Highly Efficient One-Step Direct Synthesis of Monocyclopentadienyltitanium Complexes

Yuetao Zhang and Ying Mu*

Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, School of Chemistry, Jilin University, 10 Qianwei Road, Changchun 130012, People's Republic of China

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This report describes a highly efficient one-step synthetic strategy for monocyclopentadienyltitanium complexes by the direct reaction of $TiCl_4$ with substituted cyclopentadienes, without adding any other reagents. This new synthetic method is particularly efficient for cyclopentadienes with a pendant group that can bond or coordinate to the Ti atom.

Introduction

Group 4 metallocene complexes have been used as catalysts for many organic and polymerization reactions, such as the olefin polymerization reaction,[1] organosilane dehydrocoupling reaction,[2] and Diels−Alder reaction,[3] as well as the hydrogenation,[4] hydrosilation,[5] hydroamination,[6] and coupling reactions of unsaturated organic compounds,[7] of which the olefin polymerization reaction is probably the most important one for human society and thus has been extensively studied by scientists in the industrial and academic communities. Group 4 metallocene-based catalysts can produce a number of high-performance polyolefin products, including isotactic polypropylene, syndiotactic polypropylene, atactic polypropylene, linear high-density polyethylene, linear low-density polyethylene, syndiotactic polystyrene, and cycloolefin copolymer. As we know, polyolefins are the largest volume synthetic materials used in the world and have been applied in almost every aspect of our daily lives. The global polyethylene demand is expected to increase from about 55 million metric tons in 2002 to 87 million metric tons in 2010, and polypropylene demand is expected to grow from about 35 million metric tons to nearly 60 million metric tons in the same period.[8] The growing demand for high-performance polyolefin products in recent years has further inspired industrial and academic interest in developing efficient synthetic methods for metallocenes and high-performance olefin polymerization catalysts.[9] Thus far, a number of synthetic strategies, such as lithium salt elimination,[10] amine elimination,[11] alkane elimination,[12] and Me_3SiCl,[13] Me_2SnCl_2,[14] and $Al_2Me_4(\mu\text{-}NMe_2)_2$[15] elimination reactions, as well as the oxidative addition reaction of cyclopentadiene with lower halides,[16] have been developed for the synthesis of metallocene complexes. However, due to multistep syntheses, expensive reagents, and harsh reaction conditions, present synthetic techniques are still too complicated and expensive for commercial application of metallocene catalysts in polyolefin industry. We herein report a highly efficient one-step synthesis of monocyclopentadienyltitanium complexes by the direct reaction of $TiCl_4$ with substituted cyclopentadienes under mild conditions without adding any other reagents. To the best of our knowledge, this is the first time that metallocene complexes have been synthesized in high yields by such an easy synthetic approach. Similar reactions of $TiCl_4$ with cyclopentadiene and $C_5H_5(CH_2)_nN(R)H$ in the presence of Et_3N were reported before,[17] but the introduction of Et_3N makes the isolation and purification of the products complicated, and therefore, the cost of the products increased. It has been known that some monocyclopentadienyltitanium complexes,[18] especially the so-called constrained-geometry titanium complexes,[19] are excellent catalysts for producing syndiotactic polystyrene and high-molecular-weight atactic

* To whom correspondence should be addressed. Fax: (+86) 431-5193421. Tel: (+86) 431-5168472. E-mail: ymu@mail.jlu.edu.cn.

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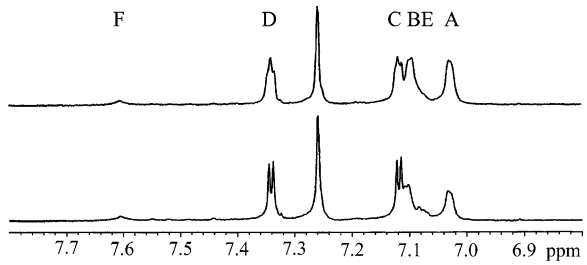


Figure 1. Stack plot of the aromatic region of ^{1}H NMR spectra recorded from the NMR tube reaction of $TiCl_4$ with $(TCDBP)H_2$ at 15 min and 40 min.

polypropylene, as well as copolymers of ethylene with propylene, α-olefins, styrene, and norbornene. Some of the constrained-geometry titanium complexes have been applied as catalysts in the industrial production of polyolefins.[20] Our new synthetic technique is undoubtedly a breakthrough in the methodology and concept of preparing metallocene complexes and might be helpful in promoting the application of metallocene catalysts.

Results and Discussion

Synthesis of Constrained-Geometry Titanium Dichloride Complexes 1−4. We reported recently a series of constrained-geometry cyclopentadienylphenoxytitanium(IV) dichloride complexes synthesized by a template lithium salt elimination approach.[21] These complexes show catalytic performance similar to that of the constrained-geometry titanium catalysts used currently in industry.[20] To understand the reaction mechanism, the interaction of 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenol ($TCDBPH_2$) with $TiCl_4$ in $CDCl_3$ was followed by ^{1}H NMR. It was a great surprise to us that the signals of the final products, (2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenoxy)titanium dichlorides ($TCDBPTiCl_2$), were observed before the addition of ^{n}BuLi. This result promoted us to investigate the reaction in detail on the NMR tube and flask scales, and a highly efficient one-step synthetic method for the monocyclopentadienyltitanium complexes was finally developed. The important feature of this new method is that the monocyclopentadienyltitanium complexes can be easily synthesized in high yields by the direct reaction of cyclopentadiene derivatives with $TiCl_4$ in a 1:1 molar ratio without using any other reagents. The new method was first tested for the reactions of $TiCl_4$ with 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenol ($(TCDBP)H_2$), 2-(tetramethylcyclopentadienyl)-6-*tert*-butylphenol ($(TCBP)H_2$), 2-(tetramethylcyclopentadienyl)-6-phenylphenol ($(TCPP)H_2$), and 2-(tetramethylcyclopentadienyl)-6-methylphenol ($(TCMP)H_2$) in toluene at room temperature, and the corresponding complexes $(TCDBP)TiCl_2$ (**1**), $(TCBP)TiCl_2$ (**2**), $(TCPP)TiCl_2$ (**3**), and $(TCMP)TiCl_2$ (**4**) were obtained in high yields of 92.4, 89.3, 75.3, and 64.7%, respectively. During the reactions of $TiCl_4$ with free ligands in NMR tubes, a small amount of an intermediate was observed by ^{1}H NMR for these systems. Figure 1 shows the aromatic region of a ^{1}H NMR spectrum recorded from the NMR tube reaction of $TiCl_4$ with $(TCDBP)H_2$. Peaks A and B are the signals of the Ph protons of the free $(TCDBP)H_2$ and C and D are the signals of the Ph protons of the $(TCDBP)TiCl_2$ complex, while E and F

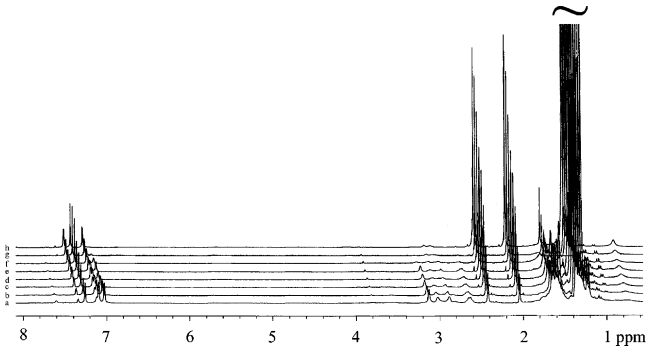
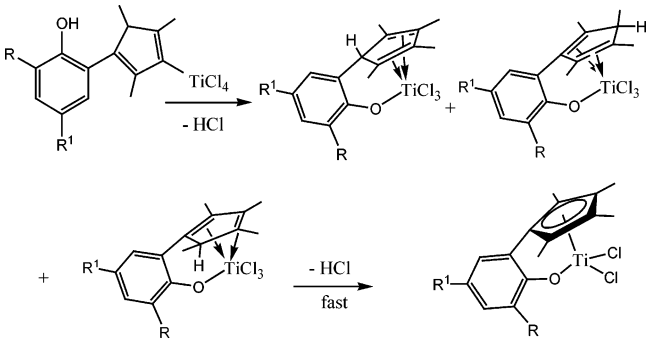


Figure 2. ^{1}H NMR spectra recorded from the free ligand ($(TCDBP)H_2$) to the $(TCDBP)TiCl_2$ complex at 30 °C. The initial concentration of $(TCDBP)H_2$ is 0.054 mol/L. Time: (a) 3 min; (b) 7 min; (c) 15 min; (d) 20 min; (e) 30 min; (f) 40 min; (g) 80 min; (h) 180 min.

Scheme 1. Possible Mechanism for the One-Step Synthetic Reaction



R = ^{t}Bu (**1**), ^{t}Bu (**2**), Ph (**3**), Me (**4**)
R^1 = ^{t}Bu (**1**), H (**2**, **3**, **4**)

are the signals of the Ph protons of the intermediate. During the course of the reaction, the amount of the intermediate changed very little, as can be seen by viewing the spectra obtained at different times (Figure 2). On the basis of our observations on these reaction systems, the intermediates in these reactions are presumably the reaction products of $TiCl_4$ with the phenol group of the free ligands. It has been reported that the reaction of $TiCl_4$ with a phenol can take place easily.[22] The fact that the intermediate does not accumulate during the reaction implies that the following intramolecular reaction between the $-TiCl_3$ and $-Me_4CpH$ moieties is relatively fast, which is understandable, since the two moieties are very close to each other and the probability for reaction to take place is increased greatly. The yields for complexes **1**−**4** under similar conditions is **1** > **2** > **3** > **4**, which could be attributed to the steric effects of the R group at the ortho position of the phenolate in these complexes. The smallest R group, methyl, results in the lowest yield of **4**, while the bulky ^{t}Bu group leads to higher yields of **1** and **2**. The more bulky the R group, the longer the distance between the R and $-TiCl_3$ moieties. In contrast, the $-TiCl_3$ and $-Me_4CpH$ moieties are closer and the reaction between them is faster. On the basis of the above discussions, a possible reaction mechanism for the one-step synthetic reaction, as shown in Scheme 1, could be proposed.

Synthesis of Monocyclopentadienyltitanium Trichloride Complexes 5−7. To validate the universality of the one-step synthetic reaction, reactions of $TiCl_4$ with cyclopentadiene

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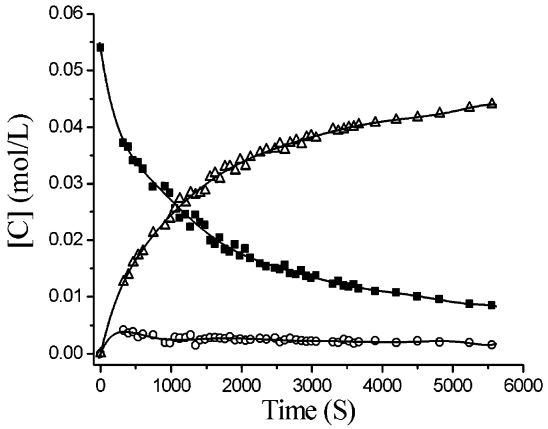

Figure 3. Plot of the concentration of components vs time of the reaction of $TiCl_4$ with $(TCDBP)H_2$ at 30 °C: (■) $(TCDBP)H_2$; (△) $(TCDBP)TiCl_2$; (○) intermediate.

(CpH), methylcyclopentadiene (Cp′H), pentamethylcyclopentadiene (Cp*H), 1-butyl-2,3,4,5-tetramethylcyclopentadiene ($Cp^{\#}H$), and tetramethylcyclopentadiene (Cp″H) were also studied. Experimental results indicated that both CpH and Cp′H were polymerized to produce a black tar under different conditions, which is consistent with the results previously reported by Wilkinson et al.[17a] The complexes Cp^*TiCl_3 (**5**), $Cp^{\#}TiCl_3$ (**6**), and $Cp''TiCl_3$ (**7**) were obtained from the corresponding reactions at 80 °C in yields of 58.2, 53.1, and 49.0%, respectively. NMR tube reactions indicated that the reactions could not go to completion at room temperature. From the synthetic reaction of Cp^*TiCl_3, a small amount of tetramethylfulvene, identified by ^1H and ^{13}C NMR spectroscopy, was obtained as a byproduct. Freshly prepared $Cp^{\#}TiCl_3$ was a viscous red oil that crystallized slowly when the crude product was allowed to stand at room temperature for several weeks. The above results could cause us to draw the conclusion that the one-step synthetic reaction is a versatile method for the synthesis of monocyclopentadienyltitanium complexes and can be applied to all multiply substituted cyclopentadienes only if polymerization does not take place in the presence of $TiCl_4$. A side chain on the Cp ring, which can bond or coordinate to the Ti atom, might accelerate the reaction between the −CpH and $-TiCl_n$ moieties and hence increase the yield of product.

Kinetic Studies on the Reaction of $TiCl_4$ with $(TCDBP)H_2$. By following the reaction of $TiCl_4$ with $(TCDBP)H_2$ (1:1) with ^1H NMR, it was found that the signals for the free ligand $(TCDBP)H_2$, the product **1**, and the intermediate in the aromatic region of the ^1H NMR spectrum of the reaction mixture can be identified clearly (Figure 1) and the concentrations of these species can be calculated, which is suitable for kinetic studies. We therefore studied the kinetics of the reaction at different temperatures. Figure 2 shows the ^1H NMR spectra obtained at different times at 30 °C. After the resulting integrals were scaled by the initial concentration, a plot of the concentration of components vs time (Figure 3) was obtained, which shows that the concentration of the intermediate is very low during the whole reaction, indicating the following reaction is relatively fast. Since the concentration of $(TCDBP)H_2$ is equivalent to that of $TiCl_4$ and the plot of 1/(concentration of the free ligand, mol/L) vs time gives a good straight line, the reaction should be a second-order reaction and the slope of the line is the rate constant (k). The experiment was repeated for several temperatures (15, 20, 25, 30, and 35 °C), each leading to similar linear plots (Figure 4), and the resulting rate constants (Table 1) were used to construct the Arrhenius plot that is shown in Figure 5.

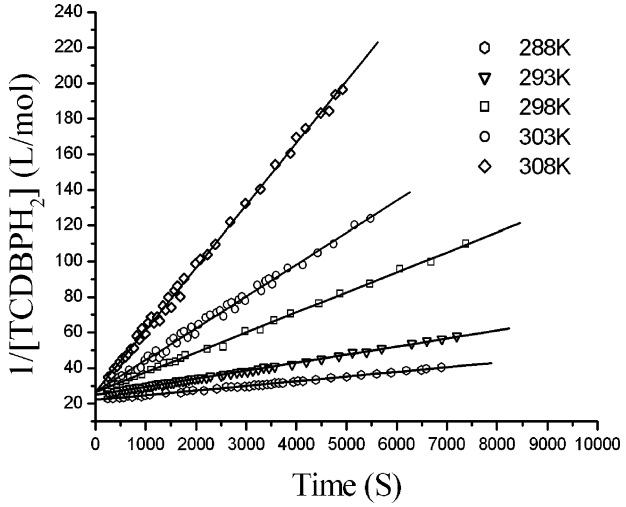

Figure 4. Second-order plots of rate data of the reaction of $TiCl_4$ with $(TCDBP)H_2$.

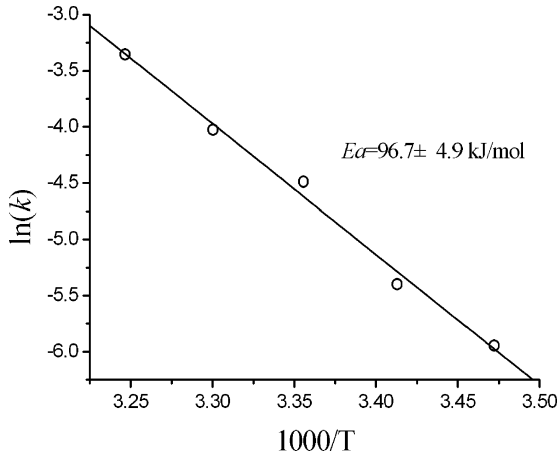

Figure 5. Arrhenius plot of the reaction of $TiCl_4$ with $(TCDBP)H_2$.

Table 1. Rate Constants and Activation Parameters for the Reaction of $TiCl_4$ with $(TCDBP)H_2$

T (K)	10^5k (L/(mol S))	E_a (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/(mol K))
288	262 ± 2.3			
293	452 ± 2.4			
298	1123 ± 9.0	96.7 ± 4.9	94.3 ± 4.9	33.0 ± 16.5
303	1789 ± 22.8			
308	3496 ± 27.4			

The kinetic results are consistent with the ^1H NMR observations and support the proposed mechanism shown in Scheme 1. The bimolecular reaction of $TiCl_4$ with the phenol group of the free ligand should be the rate-controlling step of the whole reaction. The apparent activation energy (E_a = 96.7 kJ/mol) is in a reasonable range for a reaction that can go to completion at room temperature.[23] The activation enthalpy ($\Delta H^{\ddagger}$ = 94.3 kJ/mol) and entropy ($\Delta S^{\ddagger}$ = 33.0 J/(mol K)) for the reaction were also calculated according to the transition-state theory expression for the rate constant. A plot of $\ln(hk/k_BT)$ vs $1/T$ gives a straight line. The activation enthalpy is obtained from the slope and the activation entropy from the intercept (see the Supporting Information). The rate constants and activation parameters are given in Table 1.

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Conclusions

We have developed a highly efficient synthetic method for the monocyclopentadienyltitanium complexes by the direct reaction of $TiCl_4$ with substituted cyclopentadienes that do not polymerize under the reaction conditions. This new method is versatile and especially efficient for cyclopentadienes with a side chain containing a group that can bond or coordinate to the Ti atom. At present, further investigations exploring possibilities of applying this method to synthesizing cyclopentadienyl complexes of other metals are under way.

Experimental Section

All operations were performed under an inert atmosphere of nitrogen using standard Schlenk-line or glovebox techniques. Solvents were dried and distilled prior to use. $TiCl_4$, Cp″H, and Cp*H were purchased from Aldrich. (TCDBP)H_2, (TCBP)H_2, (TCPP)H_2, and (TCMP)H_2 were prepared according to literature procedures. [21] All NMR experiments were carried out in sealed NMR tubes on a Varian Mercury-300 NMR spectrometer. Kinetic experiments were performed with a delay time (d1) of 12 s, a number of data points (np) of 32 k, an acquisition time (at) of 2.666 s, and a pulse width (pw) of 90°.

Synthesis of 1-Butyl-2,3,4,5-tetramethylcyclopentadiene (Cp$^{\#}$H). A solution of 2,3,4,5-tetramethyl-2-cyclopentenone (2.64 mL, 17.5 mmol) in Et_2O (60 mL) was added dropwise to a solution of ^{n}BuLi (17.5 mmol) in Et_2O (40 mL) at −15 °C. The mixture was slowly warmed to room temperature and stirred overnight. The reaction mixture was hydrolyzed with 20 mL of saturated NH_4Cl(aq). The organic layer was separated and treated three times with 20 mL of concentrated HCl and then washed three times with water (50 mL), dried over $MgSO_4$, filtered, and evaporated to dryness, affording a brown oil. Pure product (2.1 g, 67%) was obtained by column chromatography over silica (hexanes/CH_2Cl_2, 5:1) as a yellow oil. ^{1}H and ^{13}C NMR spectroscopic analysis indicates that the samples are mixtures of three isomers.

One-Step Synthesis of (TCDBP)$TiCl_2$ (1). A solution of (TCDBP)H_2 (1.0 g, 3.1 mmol) in toluene (20 mL) was added dropwise to a solution of $TiCl_4$ (3.1 mmol) in toluene (40 mL) at room temperature. The mixture was heated with stirring at 40 °C overnight. The precipitate was filtered off, and the solvent was removed to leave a red crystalline solid (1.28 g, 93%). Mp: 238−240 °C. Anal. Calcd for $C_{23}H_{32}Cl_2OTi$ (443.27): C, 62.32; H, 7.28. Found: C, 62.23; H, 7.24. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.33 (s, 1H, Ph), 7.11 (s, 1H, Ph), 2.42 (s, 6H, C_5Me_4), 2.04 (s, 6H, C_5Me_4), 1.353 (s, 9H, ^{t}Bu), 1.347 (s, 9H, ^{t}Bu). ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K): δ 171.60, 146.86, 145.72, 143.59, 134.82, 130.14, 128.88, 123.40, 123.11, 35.02, 34.76, 31.72, 29.52, 13.49, 13.00 ppm.

One-Step Synthesis of (TCBP)$TiCl_2$ (2). The reaction of (TCBP)H_2 (3.5 mmol) and $TiCl_4$ (3.5 mmol) was carried out in the same way as described above for the synthesis of **1**. Pure **2** (1.21 g, 89%) was obtained as a red crystalline solid. Mp: 138−140 °C. Anal. Calcd for $C_{19}H_{24}Cl_2OTi$ (387.17): C, 58.94; H, 6.25. Found: C, 58.89; H, 6.20. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.33−7.36 (m, 1H, Cp), 7.11−7.13 (m, 2H, Ph), 2.43 (s, 6H, C_5Me_4), 2.04 (s, 6H, C_5Me_4), 1.35 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 174.18, 146.05, 143.43, 136.53, 130.62, 129.47, 126.93, 126.79, 123.97, 35.14, 29.68, 13.73, 13.31 ppm.

One-Step Synthesis of (TCPP)$TiCl_2$ (3). The reaction of (TCPP)H_2 (3.0 mmol) and $TiCl_4$ (3.0 mmol) was carried out in the same way as described above for the synthesis of **1**. Pure **3** (0.92 g, 75%) was obtained as a red crystalline solid. Mp: 289−291 °C. Anal. Calcd for $C_{21}H_{20}Cl_2OTi$ (407.16): C, 61.95; H, 4.95. Found: C, 61.89; H, 4.92. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.24−7.64 (m, 8H, Ph), 2.44 (s, 6H, C_5Me_4), 2.11 (s, 6H, C_5Me_4). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 171.97, 145.85, 142.68, 136.44, 130.76, 130.24, 129.26, 129.01, 128.36, 127.81, 127.38, 126.61, 124.23, 13.60, 13.12 ppm.

One-Step Synthesis of (TCMP)$TiCl_2$ (4). The reaction of (TCMP)H_2 (3.0 mmol) and $TiCl_4$ (3.0 mmol) was carried out in the same way as described above for the synthesis of **1**. Pure **4** (0.67 g, 65%) was obtained as a red crystalline solid. Mp: 155−157 °C. Anal. Calcd for $C_{16}H_{18}Cl_2OTi$ (345.09): C, 55.69, H; 5.26. Found: C, 55.60; H, 5.20. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.19−7.23 (m, 1H, Ph), 7.04−7.12 (m, 2H, Ph), 2.43 (s, 6H, C_5Me_4), 2.18 (s, 3H, Ph−Me), 2.06 (s, 6H, C_5Me_4). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 173.65, 145.95, 143.16, 131.22, 130.55, 128.01, 126.20, 123.67, 123.55, 15.31, 13.53, 13.12 ppm.

One-Step Synthesis of Cp*$TiCl_3$ (5). A solution of Cp*H (1.0 g, 7.3 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of $TiCl_4$ (7.3 mmol) in CH_2Cl_2 at room temperature. The mixture was heated with stirring at 80 °C overnight. The precipitate was filtered off, and the solvent was removed in vacuo. Then the red residue was dried in vacuo at 100 °C to leave a red crystalline solid (1.23 g, 58%). Mp: 223−225 °C. Anal. Calcd for $C_{10}H_{15}Cl_3Ti$ (289.45): C, 41.49; H, 5.22. Found: C, 41.45; H, 5.20. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 2.38 (s, 15H, Cp−CH_3). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 138.18 (Cp), 14.70 (Cp−CH_3) ppm.

One-Step Synthesis of Cp$^{\#}$$TiCl_3$ (6). The reaction of Cp$^{\#}$H (5.0 mmol) with $TiCl_4$ (5.0 mmol) was carried out in the same way as described above for the synthesis of **5**. Pure **6** (0.88 g, 53%) was obtained as a red crystalline solid. Mp: 106−108 °C. Anal. Calcd for $C_{13}H_{21}Cl_3Ti$ (331.53): C, 47.10; H, 6.38. Found: C, 47.06; H, 6.35. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 2.85 (t, 2H, ^{n}Bu CH_2), 2.38 (s, 12H, Cp−Me), 1.38 (m, 4H, ^{n}Bu CH_2), 0.94 (t, 3H, ^{n}Bu Me). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 142.48, 138.36, 137.66, 32.34, 29.41, 23.03, 14.64, 14.15 ppm.

One-Step Synthesis of Cp″$TiCl_3$ (7). The reaction of Cp″H (6.0 mmol) with $TiCl_4$ (6.0 mmol) was carried out in the same way as described above for the synthesis of **5**. Pure **7** (0.81 g, 49%) was obtained as a red crystalline solid. Mp: 145−147 °C. Anal. Calcd for $C_9H_{13}Cl_3Ti$ (275.43): C, 39.25; H, 4.76. Found: C, 39.19; H, 4.73. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 6.65 (s, 1H, Cp H), 2.41 (s, 6H, Cp−Me), 2.36 (s, 6H, Cp−Me). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 139.30, 138.11, 124.54, 16.61, 14.26 ppm.

Kinetic Experiment on the Reaction of $TiCl_4$ with (TCDBP)H_2. A solution of $TiCl_4$ (0.03 mmol) in $CDCl_3$ (0.25 mL) was added to a solution of (TCDBP)H_2 (10 mg, 0.03 mmol) in $CDCl_3$ (0.25 mL) in a NMR tube. The reaction was followed immediately by ^{1}H NMR at the appropriate temperature (15, 20, 25, 30, and 35 °C, respectively).

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Supporting Information Available: Figures giving ^{1}H and ^{13}C NMR spectra for the complexes in this article. This material is available free of charge via the Internet at http://pubs.acs.org.

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