Notes

Unexpected Binuclear Bis(phenolato) Titanium (IV) {[(L)Ti(Ph)]$_2$(μ-OEt)$_2$} Assisted by Carbon−Oxygen Bond Cleavage and Alkali-Metal-Containing Titanium(III) Complexes [Ti(L)$_2$·M(solv)$_2$] (M = Li, Na, K; solv = THF, DME)

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*Summary: Titanium complex [(**L**)Ti(CH$_2$Ph)$_2$] (**2**) was prepared by reaction of [(**L**)TiCl$_2$] (**L** = 2,2′-methylenebis(6-tert-butyl-4-methylphenolato)) (**1**) with PhCH$_2$MgCl in a 1:2 ratio in Et$_2$O in 69% yield, while the reaction of **1** with PhLi under the same conditions yields [(**L**)Ti(Ph)$_2$] (**3**) in less than 40% yield and an unexpected rare phenyl alkoxide-bridged compound {[(**L**)-Ti(Ph)]$_2$(μ-OEt)$_2$}(**4**) in ca. 9% yield. According to the crystal structure, **2** and **3** are monomeric and tetrahedral, with boat-conformation ligands. The X-ray structure of **4** showed the complex to be dimeric, with titanium in a distorted pyramidal coordination geometry. The reduction of **1** with 1.0 equiv of LiBEt$_3$H, excess Na/Hg, or 1.0 equiv of KC$_8$ gave the titanium-(III) salts [Ti(**L**)$_2$·M(THF)$_2$] (M = Li, **5**; M = Na, **6**) and [Ti-(**L**)$_2$·K(DME)$_2$] (**7**), respectively. The molecular structures of **5** and **7** were confirmed by single-crystal X-ray analysis. The titanium atom in complexes **5** and **7** is four-coordinate, with a distorted tetrahedral arrangement and the same ligand orientations as in **2**−**4**. The lithium atom in **5** is four-coordinate with two coordinated THF molecules, while the big potassium ion in **7** is six-coordinate with two chelated DME molecules added to the two bridging oxygen atoms of the bis(phenolato) ligands.*

Introduction

Group 4 transition metal complexes have been the most extensively studied for their promotion of numerous organic transformations, in part due to their steric and electronic modularity and convenient synthetic access to low-valent derivatives by treatment with alkyl lithium reagents or alkali metal reductants.[1] However, a better understanding of the synthesis, structure, and reactivity of reduced titanium complexes is needed in order to achieve a greater mechanistic understanding and better control over selectivity of the reactions. Hence, increased effort has been focused on developing the synthesis and reactivity of well-characterized low-valent group 4 metal complexes. For example, some titanium complexes have been investigated for their promotion of small molecule activation processes and carbon−oxygen bond cleavage.[2,3]

The aryloxide-based multidentate ligands continue to attract considerable attention for their use in stabilizing reactive metal centers for a number of unusual reactions.[4] So we chose to explore the chemistry of transition metal complexes with such ligands. Over the last several years, we have been investigating the use of multidentate aryloxides ligands to generate *S*-block and group 4 metal species and nickel complexes.[5] Aiming to explore more unusual aryloxide-containing compounds such as low-valent metal derivatives, we have now turned to the study of the reactivity of these mononuclear Ti-aryloxide complexes. Recently, we reported the facile formation of six-membered ring [Al$_3$O$_2$Cl] aluminum and alkoxide-bridged titanium complexes by the reactions of AlMe$_3$ with [(**L**)TiCl$_2$] (**L** = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)) (**1**).[5a] The present work describes the synthesis and characterization of the unexpected alkoxide-bridged titanium product generated from C−O bond rupture of diethyl ether as well as the reduction of dichloride titanium(IV) compound **1** by different reducing agents to generate some alkali-metal-containing low-valent titanium species (Scheme 1).

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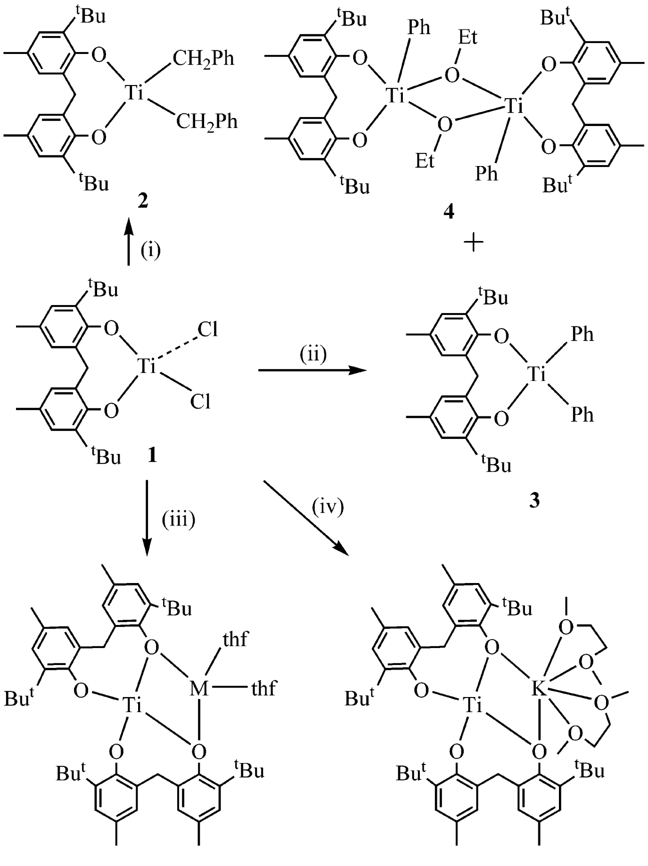
10.1021/om700298f CCC: $37.00

Scheme 1. Synthesis of Titanium Complexes 2−7[a]

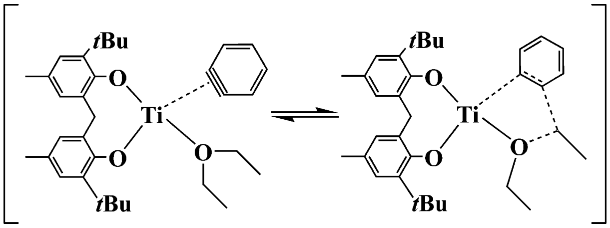


[a] Reagents and conditions: (i) 2 $PhCH_2MgCl/Et_2O$, −78 °C to rt, overnight; (ii) 2 $PhLi/Et_2O$, −78 °C to rt, 3 days; (iii) for **5**: $LiBEt_3H$/THF, −78 °C to rt, overnight; for **6**: excess Na/Hg/THF, rt, 2 days; (iv) KC_8/DME/toluene, −29 °C to rt, overnight.

Results and Discussion

Complex [(**L**)$TiCl_2$] (**1**) could readily be converted to the bis(alkyl) or bis(aryl) compounds [(**L**)TiR_2] by salt metathesis using Grignard or organolithium reagents.[6] In this way complex [(**L**)-$Ti(CH_2Ph)_2$] (**3**) was made by addition of $PhCH_2MgCl$ reagent to a cooled (−78 °C) suspension of dichloride complex in ether and subsequent workup from pentane in 69% yield. Moreover, protonolysis of the readily available precursor $Ti(CH_2Ph)_4$ with chelating bisphenol at 20 °C could yield **3** with concomitant liberation of toluene, but the product includes a small amount of impurities. In a similar way, complex **1** reacts with 2.0 equiv of PhLi in diethyl ether to give the corresponding diphenyl complex [(**L**)$TiPh_2$] (**2**) in less than 40% yield. The syntheses of **2** and **3** have been described elsewhere,[6a,c] but no detailed NMR spectra and X-ray single-crystal analyses have been given due to their thermal- and light-instability. In this paper complexes **2** and **3** were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and X-ray single-crystal determination (see Experimental Section and the Supporting Information).

Chart 1



The yield of diphenyl titanium complex **3** is very low, less than 40%, which made us wonder what the other products are. After complex **3** was completely extracted with pentane, the resultant crude was washed with hexane and treated with toluene to afford a red crystalline compound, $\{[(\mathbf{L})TiPh]_2(\mu\text{-}OEt)_2\}$(**4**) (Scheme 1). Complex **4** is stable in the solid state but slowly decomposed to unidentified compounds in C_6D_6 at room temperature. Single-crystal X-ray analysis confirms that compound **4** is a dimer, with two ethoxo-oxygens bridging the two titanium atoms (see the Supporting Information).

The unexpected formation of **4** clearly indicates the alkyl−oxygen bond cleavage of diethyl ether. It has been observed that some Sc, Ti, and Zr complexes could promote C−O bond cleavage of Et_2O and THF.[3e,g] The force of this process is ascribed to the low oxidation states of the transition metal. For example, the η^9,η^5-bis(indenyl)zirconium sandwich complex was just reported to promote the C−O bond cleavage of dialkyl ethers such as diethyl ether, CH_3OR (R = Et, *n*Bu, *t*Bu), *n*Bu_2O, or *i*Pr_2O by Chirik et al.[3a] The η^2-benzyne titanium intermediate complex could be generated from the thermolysis of diphenylzirconocene, and the nascent benzyne complex can be used as a means for carbon−carbon bond formation in organic synthesis.[7] Herein we suppose that the titanium(II) complexes, e.g., the η^2-benzyne titanium complex (Chart 1), are possible intermediates in the formation of **4**. Although trace ethylbenzene was detected in reaction mixture by GC-MS, unfortunately until now it is not clear which phenyl carbon the ethyl migrates to because there are five H atoms on the phenyl ring and a hydride shift is required.

Given that only few low-valent species of phenolato titanium complexes have been reported,[8] several kinds of reducing agents including Mg powder, Na/Hg, $LiBEt_3H$, and KC_8 were used to reduce dichloride titanium complex **1**. The experimental results showed that Mg powder almost has no reducing ability and compound **1** could be retrieved from the reaction mixture in 87% yield. Treatment of **1** with $LiBEt_3H$ in THF at −78 °C led to a color change from yellow to pale green, which changed to yellow-green on warming to room temperature. The Ti(III) reduction product, $[Ti(\mathbf{L})_2\cdot Li(THF)_2]$ (**5**), was isolated as yellow-green plate crystals. Titanium complexes $[Ti(\mathbf{L})_2\cdot Na(THF)_2]$ (**6**) and $[Ti(\mathbf{L})_2\cdot K(DME)_2]$ (**7**) were similarly prepared from the reaction of **1** with excess sodium amalgam in THF and 1.0 equiv of KC_8 in toluene/DME, respectively (Scheme 1). The compositions of **5**, **6**, and **7** were confirmed by elemental analysis, and the X-ray structures of complexes **5** and **7** were determined (see the Supporting Information).

The titanium atom in complex **5** is four-coordinate, with a distorted tetrahedral arrangement and the same ligand orientations as in **2**−**4**. Two oxygen atoms from the aryloxide ligands are also involved in oxygen bridges between the lithium and titanium atoms. The lithium atom is four-coordinate, with two coordinated THF molecules added to the bridging oxygen atoms. The titanium(III) coordination geometry in **7** (a distorted

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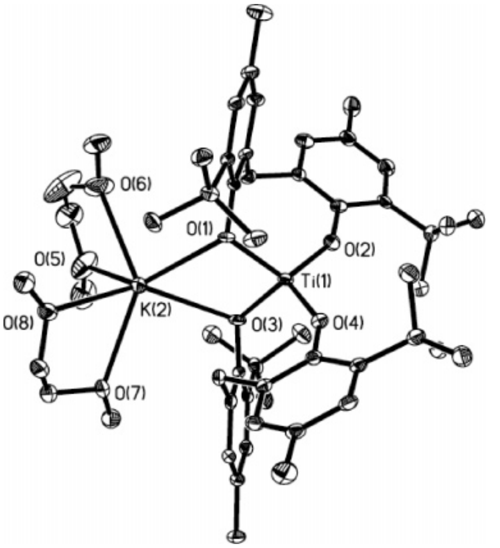


Figure 1. Molecular structure of **7**. All hydrogen atoms are omitted for clarity.

tetrahedral arrangement) is very similar to that in complex **5**. The big potassium ion is six-coordinate, with two chelated DME molecules added to the two bridging oxygen atoms of the bis(phenolato) ligands (Figure 1).

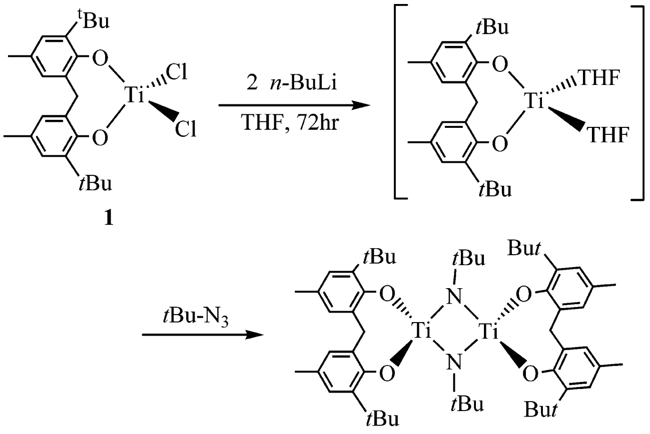
Although we did not isolate the titanium(II) compounds using the above-mentioned reducing agents, treatment of **1** with 2 equiv of *n*BuLi in THF for 3 days at room temperature afforded a dark blue mixture that continuously reacted with 1.0 equiv of *t*Bu-N_3 to afford the yellow-orange titanium(IV) complex [Ti_2-(μ-NBu^t)$_2$(L)$_2$] (**8**) (Scheme 2). The ^{1}H NMR spectrum of **8** exhibits a singlet for the *tert*-butyl imido group at δ 0.98 ppm and two doublets for bridged methylene at δ 4.41 and 3.53 ppm with the coupling constant $J_{H-H} = 14.2$ Hz. Orange crystals of complex **8** suitable for X-ray analysis could be obtained although their quality was not ideal because they are very thin platelets. The outline of the solid-state structure of **8** clearly indicates its dimeric structure with two bridged imido (μ-N*t*Bu) moieties.[9] Clearly the process includes a dark blue titanium(II) intermediate compound.

In summary, we have demonstrated the formation of an unexpected alkoxide-bridged diphenyl titanium(IV) bis(phenolate) complex by carbon−oxygen bond cleavage. Upon reduction, some alkali-metal-containing low-valent titanium species can be achieved. Further experiments are now in progress.

Experimental Section

General Procedures. Unless otherwise noted, all operations were performed either under an inert atmosphere of argon using standard Schlenk techniques or under nitrogen in an MBraun glovebox. All dried solvents and chemicals commercially available were used as received without further purification. C_6D_6 was dried and degassed over a potassium mirror and vacuum transferred prior to use. H_2-(**L**) (**L** = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)) and [(**L**)$TiCl_2$] (**1**) were prepared by a literature procedure.[6] NMR spectra were recorded on a Bruker AVANCE-DMX 500 spectrometer. ^{1}H and $^{13}C\{^1H\}$ NMR are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, δ 7.15 and 128.0 ppm). Elemental analysis was performed on an Elementar Vario EL III analyzer.

Scheme 2. Synthesis of Complex 8



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Synthesis of [(L)Ti(CH_2Ph)$_2$] (2). Path A.[6c] $C_6H_5CH_2MgCl$ (1.6 mL, 1.0 M solution in diethyl ether, 1.6 mmol) was added dropwise to a precooled suspension of **1** (0.373 g, 0.816 mmol) in Et_2O (30 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed under vacuum, and CH_2Cl_2 (20 mL) was added to the solid residue. The suspension was centrifuged to remove formed salt, and the upper clear solution was evacuated to dryness. The orange-red crude was purified by recrystallization from hexane/Et_2O to afford 0.32 g of orange, block-like crystals in 69% yield.

Path B. A sample of Ti(CH_2Ph)$_4$ (0.405 g, 1.0 mmol) in 20 mL of hexane, precooled to −40 °C, was added dropwise to a suspension of H_2**L** (0.340 g, 1.0 mmol) in 20 mL of hexane, also cooled to −40 °C. After addition, the reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The resulting red-colored solution was stripped under vacuum to give a red foam. Crystallization of a concentrated hexane solution at −30 °C gave 0.31 g of a microcrystalline solid in 55% yield. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.37 (d, 2H, $J_{H-H} = 7.08$), 7.23 (m, 2H, H-Ar), 7.06−6.88 (m, 10H, H-Ar), 6.75 (m, 1H, H-Ar), 3.25, 3.22 (d, 1H, $J_{H-H} = 14.4$, 1H, CH_2), 3.16, 3.13 (d, 1H, $J_{H-H} =$ 14.4, CH_2), 3.14 (s, 1H, Ti-CH_2Ph), 2.77 (s, 1H, Ti-CH_2Ph), 2.08 (s, 6H, *p*-CH_3), 1.54 (s, 18H, *o*-C(CH_3)$_3$). $^{13}C\{1H\}$ NMR (C_6D_6, 127 MHz): δ 160.95 (O-C_{Ar}), 146.48, 141.24, 135.92, 135.37, 131.73, 130.02, 129.56, 129.23, 128.81, 128.30, 127.37, 125.83, 125.43, 123.33 (CH_{Ar}), 83.39 (d, $J = 69.5$ Hz, Ti-CH_2Ph), 35.24 (Ar-CH_2-Ar), 34.15, (*o*-C(CH_3)$_3$), 30.41 (*o*-C(CH_3)$_3$), 21.03 (*p*-CH_3). Anal. Calcd for $C_{37}H_{44}O_2Ti$: C, 78.15; H, 7.80. Found: C, 77.94; H, 7.82.

Synthesis of [(L)TiPh$_2$] (3) and {[(L)Ti(Ph)]$_2$(μ-OEt)$_2$} (4). LiPh (1.2 M, 1.65 mL, 1.98 mmol) was added to a diethyl ether solution (20 mL) of **1** (0.432 g, 0.94 mmol) at room temperature. The resulting solution was allowed to stand for 3 days, then evaporated to dryness. The resulting solid was extracted with pentane (20 mL), and LiCl was removed by centrifugation. The pentane solution, upon cooling to −30 °C, gave green needles of **3** in 40% yield (0.20 g). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.23 (d, 1H, $J_{H-H} = 1.95$, *H*-Ar), 8.22 (m, 1H, *H*-Ar), 8.13 (m, 1H, *H*-Ar), 8.12 (d, 1H, $J_{H-H} = 1.95$, *H*-Ar), 7.11 (d, 1H, $J_{H-H} = 1.95$, *H*-Ar), 7.09 (d, 1H, $J_{H-H} = 1.95$, *H*-Ar), 7.07 (d, 1H, $J_{H-H} = 2.2$, *H*-Ar), 7.06 (d, 1H, $J_{H-H} = 1.2$, *H*-Ar), 7.02 (q, 2H, $J_{H-H} = 1.95$, *H*-Ar),

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3.97 (d, $J_{\mathrm{H-H}} = 14.65$ Hz, 1H, CH_2), 3.40 (d, $J_{\mathrm{H-H}} = 14.65$ Hz, 1H, CH_2), 2.08 (s, 6H, *p*-CH_3), 1.59 (s, 18H, *o*-C(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 127 MHz): δ 196.63, 196.35, 196.05, 161.09 (O-C_{Ar}), 150.04, 136.33, 135.90, 132.21, 131.90, 131.63, 131.22, 131.17, 129.55, 128.49, 127.92, 126.23 (CH), 36.02 (C(CH$_3$)$_3$), 35.54 (Ar-CH$_2$-Ar), 30.59 (C(CH$_3$)$_3$), 21.23 (Ar-CH$_3$). Anal. Calcd for $C_{35}H_{40}O_2Ti$: C, 77.77; H, 7.46. Found: C, 77.64; H, 7.52. The above residual crude solid was washed with hexane (5 mL) and then extracted with toluene (10 mL). The resulting red solution was concentrated to ca. 2 mL and cooled at −19 °C for several days to give 45 mg of **4** as orange-red crystals in ca. 9% yield. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.24 (d, 2H, $J_{\mathrm{H-H}} = 6.4$, *H*-Ar), 7.23 (m, 3H, *H*-Ar), 6.97 (s, 2H, *H*-Ar), 6.83 (s, 2H, *H*-Ar), 5.31 (br, 2H, CH_2), 3.26 (br, 2H, μ-OCH_2CH$_3$), 2.06 (s, 6H, *p*-CH_3), 1.47 (s, 18H, *o*-C(CH_3)$_3$), 1.24 (br, 2H, μ-OCH_2CH$_3$). Anal. Calcd for $C_{62}H_{80}O_6Ti_2$: C, 73.22; H, 7.94. Found: C, 73.14; H, 8.01.

Synthesis of [Ti(L)$_2$·Li(THF)$_2$] (5). A solution of **1** (0.229 g, 0.5 mmol) in toluene (10 mL) was cooled to −78 °C in a methanol/N_2(liquid) bath, and 1.0 equiv of LiBEt$_3$H (0.5 mL, 1.0 M solution in THF, 0.5 mmol) was added slowly via a syringe. The color changed rapidly from red to yellow. The mixture was allowed to warm to room temperature and was stirred another 4 h, when the color gradually turned very dark green. The solution was filtered, and the solvent was concentrated to ca. 2 mL under vacuum, layered with 1 mL of hexane, and cooled at −29 °C for a week to afford 0.21 g of **5**·(C_6H_{14}) as yellow-green plate crystals in 43% yield. Anal. Calcd for $C_{60}H_{90}LiO_6Ti$: C, 74.90; H, 9.43. Found: C, 74.86; H, 9.42. The paramagnetic nature of **5** precluded the acquisition of suitable NMR data.

Synthesis of [Ti(L)$_2$·Na(THF)$_2$] (6). THF (15 mL) was added at −78 °C to a freshly prepared sodium amalgam (mercury: 2.0 g, 10.1 mmol; sodium: 0.02 g, 0.85 mmol). A solution of **1** (0.229 g, 0.5 mmol) in THF (20 mL) was cooled to −78 °C and added slowly to the Hg/Na amalgam. The mixture was allowed to warm to room temperature and was stirred 2 days, when the color gradually turned very dark green. The solution was filtered to remove the excess of Hg/Na, and the solvent was removed under vacuum to yield **6** as a green crystalline compound. Yield: 0.19 g (42%). We tried but failed to obtain X-ray quality crystals. Anal. Calcd for $C_{54}H_{76}NaO_6Ti$: C, 72.71; H, 8.59. Found: C, 72.36; H, 8.32. The paramagnetic nature of **6** precluded the acquisition of suitable NMR data.

Synthesis of [Ti(L)$_2$·K(DME)$_2$] (7). A solution of **1** (0.229 g, 0.5 mmol) in toluene/DME (20/10 mL) was cooled to −29 °C, and 1.0 equiv of KC$_8$ (0.068 g, 0.5 mmol) was added slowly in a glovebox. The color changed rapidly from red to yellow-green. The mixture was allowed to warm to room temperature and was stirred overnight, when the color gradually turned very dark green. The solution was filtered to remove the carbon, and the solvent was removed to give a blue-green powder in 38% yield. Blue-green, needle-like, X-ray quality crystals were obtained by storing its saturated solution of hexane/toluene/DME (0.5/0.5/0.5) at 4 °C for 2 weeks. Anal. Calcd for $C_{54}H_{80}KO_8Ti$: C, 68.69; H, 8.54. Found: C, 68.46; H, 8.43. The paramagnetic nature of **7** precluded the acquisition of suitable NMR data.

Synthesis of [Ti$_2$(μ-N*t*Bu)$_2$(L)$_2$] (8). To a solution of **1** (0.229 g, 0.5 mmol) in THF (20 mL) was slowly added the hexane solution of *n*BuLi (0.6 mL, 1.6 M, 1.0 mmol) at −78 °C. The mixture was slowly warmed to room temperature and continuously stirred for 72 h to give a dark blue solution. Then *t*Bu-N$_3$ (0.050 g, 0.5 mmol) was added at −40 °C. The reaction mixture was slowly warmed to room temperature and stirred for another 8 h. The solvent was evaporated to dryness. Extraction of the residue with THF/hexane gave an orange solid (0.133 g) in 58% yield. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.01 (s, 2 H, H-Ar) 6.93(s, 2 H, H-Ar), 4.41 (d, 1H, $J_{\mathrm{H-H}} = 14.2$, 1H, CH_2), 3.57 (br, 2H, THF), 3.53 (d, 1H, $J_{\mathrm{H-H}} = 14.2$, 1H, CH_2), 2.06 (s, 6H, *p*-Me), 1.58 (s, 18H, *o*-C(CH_3)$_3$), 1.41 (br, 2H, THF), 0.98 (s, =NC(CH_3)$_3$). Anal. Calcd for $C_{54}H_{78}N_2O_4Ti_2$: C, 70.89; H, 8.59; N, 3.06. Found: C, 70.46; H, 8.63; N, 3.12.

Crystallographic Data. 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. Diffraction experiments were performed with Mo Kα radiation ($\lambda = 0.710\ 70$ 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 Crystal Clear Processing packages.[10] The structures were determined by routine heavy-atom and Fourier methods by using SHELXS 97[11] and refined by full-matrix least-squares with the non-hydrogen atoms anisotropic and hydrogen with fixed isotropic thermal parameters of 0.07 Å by means of the SHELXL 97 program.[12] The hydrogens were partially located from difference electron-density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources.[13] Some details of data collection and refinement are given in the Supporting Information.

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Supporting Information Available: For compounds **2**−**5** and **7**, crystallographic data in CIF format, figures of the molecular structure, tables of selected bond lengths and angles, and a discussion of the X-ray data of these compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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