	0.092/0.182
Gof	1.000	1.001	1.217
Min./max. electron density [e Å^{-3}]	–2.38/0.82	–1.15/3.59	–1.10/2.25

[a] Definitions: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

night at room temperature and was evaporated to dryness. The crude mixture was recrystallized from THF/hexane to give 0.167 g of **5** as light yellow plate crystals. Yield 84%. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.43 (s, 36 H, CH_3 of *t*Bu), 1.63 (s, 36 H, CH_3 of *t*Bu), 3.96, 3.99 (br. s, 4 H, N–CH_2–Ar), 5.74 (s, 4 H, N–CH=), 6.04, 6.07 (br. s, 4 H, N–CH_2–Ar), 7.07 (d, *J* = 2.5 Hz, 4 H, H-Ar), 7.51 (d, *J* = 2.5 Hz, 4 H, H-Ar) ppm. ^{13}C{^{1}H} NMR (127 MHz, $CDCl_3$): δ = 30.8, 32.0 (CH_3 of *t*Bu), 34.4, 35.4 (*C*Me$_3$), 53.1 (N–CH_2–Ar), 119.2 (CH of imidazol), 124.4, 124.6, 124.7, 128.3 138.2, 140.6 (arom.), 162.5 (Ti–O–C), 188.4 (NCN) ppm. $C_{66}H_{94}N_4O_6Ti_2$ (1135.21): calcd. C 69.83, H 8.35, N 4.94; found C 69.74, H 8.43, N 4.97.

Ethylene Polymerization: A 500-mL autoclave was charged with 240 mL of toluene under argon and a mixture of titanium complex/MAO (the molar ratio of Al:Ti was 1000) in 10 mL toluene was added. After three ethylene gas exchanges, the ethylene pressure was raised to 7 bar and maintained for 1 h. The polymerization was terminated by the addition of methanol and diluted HCl (10%). The solid polyethylene was filtered, washed with methanol, and dried at 40 °C in vacuo.

X-ray Crystal Structure Determination: A suitable crystal was immersed in mineral oil and mounted on a nylon loop in a random orientation under a cold stream of dry nitrogen (Rigaku GNNP low-temperature device). Diffraction experiments were performed with Mo-K_α radiation (α = 0.71070 Å) on a Rigaku CCD diffractometer. The data were collected in a hemisphere of data in 720 frames with 20–40-s exposure times. The data sets were collected ($4.0 < 2\theta < 45$–$55°$). The data were processed using CrystalClear (Rigaku) Processing packages.[21] The structures were determined by routine heavy-atom and Fourier methods by using SHELXS-97[22] and refined by full-matrix least-squares. The non-hydrogen atoms were refined with anisotropic parameters and the hydrogen atoms with fixed isotropic thermal parameters of 0.07 Å by means of the SHELXL-97[23] program. The hydrogen atoms were partially located from difference electron-density maps and the rest were fixed at predetermined positions. Scattering factors were from common sources. Some details of data collection and refinement are given in Table 4.

CCDC-639449, -639453, and -639454 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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