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Facile Formation of Hexacyclic [Al_3O_2Cl] Aluminum and Alkoxide-Bridged Titanium Complexes: Reactions of $AlMe_3$ with [Ti(L)Cl_2] [L = 2,2′-Methylenebis(6-*tert*-butyl-4-methylphenolato)]

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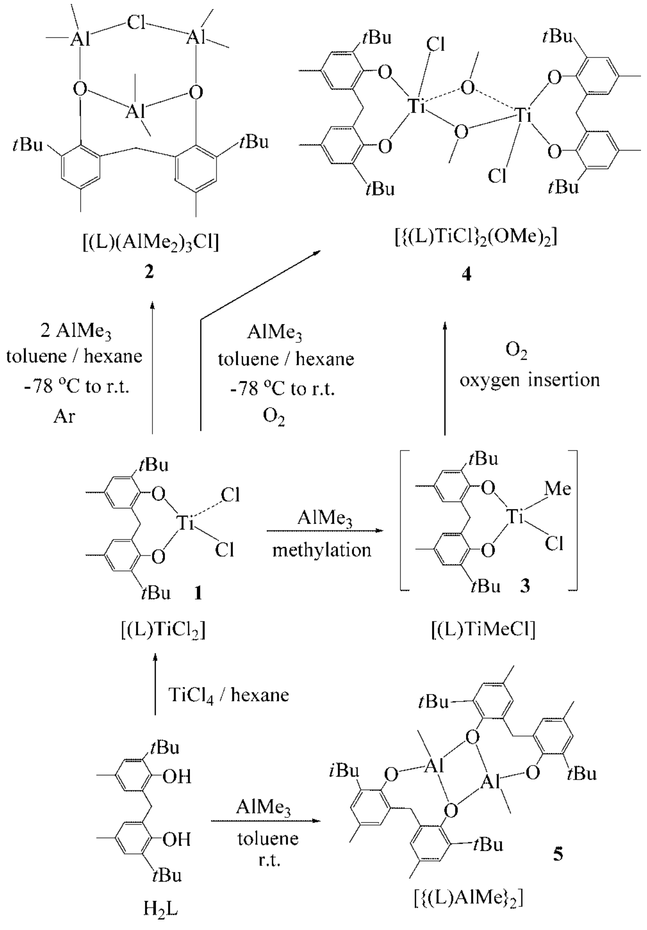
The titanium dichloride complex [(L)$TiCl_2$] [L = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)] (**1**) reacted with trimethylaluminum ($AlMe_3$) in a 1:2 ratio to give a trimetallic aluminum complex of the composition [(L)$(AlMe_2)_3$(μ-Cl)] (**2**) with a symmetric six-membered ring [$Al_3(\mu_2\text{-}O)_2(\mu_2\text{-}Cl)$] and a four-coordinate aluminum center in the solid state. The reaction of 1 equiv. $AlMe_3$ gave [(L)TiMeCl] (**3**), which could absorb O_2 gas to afford the oxygen-insertion product [{(L)-TiCl}$_2$(μ-OMe)$_2$] (**4**) with a five-coordinate metal center. Upon reaction of H_2L with $AlMe_3$, the binuclear, four-coordinate adduct [{(L)AlMe}$_2$] (**5**) was formed. Complex **4** supported on $MgCl_2$ and activated with aluminum alkyls reveals high catalytic activity for ethylene polymerization to produce polymers with molecular weight distributions of ca. 3.1.

Introduction

Reactions of organometal(IV) halides with alkyls of group 13 elements, especially those of aluminum, have attracted much interest because of their inherent fundamental chemistry as well as their potential applications. The methylation of a metallocene(IV) chloride is assumed to be the first step of activation of a polymerization catalyst and one of the first well-defined products is Tebbe's reagent, [$Cp_2Ti(\mu_2\text{-}CH_2)(\mu_2\text{-}Cl)AlMe_2$], derived from Cp_2TiMe_2 and $AlMe_3$.[1] Later, methyl nonmetallocene transition-metal complexes could be conveniently prepared with the Jordan amido/alkyl exchange protocol using $AlMe_3$, a technique primarily utilized with complexes of the metallocene type.[2] Several novel aluminum-containing clusters, [$(Cp^*M)_3Al_6Me_8(CH)_5(CH_2)_2$] (M = Zr, Hf),[3] [($t$$Bu_3$PN)Ti(μ-Me)($\mu_4$-C)-$(AlMe_2)_2$]$_2$,[4] and [$Cp^*_4Y_4(\mu_2\text{-}CH_3)_2\{(CH_3)Al(\mu_2\text{-}CH_3)_2\}_4(\mu_4\text{-}CH)_2$],[5] have been developed by the reactions of the corresponding metal complexes with $AlMe_3$ that could perform the abstraction of hydrogen from methyl groups. Nevertheless, such clusters, particularly those bearing two or more different metals, are very rare because of the limitations inherent in available synthetic methods. Moreover, a surprisingly facile transmetalation of the multidentate ligands from a transition metal such as zirconium or iron to aluminum was reported by using AlR_3 (R = Me or Et).[6,7]

As part of an ongoing project whose aim is to study the chemistry of olefin polymerization catalysis, some novel metal catalysts have been designed and successfully pre-



Scheme 1. Synthesis of aluminum and titanium complexes **2**–**5** using $AlMe_3$.

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pared.[8] Our goal is to create highly active, single-site heterogeneous systems for the ethylene polymerization process. Some titanium complexes supported on $MgCl_2$, which is a widely used support in conventional Z–N catalysts, and activated with aluminum alkyls are highly effective ethylene polymerization catalysts.[9] Especially the interaction of titanium compounds with aluminum derivatives was of great interest to us for understanding the high activity of titanium aryloxides in the ethylene polymerization process.[10]

In the present report, we aim to present the synthesis and structures of an unexpected trimetallic, hexacyclic aluminum and alkoxide-bridged titanium complex by the reaction of trimethylaluminum with $[(L)TiCl]_2$ [(L) = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)] (**1**) (Scheme 1). To the best of our knowledge, such examples have never been demonstrated. Ethylene polymerization with an alkoxide-bridged titanium complex supported on $MgCl_2$ and activated with alkylaluminum compounds is also included.

Results and Discussion

Reaction of $AlMe_3$ solved in toluene with **1** at a 2:1 molar ratio at room temp. leads to a color change from red to dark brown, and the air- and moisture-sensitive complex, $[(L)(AlMe_2)_3Cl]$ (**2**), is formed as dark green crystals and isolated by filtration in 31 % yield after the reaction solution is cooled to –20 °C overnight. Compound **2** does not react further with $AlMe_3$, even not at 100 °C in [D$_8$]toluene, and is soluble and stable in benzene and toluene.

The ^1H (see Figure 1) and ^{13}C NMR spectra of **2** are in good agreement with the crystal structure obtained from X-ray diffraction techniques. The alkyl groups attached to the metal centers are not equivalent and are in the expected chemical shift ranges; both the ^1H and ^{13}C signals are shifted distinctly from the starting $AlMe_3$. ^1H NMR spectroscopic data for **2** reveals the presence of three different methyl ($AlMe_2$) environments at δ = –1.19, –0.52, and 0.17 ppm in [D$_6$]benzene (δ = –1.26, –0.57, and 0.12 ppm in [D$_8$]toluene) with integral intensity ratios of 3:6:9 (Figure 1). Also observed is one set of resonances for the L ligand. These observations suggest that compound **2** has the same structure in solution and in the solid state.

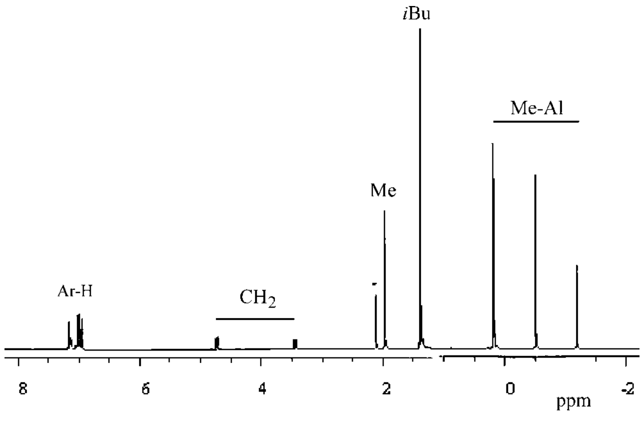

Figure 1. ^1H NMR spectra of **2** (containing toluene marked with *) in [D$_6$]benzene.

In the solid state, compound **2** forms unexpected trinuclear aluminum molecules in which there are no titanium atoms, indicating that transmetalation occurs (Figure 2 and Table 1). The central, nearly symmetrical, hexacyclic $[Al_3(\mu_2\text{-}O)_2(\mu_2\text{-}Cl)]$ is composed of three aluminum atoms, one bridging chlorine, and two bridging oxygen atoms [O(1), O(1A)] of the L ligand. This type of bridging has been rarely observed in phenolate aluminum compounds. Each aluminum atom is coordinated in a distorted tetrahedral fashion by oxygen [O(1), O(1A)] of the L ligands or chloride besides two methyl groups. The Al–O bond lengths are similar to those found in other structures of four-coordinate aluminum aryloxides.[11] The Al–Cl distance of 2.321(2) Å lies in the range of 2.2695(17)–2.3224(11) Å observed for other chlorine-bridged aluminum complexes with multidentate aryloxide ligands linked by three different spacers.[12]

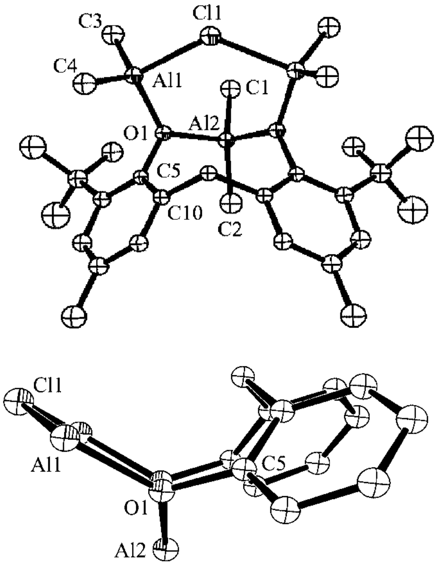

Figure 2. Molecular structure of **2**.

Table 1. Selected bond lengths [Å] and angles [°] for **2**.

Cl(1)–Al(1)	2.321(2)	Al(1)–O(1)	1.855(5)
Al(1)–C(3)	1.954(6)	Al(1)–C(4)	1.935(8)
Al(2)–O(1)	1.890(5)	Al(2)–C(1)	1.929(7)
Al(2)–C(2)	1.96(1)	O(1)–C(5)	1.436(5)
C(5)–C(10)	1.397(7)	C(10)–C(11)	1.521(8)
O(1)–Al(1)–C(3)	115.4(3)	O(1)–Al(1)–C(4)	111.5(2)
O(1)–Al(1)–Cl(1)	99.9(1)	C(3)–Al(1)–C(4)	119.3(3)
C(3)–Al(1)–Cl(1)	102.3(2)	C(4)–Al(1)–Cl(1)	105.3(3)
O(1)–Al(2)–C(1)	106.6(2)	O(1)–Al(2)–C(2)	108.2(2)
C(1)–Al(2)–C(2)	123.8(5)	C(5)–O(1)–Al(1)	117.1(4)
C(5)–O(1)–Al(2)	114.9(3)	Al(1)–O(1)–Al(2)	126.6(2)
C(10)–C(5)–O(1)	116.3(5)	C(11)–C(10)–C(5)	123.4(4)

However, treatment of **1** with precisely 1 equiv. $AlMe_3$ in [D$_6$]benzene in a J-Young tube under argon resulted in the formation of an unidentified mixture (^1H NMR), and no [(L)TiMeCl] (**3**) could be isolated. Interestingly, the same reaction carried out under O_2 affords small amount of yellow, very thin, needle-like crystals of $\{[(L)TiCl]_2(\mu\text{-}OMe)_2\}$ (**4**). The formation of **4** clearly indicates the insertion of dioxygen into "M–R" bonds of the resultant intermediate titanium complex **3**.[13] The presence of ν(Ti–Cl) frequencies at ca. 419 cm^{-1} in the IR spectra of **4** indicates characteristic modes for terminally coordinated chlorine. The methoxy groups bridging the two titanium centers are equivalent, giving rise to one singlet at δ = 4.12 ppm in the ^{1}H NMR spectra. Also, one set of resonances due to the (L) ligand, slightly shifted from that detected for **1**, was observed.

The X-ray crystal structure of **4** (Figure 3 and Table 2) shows that the binuclear molecule contains a core of two internal aluminum atoms linked by oxygen atoms from the two OMe groups. The remaining two chlorine atoms are bonded terminally to the titanium atoms. Two boat-conformation L ligands are bonded similarly, having two oxygen atoms in the same titanium coordination sphere. The coordination sphere around the titanium center can be described as distorted square pyramidal, the oxygen atoms of the L ligand [O(1), O(2)] and of two bridging OMe groups [O(3), O(3A)] forming the equatorial plane, while the chlorine atom [Cl(1)] occupies the apical sites. As expected, the average Ti–μ-O (methoxo) distance of 1.962(2) Å is significantly longer than the terminal ones [av. 1.788(3) Å] but similar to those observed in [(tritox)$_2$Ti$_2$(μ-OMe)$_2$Me$_2$] [2.015(10) Å].[13a] The Ti–Cl distance of 2.2599(1) Å is shorter than that detected in [(tbmp)Ti (η^5-C$_5$H$_5$)Cl] [2.343(2)] and Ti(tmbp)Cl$_2$ [2.236(2) Å] (tmbp = 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo)[14] and is only surpassed by the values of 2.252(2) and 2.237(2) Å found in [(tbop)$_2$Ti$_3$(OEt)$_2$Cl$_6$].[15]

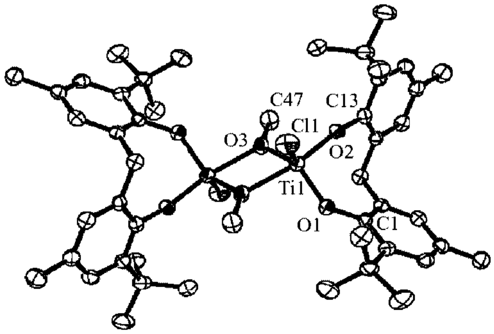

Figure 3. Molecular structure of **4**.

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

Ti(1)–Cl(1)	2.259(1)	Ti(1)–O(1)	1.805(2)
Ti(1)–O(2)	1.776(2)	Ti(1)–O(3)	1.962(2)
Cl(1)–Ti(1)–O(1)	112.52(8)	Cl(1)–Ti(1)–O(2)	98.95(9)
Cl(1)–Ti(1)–O(3)	121.75(8)	O(1)–Ti(1)–O(2)	98.0(1)
O(1)–Ti(1)–O(3)	122.2(1)	O(2)–Ti(1)–O(3)	92.1(1)
Cl(2)–Ti(2)–O(4)	112.67(8)	C(1)–O(1)–Ti(1)	140.9(2)
C(13)–O(2)–Ti(1)	155.4(3)	C(47)–O(3)–Ti(1)	129.6(2)

The reaction of H$_2$L and AlMe$_3$ in an equimolar ratio in toluene as well as in *n*-hexane leads to formation of the dimer {[(L)AlMe]$_2$} (**5**) in good yield.[12d] There is no OH resonance in the ^{1}H NMR spectrum, indicating a loss of hydroxy protons. The methyl groups attached to the metal centers are equivalent and are in the expected chemical shift ranges; both the ^{1}H and ^{13}C signals are shifted slightly from the starting AlMe$_3$.

Crystals of **5** suitable for X-ray structure determination were obtained from hexane/toluene. The molecular structure of **5** is shown in Figure 4, and selected bond lengths and angles are listed in Table 3. Crystals of **5** comprise a centrosymmetric dimer with a planar Ti$_2$O$_2$ core. The titanium atoms in **4** have tetrahedral geometry. The two Al–O(aryloxo) distances of 1.693(1) and 1.856(1) Å are in the expected range for Al^{III} complexes with facially coordinated bis(aryloxo) ligands. The Ti–C(methyl) distance of 1.941(3) Å is typical for Ti$_2$O$_2$ moieties and similar to those observed in [(tritox)$_2$Ti$_2$(μ-OMe)$_2$Me$_2$] [2.063(10) Å][13a] and [(L)TiMe$_2$] [2.090(9) and 2.030(10) Å].[16]

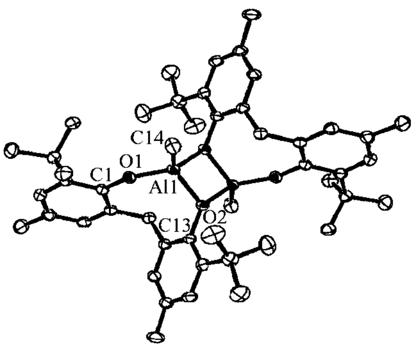

Figure 4. Molecular structure of **5**.

Table 3. Selected bond lengths [Å] and angles [°] for **5**.

Al(1)–O(1)	1.693(1)	Al(1)–O(2)	1.856(1)
Al(1)–C(14)	1.941(3)	O(1)–Al(1)–O(2)	108.93(6)
O(1)–Al(1)–C(14)	108.1(1)	O(2)–Al(1)–C(14)	125.64(8)
C(1)–O(1)–Al(1)	158.2(2)	C(13)–O(2)–Al(1)	124.8(1)

Titanium complex **4** was tested in an ethylene polymerization process. The catalyst was prepared in *n*-hexane by milling a slurry of [MgCl$_2$(thf)$_2$] with **4** (the molar ratio is 10:1) and AlEt$_2$Cl as the cocatalyst (see Exp. Sect.). Prior to the polymerization, ethylene was passed through the suspension of the catalyst. Then, MAO was added to the catalyst and dispersed in the prepolymer to form a highly active catalyst. Thus, the polymerization of ethylene was performed in a two-step process. The aim of the first step (very low Al:Ti molar ratio, normal pressure of monomer, very low rate of polymerization) was to prepare granules of polymer containing dispersed catalyst. These granules acted as a "microreactor" in the second step of polymerization with a high rate (Granular Reactor Technology). This method gave PE yields twice as high as those obtained with the one-stage activation process. The ethylene polymerization results and polymer characterization data are summarized in Table 4.

Table 4. Results of ethylene polymerization.[a]

Entry	Complex	T [°C]	Activity[b]	M_w/M_n
1	**4**	50	123	3.08
2	**4**	70	149	3.11
3[c]	**4**	50	278	n.d.[d]
4	Cp_2TiCl_2	50	108	2.94

[a] Polymerization conditions: MAO (Al:Ti = 4000) as the cocatalyst, ethylene pressure: P_{gauge} = 70 psi, 0.5 h. [b] kg PE g^{-1} Ti h^{-1}. [c] Ethylene pressure is P_{gauge} = 100 psi. [d] Not determined.

For comparison of catalyst activities, titanocene dichloride (Cp_2TiCl_2) was used as a reference under the same conditions (Table 1, entry 4). It turned out that the catalysts based on complex **4** (entries 1–3) exhibited comparable catalytic activity (about 120 kg PE g^{-1} Ti h^{-1}) for ethylene polymerization. This is compared with the titanocene catalyst, and much less than that originally reported for [(tbmp)TiX$_2$]/MAO (820 kg PE/g of Ti h for X = Cl and 677 kg PE/g of Ti h for X = O*i*Pr; 20 °C, 3 MPa, 1 μmmol catalyst)[17] and [(tbop)$_2$Ti$_3$(OEt)$_2$Cl$_6$]/MAO (353 kg PE/g of Ti h; 50 °C, 0.5 MPa, 1 μmmol catalyst)[15] systems. The molecular weights (M_w) of the polyethylene produced range from 9.18 to 11.97×10^5, and the molecular weight distributions (M_w/M_n) are narrower than those reported for ethylene polymerization with catalysts.[18,19] It would appear that, for polymerization of ethylene, activation of systems based on complex **4** affords a single well-defined active species. This indicates that the cocatalyst does not abstract the ligand L from the titanium center to the aluminum. The nature of the active center in the catalyst based on the L–titanium complexes is currently being investigated.

Conclusions

In contrast to methylation of some organometal chlorides with $AlMe_3$, the unexpected transmetalation reaction of the corresponding titanium chloride complex **1** with $AlMe_3$ in a 1:2 ratio occurs with the generation of trialuminum complex **2** with a symmetrical, hexacyclic [$Al_3(\mu_2\text{-}O)_2(\mu_2\text{-}Cl)$] core. The reaction of **1** with $AlMe_3$ in an equimolar ratio affords the methoxy-bridged dimeric titanium chloride complex **4**, which suggests the formation of the monomethyl titanium complex **3** that easily absorbs O_2 to give an oxygen-insertion product. Treatment of H_2mbmp with $AlMe_3$ leads to the formation of the dimeric methyl titanium complex **5**. Complex **4** supported on $MgCl_2$ and activated with aluminum alkyls is highly effective as an ethylene polymerization catalyst. The narrow molecular weight distribution for this system suggests the operation of a well-defined, heterogeneous single-site catalyst.

Experimental Section

General Considerations: All operations were carried out under a dry argon atmosphere, using standard Schlenk techniques. All of the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. [D$_6$]Benzene and [D$_8$]toluene were distilled from K metal and degassed by three freeze-pump-thaw cycles prior to use. The $TiCl_4$, $AlMe_3$ solution (1.0 M in hexane), and MAO compounds were obtained from the Aldrich Chemical Co. and were used without further purification unless stated otherwise. 2,2′-Methylenebis(6-*tert*-butyl-4-methylphenol) [H$_2$(L)] and [Ti(L)Cl$_2$] (**1**) were synthesized according to literature methods.[20] ^{1}H and ^{13}C NMR spectra were recorded with a JEOL Lambda-500 spectrometer. Chemical shifts are reported in parts per million. Elemental analyses were measured with Yanaco MT-6 and MSU-32 microanalyzers. Infrared spectra were recorded with a Perkin–Elmer 180 spectrophotometer in Nujol mulls.

Synthesis of [(L)(AlMe$_2$)$_3$(μ-Cl)] (2): $AlMe_3$ (1.0 M Me$_3$Al, 0.82 mL in hexane, 0.82 mmol) was added to a toluene/hexane solution (10/40 mL) of Ti(L)Cl$_2$ (**1**) (188 mg, 0.41 mmol) at –78 °C. The mixture was slowly warmed to room temp., and the color of the solution changed from red to brown-yellow and finally dark brown. After the resulting solution was stirred for another 8 h, the blue precipitate was separated by filtration. The clear solution was cooled to –20 °C for about one week to afford **2** as dark green crystals in 31% yield (46 mg based on $AlMe_3$). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = –1.19 (s, 3 H, CH$_3$-Al), –0.52 (s, 6 H, CH$_3$-Al), 0.17 (s, 9 H, CH$_3$-Al), 1.38 (s, 18 H, C(CH$_3$)$_3$), 1.97 (s, 6 H, CH$_3$), 2.11 (s, 3 H, toluene), 3.45 (d, $J_{H\text{-}H}$ = 13.65 Hz, CH$_2$), 4.73 (d, $J_{H\text{-}H}$ = 13.65 Hz, CH$_2$), 6.96 (s, 2 H, Ar), 7.00–7.13 (m, 5 H, toluene), 7.16 (s, 2 H, Ar) ppm. ^{1}H NMR (500 MHz, C$_7$D$_8$): δ = –1.26 (s, 3 H, CH$_3$-Al), –0.57 (s, 6 H, CH$_3$-Al), 0.12 (s, 3 H, CH$_3$-Al), 0.13 (s, 6 H, CH$_3$-Al), 1.40 (s, 18 H, C(CH$_3$)$_3$), 2.01 (s, 6 H, CH$_3$), 2.14 (s, toluene), 3.38 (d, $J_{H\text{-}H}$ = 13.65 Hz, CH$_2$), 4.66 (d, $J_{H\text{-}H}$ = 13.65 Hz, CH$_2$), 6.94 –7.12 (m, H-Ar, toluene) ppm. ^{13}C NMR (126 MHz, C$_6$D$_6$): δ = 147.35, 140.60, 137.84, 135.23, 134.69, 130.32, 129.28, 129.18, 128.51, 128.29, 128.10, 127.91, 125.64, 35.68, 34.48, 32.75, 21.36, 20.85, –2.85, –6.00, –7.42, –8.75 ppm. $C_{29}H_{48}Al_3ClO_2$ (545.09): calcd. C 63.90, H 8.88; found C 63.77, H 8.91.

Synthesis of [{(L)TiCl}$_2$(μ-OMe)$_2$] (4): $AlMe_3$ (1.0 equiv. $AlMe_3$, 1.64 mL in hexane, 1.64 mmol) was added to a toluene/hexane solution (10/40 mL) of [(L)TiCl$_2$] (**1**) (0.375 g, 0.82 mmol) at –78 °C. The mixture was slowly warmed to room temp., and the color of the solution changed from red to orange. After the resulting solution was stirred for another 8 h under a dioxygen atmosphere, the precipitate was separated by filtration. The clear solution was cooled to –35 °C for about one week to afford orange crystals in 21% yield. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 1.47 (s, 9 H, CH$_3$), 1.52 (s, 9 H, CH$_3$), 2.05 (s, 3 H, CH$_3$), 2.08 (s, 3 H, CH$_3$), 3.42 (d, $J_{H\text{-}H}$ = 14.0 Hz, CH$_2$), 3.95 (d, $J_{H\text{-}H}$ = 14.0 Hz, CH$_2$), 4.12 (s, 6 H), 6.87 (s, 1 H, Ar), 6.92 (s, 3 H, Ar), 6.70 (s, 2 H, Ar) ppm. ^{13}C NMR (126 MHz, C$_6$D$_6$): δ = 161.73, 161.52 ($\triangle\delta$ = 0.208, O-C$_{Ar}$), 136.44, 136.37, 136.01, 135.28, 133.17, 133.06, 129.28, 129.02, 128.97, 128.51, 128.41, 128.30, 128.10, 127.91, 126.11, 126.08, 69.81, 64.56, 35.38, 35.22, 35.16, 34.65, 30.32, 30.21, 21.05, 21.01 ppm. $C_{48}H_{66}Cl_2O_6Ti_2$ (905.67): calcd. C 63.66, H 7.35; found C 63.91, H 7.42.

Synthesis of {[(L)AlMe]$_2$} (5): Complex **5** was prepared by using a modification of the technique used in ref.[12d]. $AlMe_3$ (1.0 equiv. $AlMe_3$, 1.5 mL in hexane, 1.5 mmol) was added to a toluene/hexane solution (10/15 mL) of H$_2$L (0.5 g, 1.5 mmol) at –78 °C. The mixture was slowly warmed to room temp. and a white solid appeared. After the resulting mixture was stirred for another 8 h, the precipitate was separated by filtration and washed with hexane to give 0.29 g of **5** as a white solid in 52% yield. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 0.144 (s, 3 H, Al-CH$_3$), 1.37 (s, 9 H, CH$_3$), 1.40 (s, 9 H, CH$_3$), 1.84 (s, 3 H, CH$_3$), 2.32 (s, 3 H, CH$_3$), 3.69 (d, $J_{H\text{-}H}$ = 12.95 Hz, CH$_2$), 4.69 (d, $J_{H\text{-}H}$ = 12.95 Hz, CH$_2$), 6.88 (s, 1 H, Ar), 7.04 (s, 1 H, Ar) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = 161.73, 161.52 ($\triangle\delta$ = 0.208, O-C_{Ar}), 136.44, 136.37, 136.01, 135.28, 133.17, 133.06, 129.28, 129.02, 128.97, 128.51, 128.41, 128.30, 128.10, 127.91, 126.11, 126.08, 69.81, 64.56, 35.38, 35.22, 35.16, 34.65, 30.32, 30.21, 21.05, 21.01 ppm. $C_{48}H_{66}Al_2O_4$ (761.00): calcd. C 75.76, H 8.74; found C 75.67, H 8.71.

Ethylene Polymerization: To a slurry of [$MgCl_2(thf)_2$] (10 mmol) in *n*-hexane milled under argon in a glass mill (250 mL capacity, with 20 balls) at room temp. for 10 h, were added the titanium compound **4** (1 mmol) and *n*-hexane (50 mL). After the mixture was milled for an additional 24 h, the sample of precatalyst suspension (containing 0.01 mmol of titanium) was activated with $AlEt_2Cl$ (the molar ratio Al:Ti is 150) for 15 min at 50 °C under argon. Prior to polymerization, ethylene was passed through the suspension of the catalyst (10 mL) in a Schlenk ampoule for 15 min at room temp. and normal pressure, and the prepolymer was obtained. Then, MAO was added to the catalyst and dispersed in the prepolymer to form a highly active catalyst. The polymerization of ethylene was carried out in *n*-hexane at 50 or 70 °C in a stainless steel reactor (1 L), equipped with a stirrer, at P_{gauge} = 70 or 100 psi pressure. The polymerization was quenched with a solution of HCl (5% in methanol) and dried under vacuum. The molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polypropylenes were determined by GPC in 1,2,4-trichlorobenzene using standard polystyrenes as a reference.

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 (λ = 0.71070 Å) in a Rigaku CCD diffractometer. The data were collected in a hemisphere in 720 frames with 20–40-s exposure times ($4.0° < 2\theta < 45–55°$). The data were processed by using CrystalClear (Rigaku) processing packages.[21] The structures were determined by routine heavy-atom and Fourier methods by using SHELXS97[22] and refined by full-matrix least-squares with the non-hydrogen atoms with anisotropic and hydrogen with fixed isotropic thermal parameters of 0.07 Å by means of the SHELXL97[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.[24] Some details of data collection and refinement are given in Table 5.

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

Compound	**2**	**4**	**5**
Formula	$C_{29}H_{48}Al_3ClO_2$	$C_{56}H_{85}Cl_2O_6Ti_2$	$C_{30}H_{39}AlO_2$
F_w	545.09	1020.99	458.62
Temp. [K]	173	173	173
Crystal system	monoclinic	monoclinic	triclinic
Space group	*Cm* (#8)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a [Å]	11.677(8)	9.787(3)	9.209(3)
b [Å]	20.261(11)	12.689(4)	11.613(3)
c [Å]	9.214(6)	25.294(8)	14.466(5)
α [°]	90	73.659(10)	73.496(12)
β [°]	121.886(8)	78.020(12)	87.58(1)
γ [°]	90	76.319(12)	66.038(10)
V [Å^3]	1850.9(20)	2895.2(17)	1350.8(7)
Z	4	2	2
D_{calcd}. [g cm^{-3}]	1.956	1.171	1.127
μ (Mo-K_α) [mm^{-1}]	3.87	4.12	0.98
No. of unique reflections	2180	12712	5898
R_1/wR_2 [a]	0.090/0.144	0.076/0.161	0.057/0.172
GOF	1.053	1.035	1.001
Min./max. electron density [e Å^3]	–0.60/0.86	–0.66/1.20	–0.44/0.51

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

CCDC-631721 (for **2**), -631722 (for **4**), and -631723 (for **5**) 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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