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New Titanium Complexes with Symmetric or Asymmetric *cis*-9,10-Dihydrophenanthrenediamide Ligands Formed through Sequential Intramolecular C−C Bond-Forming Reactions

Dapeng Zhao, Bo Gao, Wei Gao, Xuyang Luo, Duihai Tang, Ying Mu,* and Ling Ye

State Key Laboratory of Supramolecular Structure and Materials, School of Chemistry, Jilin University, Chang Chun 130012, People's Republic of China

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A series of new titanium(IV) complexes with symmetric or asymmetric *cis*-9,10-dihydrophenanthrenediamide ligands, *cis*-9,10-PhenH$_2$(NR)$_2$Ti(O^{i}Pr)$_2$ [PhenH$_2$ = 9,10-dihydrophenanthrene, R = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2a**), 2,6-Et$_2$C$_6$H$_3$ (**2b**), 2,6-Me$_2$C$_6$H$_3$ (**2c**)], *cis*-9,10-PhenH$_2$(NR$_1$)(NR$_2$)Ti(O^{i}Pr)$_2$ [R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Et$_2$C$_6$H$_3$ (**2d**); R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Me$_2$C$_6$H$_3$ (**2e**)], and [*cis*-9,10-PhenH$_2$(NR$_1$)$_2$][*o*-C$_6$H$_4$(CH=NR$_2$)]TiO^{i}Pr [R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Et$_2$C$_6$H$_3$ (**3a**); R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$ (**3b**)], have been synthesized from the reactions of TiCl$_2$(O^{i}Pr)$_2$ with *o*-C$_6$H$_4$(CH=NR)Li [R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-Et$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$]. The symmetric complexes **2a**−**2c** were obtained from the reactions of TiCl$_2$(O^{i}Pr)$_2$ with 2 equiv of the corresponding *o*-C$_6$H$_4$(CH=NR)Li followed by intramolecular C−C bond-forming reductive elimination and oxidative coupling processes, while the asymmetric complexes **2d**−**2e** were formed from the reaction of TiCl$_2$(O^{i}Pr)$_2$ with two different types of *o*-C$_6$H$_4$(CH=NR)Li sequentially. The complexes **3a** and **3b** were also isolated from the reactions for complexes **2d** and **2e**. All complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, and the molecular structures of **2a**, **2b**, **2e**, and **3a** were determined by X-ray crystallography.

Introduction

Studies on transition-metal-mediated C−C bond-forming reactions have been an important research area in organic and organometallic chemistry.[1] Some of the C−C bond-forming reactions have been well documented as efficient synthetic methods for constructing the basic carbon backbone of small organic molecules, metal complexes, and extended polymeric structures.[2] It has been known that most stoichiometric and catalytic C−C bond-forming reactions mediated by transition metals can take place through several pathways, such as reductive elimination, oxidative coupling, migratory insertion, and σ- or π-bond metathesis.[3] Group 4 metal-mediated C−C bond-forming reactions take place usually through two principal mechanistic pathways: σ-bond metathesis and migratory insertion, which operate without requiring redox changes at the metal center.[4] Although some examples of C−C bond-forming reactions mediated by group 4 metals through the reductive elimination pathway are known, most of the reported C−C bond-forming reductive elimination reactions involving group 4 metal complexes are the coupling reactions of alkyl, acyl, 1-alkenyl, and 1-alkynyl groups.[5] For the aryl−aryl bond-forming

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*To whom correspondence should be addressed. E-mail: ymu@jlu.edu.cn.

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reductive elimination reactions mediated by group 4 metals, only a very few examples[6] have been reported so far. On the other hand, oxidative coupling reactions of unsaturated organic compounds on low-valent group 4 metals have been extensively studied as an efficient pathway for constructing the C−C bond.[7] The low-valent group 4 metals, such as titanium(II) or zirconium(II) reagents, are usually generated by the treatment of titanium(IV) or zirconium(IV) complexes with Grignard or organolithium reagents, followed by a reductive elimination process.[8] In principle, both the reductive elimination and the subsequent oxidative coupling processes can be used to construct the C−C bond. Recently, we reported such an example of utilizing titanium-mediated sequential reductive elimination and oxidative coupling processes to synthesize new titanium(IV) complexes with a *cis*-9,10-dihydrophenanthrenediamide ligand, *cis*-9,10-PhenH$_2$(NR)$_2$TiCl$_2$, from the reaction of TiCl$_4$ with *o*-C$_6$H$_4$(CH═NR)Li.[9] This reaction provides a very interesting synthetic strategy for the titanium(IV) complexes with a complicated diamide ligand formed in situ from easily obtained *o*-C$_6$H$_4$(CH═NR)Li reagents. However, it was found that the reaction with TiCl$_4$ as the starting material is relatively difficult to control because of the high reactivity of TiCl$_4$ and the isolated yields of the titanium(IV) diamide complexes are usually low. To further exploit the application of this reaction and increase the yield of the diamide complexes, we have studied the reaction with TiCl$_2$(O^{i}Pr)$_2$ as the starting material and found that both the controllability and selectivity of the reaction are obviously improved. From the reactions of TiCl$_2$(O^{i}Pr)$_2$ with *o*-C$_6$H$_4$(CH═NR)Li reagents, both symmetric and asymmetric titanium(IV) diamide complexes have been obtained in high yields. The development of new synthetic method for the asymmetric titanium(IV) diamide complexes is of importance, considering that the asymmetric titanium(IV) diamide complexes might be useful as chiral catalysts for some organic or polymerization reactions.

Herein we report the synthesis of the new titanium(IV) complexes with symmetric and asymmetric *cis*-9,10-dihydrophenanthrenediamide ligands, *cis*-9,10-PhenH$_2$(NR)$_2$Ti(O^{i}Pr)$_2$ [PhenH$_2$ = 9,10-dihydrophenanthrene, R = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2a**), 2,6-Et$_2$C$_6$H$_3$ (**2b**), 2,6-Me$_2$C$_6$H$_3$ (**2c**)], *cis*-9,10-PhenH$_2$(NR$_1$)(NR$_2$)Ti(O^{i}Pr)$_2$ [R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Et$_2$C$_6$H$_3$ (**2d**); R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Me$_2$C$_6$H$_3$ (**2e**)], and [*cis*-9,10-PhenH$_2$(NR$_1$)$_2$][*o*-C$_6$H$_4$(CH═NR$_2$)]TiO^{i}Pr [R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Et$_2$C$_6$H$_3$ (**3a**); R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$ (**3b**)], from the reactions of TiCl$_2$(O^{i}Pr)$_2$ with *o*-C$_6$H$_4$Li(CH═NR) [R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-Et$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$], and their spectroscopic characterization and crystal structural analysis of complexes **2a**, **2b**, **2e**, and **3a**.

Results and Discussion

Reaction of TiCl$_2$(O^{i}Pr)$_2$ with *o*-C$_6$H$_4$(CH═NR)Li. The *o*-bromophenyl Schiff base compounds *o*-C$_6$H$_4$(CH═NR)Br (**1a**−**1c**) were prepared by the condensation reaction of *o*-bromobenzaldehyde with 1 equiv of the corresponding arylamine in hexane (Scheme 1).[10] Of them, compounds **1a** and **1c** have been reported previously.[9] TiCl$_2$(O^{i}Pr)$_2$ was prepared according to a literature procedure[11] by the reaction of TiCl$_4$ and Ti(O^{i}Pr)$_4$ (mole radio 1:1). Pure product was obtained as colorless crystals by recrystallization from hexane. The treatment of compounds **1a**−**1c** with 1 equiv of ^{n}BuLi in hexane produced the corresponding ortho-lithiated Schiff base derivatives *o*-C$_6$H$_4$(CH═NR)Li.[12] The reactions were carried out at 0 °C to minimize the formation of byproducts because the lithiation reactions are usually rapid and exothermic. The ortho-lithiated Schiff base compounds were isolated in high yields as air- and moisture-sensitive precipitates, which were washed with hexanes to remove residue ^{n}BuLi. The reactions of TiCl$_2$(O^{i}Pr)$_2$ with these ortho-lithiated Schiff base derivatives were studied in detail, and a number of new symmetric and asymmetric titanium(IV) diamide complexes **2a**−**2e**, **3a**, and **3b** have been obtained, as shown in Schemes 1 and 2. It was found that the reactions of TiCl$_2$(O^{i}Pr)$_2$ with 2 equiv of an ortho-lithiated Schiff base derivative in toluene, diethyl ether, or tetrahydrofuran (THF) give the corresponding complexes **2a**−**2c** in obviously higher yields (78−88%) in comparison with those for similar complexes obtained from the corresponding reactions of TiCl$_4$.[9] The synthetic yields of complexes **2a**−**2c** are quite dependent on the solvent and decrease in the order of toluene > diethyl ether > THF. It was also found that the reactions of TiCl$_2$(O^{i}Pr)$_2$ with the ortho-lithiated Schiff base derivatives are much slower than the corresponding reactions of TiCl$_4$, and the selectivity for replacing one or two chloride(s) of TiCl$_2$(O^{i}Pr)$_2$ with the *o*-C$_6$H$_4$(CH═NR) ligand can be roughly controlled by the molar ratio of the reagents. Therefore, the asymmetric complexes **2d** and **2e** have been synthesized in good yields (57−65%) by sequential reactions of TiCl$_2$(O^{i}Pr)$_2$ with two different ortho-lithiated Schiff base reagents in toluene. In addition to **2d** and **2e**, complexes **3a** and **3b** were also obtained as byproducts from these reactions in low yields. The formation of complexes **3a** and **3b** in these reactions indicates that a small amount of **2a** was formed in the first step of these reactions, as shown in Scheme 2, even though the molar ratio of TiCl$_2$(O^{i}Pr)$_2$ to *o*-C$_6$H$_4$[CH═N(2,6-^{i}Pr$_2$C$_6$H$_3$)]Li was controlled as 1:1.

Complexes **2a**−**2e**, **3a**, and **3b** are all soluble in toluene, CH$_2$Cl$_2$, and THF and less soluble in petroleum ether and hexanes. Complexes **2a**−**2e** are air- and moisture-sensitive in both the solid state and solution, while complexes **3a** and **3b** show relatively good stability to air and moisture and can be exposed to air for several hours without obvious decomposition. Complexes **2a**−**2e**, **3a**, and **3b** all show good thermal stability in solution and can be heated in boiling toluene for hours without obvious decomposition. Complexes **2a**−**2e**, **3a**, and **3b** were all characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy, and satisfactory analytical results were obtained. Crystallographic analysis on complexes **2a**, **2b**, **2e**, and **3a** indicates that the 9,10-dihydrophenanthrenediamide ligands in these complexes are all in the cis configuration.

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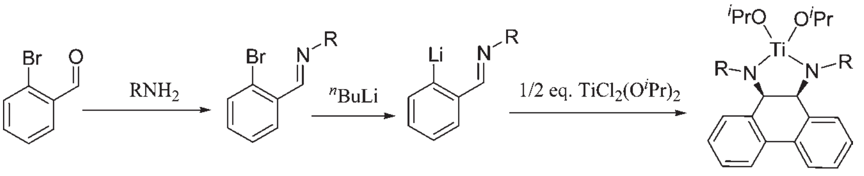
Scheme 1. Synthesis of the Symmetric Complexes **2a**−**2c**

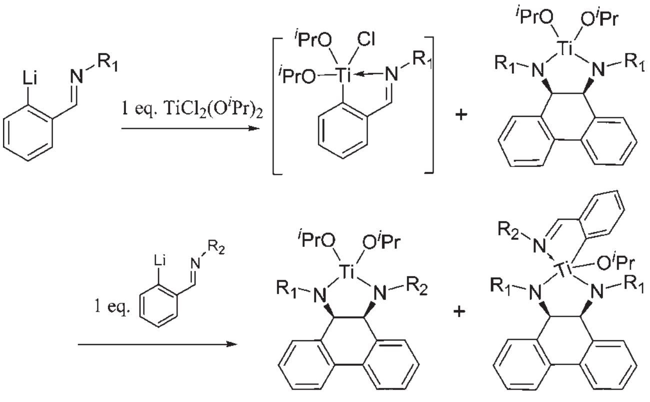


1a-c

2a-c

R = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**a**)
2,6-Et$_2$C$_6$H$_3$ (**b**)
2,6-Me$_2$C$_6$H$_3$(**c**)

Scheme 2. Synthesis of the Asymmetric Complexes **2d**−**2e**, **3a**, and **3b**



2d-e
Major product

3a-b
Minor product

R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Et$_2$C$_6$H$_3$ (**2d**)
R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Me$_2$C$_6$H$_3$(**2e**)
R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Et$_2$C$_6$H$_3$ (**3a**)
R$_1$ = 2,6-^{i}Pr$_2$C$_6$H$_3$, R$_2$ = 2,6-Me$_2$C$_6$H$_3$(**3b**)

As mentioned above, complexes **2**, instead of the intermediates [*o*-$C_6H_4(CH{=}NR)]_2Ti(O^iPr)_2$ (**A**), were always obtained from the reactions of $TiCl_2(O^iPr)_2$ with 2 equiv of the corresponding ortho-lithiated Schiff base reagents, which indicates that the intermediates **A** are unstable. As discussed in the previous publication,[9] the intermediates **A** may be formed first in these reactions and can then be converted to complexes **2** in situ through sequential C−C bond-forming reductive elimination and oxidative coupling reactions, as shown in Scheme 3. Attempts to observe the reaction intermediates by following the reaction of $TiCl_2(O^iPr)_2$ with 2 equiv of *o*-$C_6H_4[CH{=}N(2,6\text{-}^iPr_2C_6H_3)]Li$ in toluene-d_8 at different temperatures (−30, −50, and −70 °C) with ^{1}H NMR were not successful probably because the lifetime of the reaction intermediates is too short. Although the proposed intermediates **A** and **B** have not been isolated or observed in these reactions so far, the involved transition-metal-mediated reductive elimination[6,13] and oxidative coupling[7,14] reactions are well documented. Of course, it is also possible for complexes **2** to be formed through other routes, such as the direct addition of a second *o*-$C_6H_4[CH{=}NR]Li$ to the monoligated *o*-$C_6H_4[CH{=}NR]TiCl(O^iPr)_2$ to form the coupling product (rather than through reductive elimination). As was observed previously for the $TiCl_4$ reaction system,[9] the obtained titanium complexes **2a**−**2e**, **3a**, and **3b** all contain *cis*-9,10-dihydrophenanthrenediamide ligands, which indicates that the two −O^{i}Pr groups exert little steric effect on the imine oxidative coupling step.

NMR Analysis of the Complexes. All new complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy. The complexes **2a**−**2e** could be readily identified by ^{1}H and ^{13}C NMR spectroscopy. The disappearance of the signals of the imine C*H* protons and the appearance of resonances for the −C*H*N− protons in ^{1}H NMR spectra of **2a**−**2e** demonstrate the formation of the titanium diamide complexes.[15] A sharp singlet at 5.81, 5.82, and 5.83 ppm was observed in the ^{1}H NMR spectra of complexes **2a**, **2b**, and **2c**, respectively, which is representative of the −C*H*N− protons in the 9,10-dihydrophenanthrene ring. The corresponding −*C*HN− carbon resonances in these complexes were observed at 69.4, 68.8, and 66.1 ppm in their ^{13}C NMR spectra, respectively. For complexes **2d** and **2e**, two sets of doublets (5.75 and 5.91, 5.84, and 5.88 ppm) in their ^{1}H NMR spectra and two resonances (68.8 and 69.4, 66.1, and 71.0 ppm) in their ^{13}C NMR spectra were observed, indicating that the two −*CH*N− protons and carbons in the asymmetric 9,10-dihydrophenanthrene ring of **2d** and **2e** are inequivalent. The two diastereotopic isopropoxy groups in the symmetric complexes **2a**−**2c** give two sets of doublets for their methyl protons, while the four methyl groups of the two isopropoxy groups in the asymmetric complexes **2d** and **2e** show four sets of doublets because the two methyl groups in each isopropyl group are diastereotopic in the latter cases. It should be mentioned that the isopropyl units in the 2,6-^{i}Pr$_2$C$_6$H$_3$ group in complexes **2a**, **2d**, and **2e** show broad signals for both the methyl and methine protons at room temperature due to slow rotation of the 2,6-^{i}Pr$_2$C$_6$H$_3$ group about the *N*-aryl bond. When the NMR experiments were carried out at −40 °C, four sets of doublets for the methyl protons and two sets of septets for the methine protons in the two isopropyl units were observed because the two isopropyl groups in one 2,6-^{i}Pr$_2$C$_6$H$_3$ group are located at inequivalent positions at low temperatures and the two methyl groups in each isopropyl group are diastereotopic. Typical variable-temperature ^{1}H NMR spectra for complex **2e** are shown in Figure 1. Resonances for other protons and carbons in these complexes are in normal positions. Complexes **3a** and **3b**

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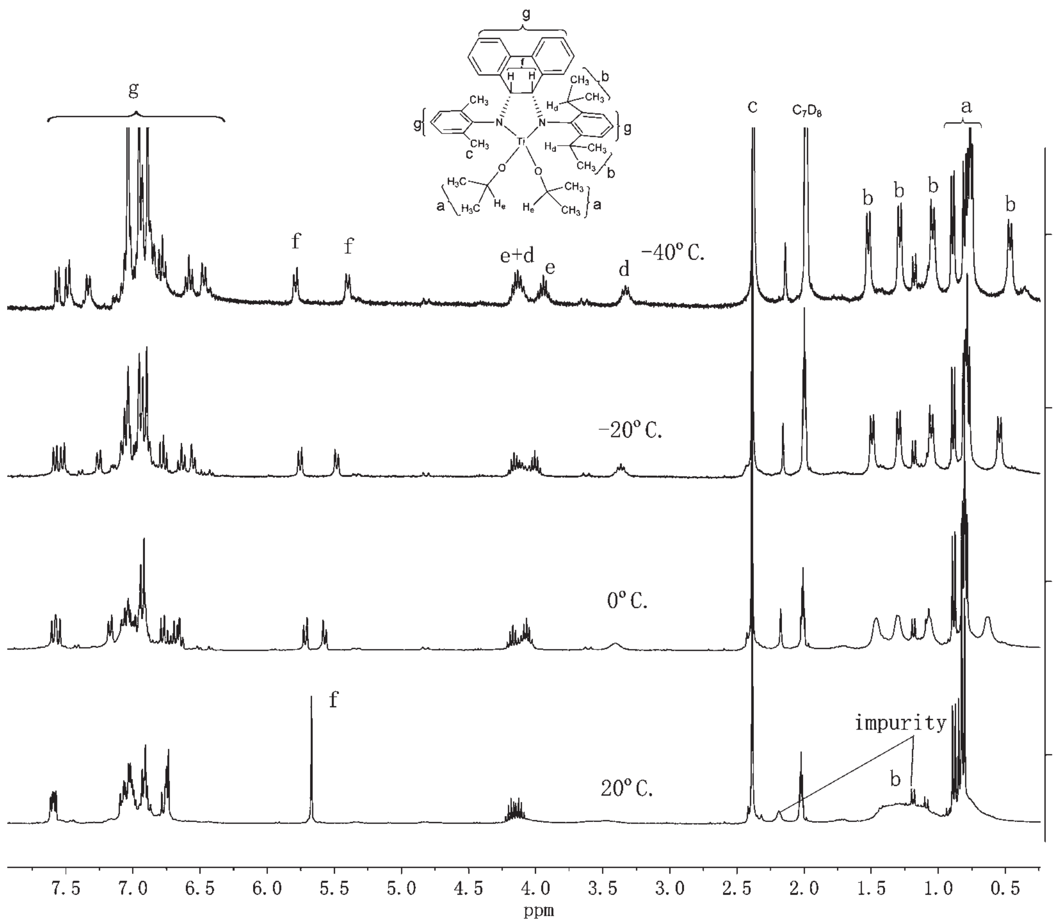
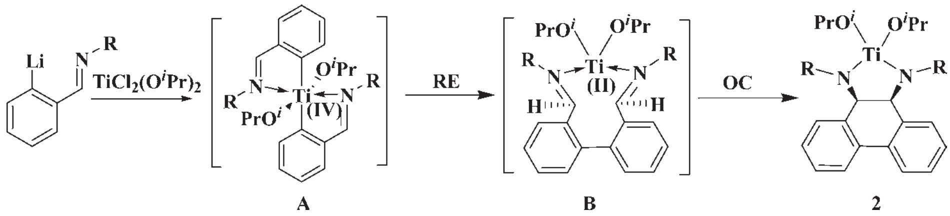


Figure 1. Variable-temperature ^{1}H NMR spectra of **2e** in toluene-d_8 at +20, 0, −20, and −40 °C.

Scheme 3. Proposed Mechanism for the Formation of **2**



could also be readily identified by ^{1}H and ^{13}C NMR spectroscopy. The presence of resonances for the −C*H*N− protons (5.80 and 5.86 ppm) and the imine C*H* protons (8.01 and 8.06 ppm) in their ^{1}H NMR spectra demonstrates the formation of titanium complexes **3a** and **3b**. The signals for the ethyl group in **3a** and the methyl group in **3b** further confirm their structures. For complexes **3a** and **3b**, four sets of doublets for the methyl protons and two sets of septets for the methine protons in the two isopropyl groups of the 2,6-^{i}Pr$_2$C$_6$H$_3$ group were observed at room temperature, which demonstrates that the 2,6-^{i}Pr$_2$C$_6$H$_3$ rotation about the *N*-aryl bond is further slowed down on the NMR time scale in these more crowded complexes.

Crystal Structures. Crystals of **2a**, **2b**, **2e**, and **3a** suitable for X-ray crystal structure determination were grown from CH$_2$Cl$_2$/*n*-hexane at ambient temperature. The ORTEP drawings of the molecular structures of **2a**, **2b**, **2e**, and **3a** are shown in Figures 2−5, respectively. X-ray analysis reveals that complexes **2a**, **2b**, and **2e** adopt a distorted tetrahedral coordination environment about the titanium center. The Ti−N bond lengths of 1.913(3) and 1.901(3) Å in **2a**, 1.896(4) and 1.901(4) Å in **2b**, and 1.900(2) and 1.917(5) Å in **2e** are in the normal range found in other titanium complexes with diamide ligands.[16] The Ti−O bond lengths of 1.787(2) and 1.781(2) Å in **2a**, 1.736(4) and 1.774(4) Å in **2b**, and 1.781(6) and 1.794(4) Å in **2e** are comparable to those reported for related titanium alkoxide complexes.[17] The O1−Ti−O2 bond angles of 108.31(11)° in **2a**, 111.0(2)° in **2b**, and

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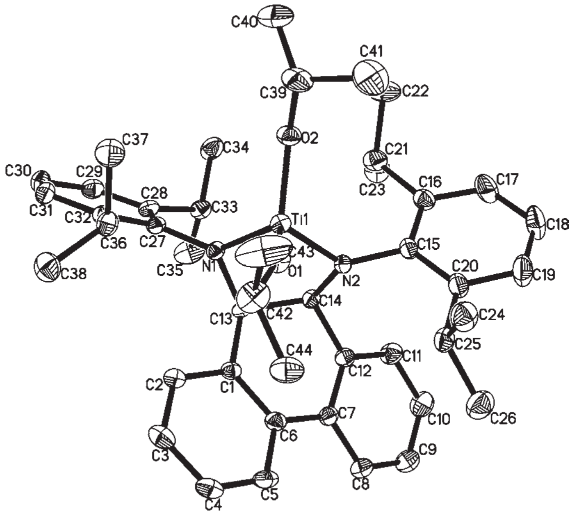

Figure 2. X-ray structure of **2a** with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ti1−N1 = 1.913(3), Ti1−N2 = 1.901(3), Ti1−O1 = 1.787(2), Ti1−O2 = 1.781(2), O1−Ti1−O2 = 108.31(11), N2−Ti−N1 = 88.15(12), N1−C13−C14−N2 = 40.08(2), C1−C6−C7−C12 = 17.63(97), C1−C13−C14−C12 = 40.92(3).

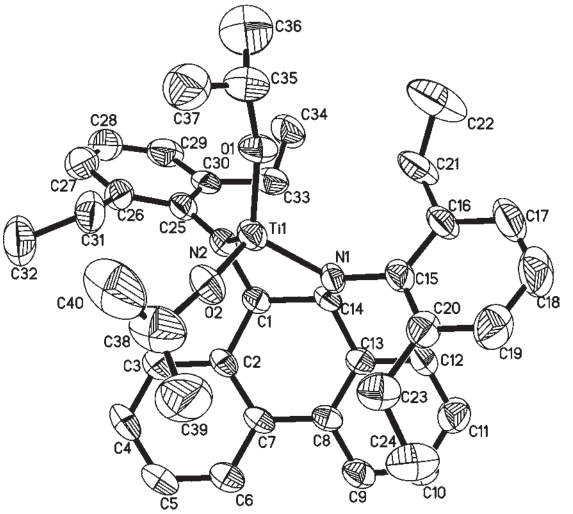

Figure 3. X-ray structure of **2b** with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ti1−N1 = 1.896(4), Ti1−N2 = 1.901(4), Ti1−O1 = 1.736(4), Ti1−O2 = 1.774(4), O1−Ti1−O2 = 111.0(2), N2−Ti−N1 = 87.97(19), N2−C1−C14−N1 = 40.80(4), C2−C1−C14−C13 = 43.22(9), C2−C7−C8−C13 = 18.60(2).

110.45(5)° in **2e** are close to the ideal bond angle in a tetrahedral coordination environment. The N1−Ti−N2 bond angles of 88.15(12)° in **2a**, 87.97(19)° in **2b**, and 87.08(9)° in **2e** are in line with those in their chloride analogues.[9] In complex **3a**, the coordination environment about the titanium atom is best described as distorted trigonal-bipyramidal, where the C39, N2, and O2 atoms form the equatorial plane [$\sum$angles X−Ti−Y = 358.52(9)°, where X, Y = O2, C39, N2] and the N1 and N3 atoms occupy the apical positions with an angle of 173.90(8)° for N1−Ti−N3. The Ti−N(amide) bond lengths of 1.938(2) and 1.945(2) Å in **3a** are comparable to those reported for related five-coordinate titanium complexes with diamide ligands[16] but longer than the corresponding ones in **2a**, **2b**, and **2e**. The Ti−N(imine) bond length of 2.423(2) Å in **3a** is close to those in related titanium complexes with imine nitrogen ligands.[18] The Ti−O bond length of 1.781(2) Å and the Ti−C bond length of 2.197(2) Å in **3a** are in normal range found in related titanium complexes.[17,19,15a] The torsion angle of N1−C1−C14−N2 [27.3(3)°] in **3a** is obviously smaller than the corresponding ones in **2a** [40.08(2)°], **2b** [40.80(4)°], and **2a** [39.34(5)°] because of the crowded coordination environment in **3a**.

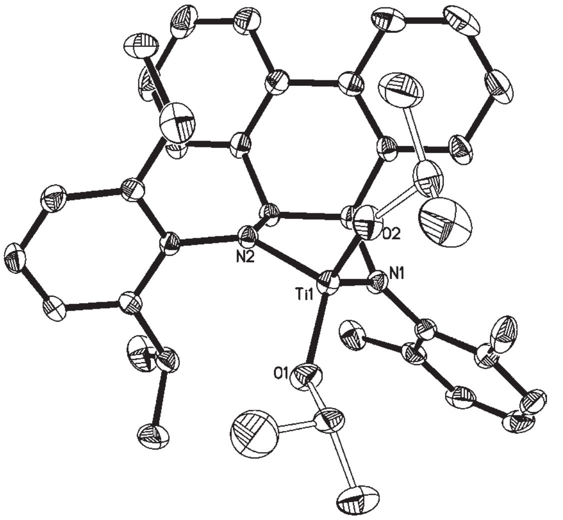

Figure 4. X-ray structure of **2e** with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ti1−N1 = 1.900(2), Ti1−N2 = 1.917(5), Ti1−O1 = 1.781(6), Ti1−O2 = 1.794(4), O1−Ti1−O2 = 110.45(2), N2−Ti−N1 = 87.08(13), N1−C1−C14−N2 = 39.34(5), C2−C7−C8−C13 = 13.26(9), C2−C1−C14−C13 = 40.37(4).

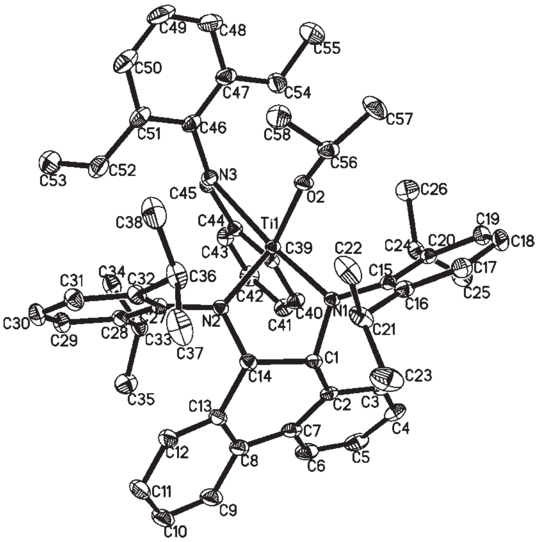

Figure 5. X-ray structure of **3a** with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ti1−N1 = 1.938(2), Ti1−N2 = 1.945(2), Ti1−N3 = 2.423(2), Ti1−O2 = 1.8188(17), Ti1−C39 = 2.197(2), O2−Ti1−C39 = 123.65(9), O2−Ti1−N2 = 134.37(9), N2−Ti1−C39 = 100.50(9), N1−Ti1−N3 = 173.90(8), N1−C1−C14−N2 = 27.2(3), C2−C7−C8−C13 = 16.3(4), C2−C1−C14−C13 = 30.6(3).

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Table 1. Crystal Data and Structural Refinement Details for **2a**, **2b**, **2e**, and **3a**

	2a	**2b**	**2e**	**3a**
formula	$C_{44}H_{58}O_2N_2Ti$	$C_{40}H_{53}O_2N_2Ti$	$C_{40}H_{50}N_2O_2Ti$	$C_{59}H_{71}Cl_2N_3OTi$
fw	694.82	641.74	638.72	956.99
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2(1)/n$	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$
a (Å)	19.693(4)	12.937(3)	17.169(1)	11.236(1)
b (Å)	10.332(2)	19.908(4)	21.062(1)	12.859(1)
c (Å)	21.764(4)	14.199(3)	20.082(1)	18.052(1)
α (deg)	90	90	90	88.233(1)
β (deg)	116.54(3)	102.68 (3)	98.021(1)	82.722(1)
γ (deg)	90	90	90	82.574(1)
v (Å^3)	3962.3(14)	3567.8(13)	7191.1(6)	2565.2(3)
Z	4	4	8	2
μ (mm^{-1})	0.253	0.275	0.273	0.314
R_{int}	0.1190	0.2002	0.0410	0.0184
GOF	1.029	0.967	1.009	1.030
R1	0.0603	0.0988	0.0535	0.0573
wR2	0.1259	0.1829	0.1275	0.1460

Conclusions

A number of new titanium complexes **2a**−**2e**, **3a**, and **3b** with an in situ formed *cis*-9,10-dihydrophenanthrenediamide ligand have been directly synthesized in high yields from the reactions of $TiCl_2(O^iPr)_2$ with corresponding *o*-C_6H_4(CH=NR)Li through sequential intramolecular C−C bond-forming reductive elimination and oxidative coupling reactions. No complexes with a *trans*-9,10-dihydrophenanthrenediamide ligand have been obtained from these reactions. The reactions of $TiCl_2(O^iPr)_2$ with the *o*-C_6H_4(CH=NR)Li reagents are much slower than the corresponding reactions of $TiCl_4$, and the selectivity for replacing one or two chloride(s) of $TiCl_2(O^iPr)_2$ with the *o*-C_6H_4(CH=NR) ligand can be controlled by the molar ratio of the reagents. The asymmetric complexes **2d** and **2e** have, therefore, been synthesized in good yields (57−65%) by sequential reactions of $TiCl_2(O^iPr)_2$ with two different *o*-C_6H_4(CH=NR)Li reagents. The cis configuration of the 9,10-dihydrophenanthrenediamide ligand in these complexes was confirmed by X-ray crystallographic analysis.

Experimental Section

General Comments. All manipulations of air- and water-sensitive compounds were performed under an inert atmosphere of nitrogen using standard Schlenk-line or glovebox techniques. Solvents were dried and purified by known procedures and distilled under nitrogen prior to use. ^{n}BuLi, $Ti(O^iPr)_4$, and $TiCl_4$ were purchased from Aldrich and used as received without further purification. $TiCl_2(O^iPr)_2$ was prepared according to literature methods.[11] ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury-300 spectrometer. Elemental analysis was performed on a Perkin-Elmer 2400 analyzer.

Synthesis of *o*-C_6H_4Br(CH=$NC_6H_3Et_2$-2,6) (1b). A mixture of *o*-bromobenzaldehyde (8.71 g, 47.1 mmol), 2,6-diethylaniline (7.8 mL, 47.1 mmol), and $MgSO_4$ (1.0 g) in *n*-hexane (30 mL) was stirred for 2 h. The mixture was filtered, and the filtrate was evaporated to dryness in vacuo to give the crude product as a yellow solid. Pure product (13.1 g, 41.6 mmol, 88%) was obtained as yellowish-green crystals by recrystallization from ethanol at −20 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (t, J = 7.5 Hz, 6 H, $CH_2C\mathit{H}_3$), 2.52 (q, J = 7.5 Hz, 4 H, $C\mathit{H}_2CH_3$), 7.04−7.12 (m, 3 H, Ph*H*), 7.36 (t, 1 H, Ph*H*), 7.45 (t, 1 H, Ph*H*), 7.64 (d, 1 H, Ph*H*), 8.28 (d, 1 H, Ph*H*), 8.61 (s, 1 H, C*H*=NAr) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.9 (*C*H_3), 24.9 (*C*H_2-CH_3), 124.3, 125.9, 126.5, 127.9, 128.3, 128.9, 132.6, 133.3, 134.6, 150.2 (*C*Br), 161.6 (*C*H=NAr) ppm. Anal. Calcd for $C_{17}H_{18}NBr$: C, 64.57; H, 5.74; N, 4.43. Found: C, 64.51; H, 5.79; N, 4.47.

Synthesis of [*cis*-9,10-($NC_6H_3{}^iPr_2$-2,6)$_2$-9,10-dihydrophenanthrene]Ti(O^iPr)$_2$ (2a). A solution of ^{n}BuLi (2.2 mmol) was added dropwise to a solution of **1a** (0.76 g, 2.2 mmol) in *n*-hexane (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The formed lithium salt of **1a** was collected on a frit, washed with *n*-hexane (2 × 5 mL), and dried under vacuum. The obtained lithium salt (0.57 g, 2.1 mmol) was dissolved in toluene (20 mL) and added to a solution of $TiCl_2$-(O^iPr)$_2$ (1.1 mmol) in toluene (10 mL) at −20 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The precipitate was filtered off, and the solvent was removed to leave a red solid. Recrystallization from CH_2Cl_2/hexane gave pure **2a** as red crystals (0.67 g, 0.97 mmol, 88%). Mp: 180−181 °C. ^{1}H NMR (300 MHz, toluene-*d*$_8$): δ 0.88 (d, J = 6.0 Hz, 6 H, OCH-(C*H*$_3$)$_2$), 0.91 (d, J = 6.0 Hz, 6 H, OCH(C*H*$_3$)$_2$), 1.0−1.5 (br, 24 H, CH(C*H*$_3$)$_2$), 3.4−3.7 (br, 2 H, C*H*(CH$_3$)$_2$), 3.9−4.2 (br, 2 H, C*H*(CH$_3$)$_2$), 4.29 (sept, J = 6.0 Hz, 1 H, OC*H*(CH$_3$)$_2$), 4.34 (sept, J = 6.0 Hz, 1 H, OC*H*(CH$_3$)$_2$), 5.81 (s, 2 H, C*H*N), 6.80−7.67 (m, 14 H, Ph*H*) ppm. ^{13}C NMR (75 MHz, toluene-*d*$_8$): δ 23.5 (br, CH(*C*H$_3$)$_2$), 25.0 (br, CH(*C*H$_3$)$_2$), 25.5 (br, CH(*C*H$_3$)$_2$), 26.1 (OCH(*C*H$_3$)$_2$), 26.2 (OCH(*C*H$_3$)$_2$), 27.3 (br, CH(*C*H$_3$)$_2$), 28.2 (br, *C*H(CH$_3$)$_2$), 29.1 (br, *C*H(CH$_3$)$_2$), 69.4 (*C*HN), 76.4 (O*C*H-(CH$_3$)$_2$), 78.1 (O*C*H(CH$_3$)$_2$), 123.5, 124.3 (br), 124.9 (br), 125.5, 125.8 (br), 126.1, 126.6 (br), 127.3, 128.3, 129.7, 132.8, 138.7 ppm. Anal. Calcd for $C_{44}H_{58}N_2O_2Ti$: C, 76.06; H, 8.41; N, 4.03. Found: C, 76.01; H, 8.39; N, 4.02.

Synthesis of [*cis*-9,10-($NC_6H_3Et_2$-2,6)$_2$-9,10-dihydrophenanthrene]Ti(O^iPr)$_2$ (2b). Complex **2b** was synthesized in the same manner as that of **2a** with compound **1b** (0.70 g, 2.2 mmol), ^{n}BuLi (2.2 mmol), and $TiCl_2(O^iPr)_2$ (1.1 mmol) as starting materials or reagents. Pure **2b** was obtained as red crystals (0.57 g, 0.90 mmol, 82%). Mp: 174−175 °C. ^{1}H NMR (300 MHz, toluene-*d*$_8$): δ 0.90 (d, J = 6.0 Hz, 6 H, OCH(C*H*$_3$)$_2$), 1.04 (d, J = 6.0 Hz, 6 H, OCH-(C*H*$_3$)$_2$), 1.35 (t, J = 7.5 Hz, 12 H, CH$_2$C*H*$_3$), 2.85−3.15 (m, J = 7.5 Hz, 8H, C*H*$_2$CH$_3$), 4.23 (sept, J = 6.0 Hz, 1 H, OC*H*(CH$_3$)$_2$), 4.32 (sept, J = 6.0 Hz, 1 H, OC*H*(CH$_3$)$_2$), 5.82 (s, 2 H, C*H*N), 6.80−7.80 (m, 14 H, Ph*H*) ppm. ^{13}C NMR (75 MHz, toluene-*d*$_8$): δ 15.1 (CH$_2$*C*H$_3$), 25.2 (*C*H$_2$CH$_3$), 26.3 (OCH(*C*H$_3$)$_2$), 26.6 (OCH-(*C*H$_3$)$_2$), 68.8 (*C*HN), 76.1 (O*C*H(CH$_3$)$_2$), 76.7 (O*C*H(CH$_3$)$_2$), 123.3, 124.6, 126.3, 126.6, 127.3, 127.6, 128.8, 129.5, 131.3, 137.7 ppm. Anal. Calcd for $C_{40}H_{50}N_2O_2Ti$: C, 75.22; H, 7.89; N, 4.38. Found: C, 75.20; H, 7.87; N, 4.37.

Synthesis of [*cis*-9,10-($NC_6H_3Me_2$-2,6)$_2$-9,10-dihydrophenanthrene]Ti(O^iPr)$_2$ (2c). Complex **2c** was synthesized in the same manner as that of **2a** with compound **1c** (0.63 g, 2.2 mmol), ^{n}BuLi (2.2 mmol), and $TiCl_2(O^iPr)_2$ (1.1 mmol) as starting materials or reagents. Pure **2c** was obtained as a red crystalline solid (0.50 g, 0.86 mmol, 78%). Mp: 172−173 °C. ^{1}H NMR (300 MHz, toluene-*d*$_8$): δ 0.83 (d, J = 6.0 Hz, 6 H, OCH(C*H*$_3$)$_2$), 0.87 (d, J = 6.0 Hz, 6 H, OCH(C*H*$_3$)$_2$), 2.41 (s, 12 H, C*H*$_3$), 4.20 (sept, J = 6.0 Hz, 1 H,

$\mathrm{OC}H(\mathrm{CH_3})_2$), 4.38 (sept, *J* = 6.0 Hz, 1 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 5.83 (s, 2 H, $\mathrm{C}H\mathrm{N}$), 6.80−7.80 (m, 14 H, $\mathrm{Ph}H$) ppm. ^{13}C NMR (75 MHz, toluene-d_8): δ 23.9 ($C\mathrm{H_3}$), 26.4 ($\mathrm{OCH(}C\mathrm{H_3})_2$), 26.7 ($\mathrm{OCH(}C\mathrm{H_3})_2$), 66.1 ($C\mathrm{HN}$), 71.5 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 76.8 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 123.5, 123.9, 124.0, 126.2, 127.5, 128.5, 129.7, 130.0, 130.2, 138.2 ppm. Anal. Calcd for $\mathrm{C_{36}H_{42}N_2O_2Ti}$: C, 74.22; H, 7.27; N, 4.81. Found: C, 74.20; H, 7.25; N, 4.80.

Synthesis of [*cis*-$\mathrm{N^9(C_6H_3Et_2}$-2,6)-$\mathrm{N^{10}(C_6H_3{}^iPr_2}$-2,6)-9,10-dihydrophenanthrene]$\mathrm{Ti(O^iPr)_2}$ (2d). The lithium salt of **1a** (0.29 g, 1.1 mmol) was dissolved in toluene (10 mL), added to a solution of $\mathrm{TiCl_2(O^iPr)_2}$ (1.1 mmol) in toluene (10 mL), and stirred for 30 min at −25 °C. Then the lithium salt of **1b** (0.25 g, 1.1 mmol) was dissolved in toluene (10 mL) and added to the reaction mixture at −25 °C. The reaction mixture was allowed to warm to room temperature and also stirred for an additional 2 h. The precipitate was filtered off, and the solvent was removed to leave a red solid. Recrystallization from $\mathrm{CH_2Cl_2}$/hexane gave pure **2d**, obtained as a red crystalline solid (0.48 g, 0.72 mmol, 65%). Mp: 154−155 °C. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 0.90 (d, *J* = 6.0 Hz, 3 H, $\mathrm{OCH(C}H_3)_2$), 0.95 (d, *J* = 6.0 Hz, 3 H, $\mathrm{OCH(C}H_3)_2$), 0.96 (d, *J* = 6.0 Hz, 3 H, $\mathrm{OCH(C}H_3)_2$), 0.97 (d, *J* = 6.0 Hz, 3 H, $\mathrm{OCH(C}H_3)_2$), 0.8−1.0 (br, 3 H, $\mathrm{CH(C}H_3)_2$), 1.1−1.5 (br, 9 H, $\mathrm{CH(C}H_3)_2$), 1.28 (t, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C}H_3$), 2.80−3.10 (m, *J* = 7.5 Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.7−3.9 (br, 1 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.9−4.1 (br, 1 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.20 (sept, *J* = 6.0 Hz, 1 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 4.29 (sept, *J* = 6.0 Hz, 1 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 5.75 (d, *J* = 7.2 Hz, 1 H, $\mathrm{C}H\mathrm{N}$), 5.91 (d, *J* = 7.2 Hz, 1 H, $\mathrm{C}H\mathrm{N}$), 6.80−7.75 (m, 14 H, $\mathrm{Ph}H$) ppm. ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$): δ 15.2 ($\mathrm{CH_2}C\mathrm{H_3}$), 23.5 (br, $\mathrm{CH(}C\mathrm{H_3})_2$), 24.4, 24.6 (br, $\mathrm{CH(}C\mathrm{H_3})_2$), 24.7, 25.5 (br, $\mathrm{CH(}C\mathrm{H_3})_2$), 25.8, 26.5 (br, $\mathrm{CH(}C\mathrm{H_3})_2$), 26.8, 28.0 (br, $C\mathrm{H(CH_3)_2}$), 28.4, 29.0 (br, $C\mathrm{H(CH_3)_2}$), 68.8 ($C\mathrm{HN}$), 69.4 ($C\mathrm{HN}$), 76.2 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 76.9 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 123.3, 123.4, 123.5, 123.7, 124.5 (br), 124.6, 125.5, 125.7 (br), 126.1, 126.4, 126.5 (br), 126.7, 127.1, 127.3 (br), 127.4, 128.2, 128.8, 129.04, 129.7, 131.5, 138.8, 139.1 ppm. Anal. Calcd for $\mathrm{C_{42}H_{54}N_2O_2Ti}$: C, 75.66; H, 8.16; N, 4.20. Found: C, 75.68; H, 8.15; N, 4.21.

Synthesis of [*cis*-$\mathrm{N^9(C_6H_3Me_2}$-2,6)-$\mathrm{N^{10}(C_6H_3{}^iPr_2}$-2,6)-9,10-dihydrophenanthrene]$\mathrm{Ti(O^iPr)_2}$ (2e). Complex **2e** was synthesized in the same manner as that of **2d** with the lithium salt of **1a** (0.29 g, 1.1 mmol), the lithium salt of **1c** (0.21 g, 1.1 mmol), and $\mathrm{TiCl_2(O^iPr)_2}$ (1.1 mmol) as starting materials or reagents. Pure **2e** was obtained as red crystals (0.40 g, 0.63 mmol, 57%). Mp: 151−152 °C. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 0.94 (d, *J* = 6.0 Hz, 6 H, $\mathrm{OCH(C}H_3)_2$), 0.98 (d, *J* = 6.0 Hz, 3 H, $\mathrm{OCH(C}H_3)_2$), 1.02 (d, *J* = 6.0 Hz, 3 H, $\mathrm{OCH(C}H_3)_2$), 0.8−1.1 (br, 3 H, $\mathrm{CH(C}H_3)_2$), 1.1−1.6 (br, 9 H, $\mathrm{CH(C}H_3)_2$), 2.54 (s, 6 H, $\mathrm{C}H_3$), 3.6−3.8 (br, 1 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.2−4.4 (br, 1 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.25 (sept, *J* = 6.0 Hz, 1 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 4.32 (sept, *J* = 6.0 Hz, 1 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 5.84 (d, *J* = 7.2 Hz, 1 H, $\mathrm{C}H\mathrm{N}$), 5.88 (d, *J* = 7.2 Hz, 1 H, $\mathrm{C}H\mathrm{N}$), 6.80−7.80 (m, 14 H, $\mathrm{Ph}H$) ppm. ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$): δ 23−24 (br, $\mathrm{CH(}C\mathrm{H_3})_2$), 24.0, 25−26 (br, $\mathrm{CH(}C\mathrm{H_3})_2$), 26.0, 26.2, 26.3, 26.6, 27−29 (br, $C\mathrm{H(CH_3)_2}$), 66.1 ($C\mathrm{HN}$), 71.0 ($C\mathrm{HN}$), 76.4 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 78.1 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 123.1, 123.6, 123.70, 123.72, 124.0 (br), 124.2, 124.5, 125.4 (br), 125.7, 127.1, 127.5 (br), 128.2, 128.7 (br), 129.4, 129.5, 129.8, 130.1, 131.3, 131.5, 133.1, 137.6, 138.3 ppm. Anal. Calcd for $\mathrm{C_{40}H_{50}N_2O_2Ti}$: C, 75.22; H, 7.89; N, 4.39. Found: C, 75.21; H, 7.88; N, 4.38.

Synthesis of [*cis*-9,10-$\mathrm{(NC_6H_3{}^iPr_2}$-2,6)$_2$-9,10-dihydrophenanthrene][*o*-$\mathrm{C_6H_4(CH{=}NC_6H_3Et_2}$-2,6)]$\mathrm{TiO^iPr}$ (3a). Complex **3a** was also isolated as a byproduct from the reaction for complex **2d**. Pure **3a** was obtained as red crystals (52 mg, 0.06 mmol, 11%). Mp: 123−124 °C. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 0.59 (d, *J* = 6.9 Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 0.87 (d, *J* = 6.0 Hz, 6 H, $\mathrm{OCH(C}H_3)_2$), 1.07 (d, *J* = 6.9 Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 1.13 (d, *J* = 6.9 Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 1.22 (d, *J* = 6.9 Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 1.27 (t, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C}H_3$), 2.53 (q, *J* = 7.5 Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.58 (sept, *J* = 6.9 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.79 (sept, *J* = 6.9 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.22 (sept, *J* = 6.0 Hz, 1 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 5.80 (s, 2 H, $\mathrm{C}H\mathrm{N}$), 6.80−7.80 (m, 21 H, $\mathrm{Ph}H$), 8.01 (s, 1H, $\mathrm{C}H\mathrm{{=}NAr}$) ppm. ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$): δ 14.9 ($\mathrm{CH_2}C\mathrm{H_3}$), 23.6, 24.8, 25.2, 25.6, 26.1, 26.6, 27.7, 28.6, 69.9 ($C\mathrm{HN}$), 77.9 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 123.3, 123.5, 124.3, 124.6, 124.7, 124.9, 125.5, 125.9, 126.6, 127.3, 128.1, 128.2, 128.4, 128.6, 128.7, 128.9, 129.4, 129.6, 132.7, 137.6, 139.0, 162.1, 177.9 ($C\mathrm{H{=}NAr}$) ppm. Anal. Calcd for $\mathrm{C_{58}H_{69}N_3OTi}$: C, 79.88; H, 7.98; N, 4.82. Found: C, 79.89; H, 7.96; N, 4.81.

Synthesis of [*cis*-9,10-$\mathrm{(NC_6H_3{}^iPr_2}$-2,6)$_2$-9,10-dihydrophenanthrene][*o*-$\mathrm{C_6H_4(CH{=}NC_6H_3Me_2}$-2,6)]$\mathrm{TiO^iPr}$ (3b). Complex **3b** was also isolated as a byproduct from the reaction for complex **2e**. Pure **3b** was obtained as a red crystalline solid (60 mg, 0.07 mmol, 13%). Mp: 118−119 °C. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 0.64 (d, *J* = 6.9 Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 0.92 (d, *J* = 6.0 Hz, 6 H, $\mathrm{OCH(C}H_3)_2$), 1.03 (d, *J* = 6.9 Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 1.15 (d, *J* = 6.9 Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 1.27 (d, *J* = 6.9 Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 2.54 (s, 6 H, $\mathrm{C}H_3$), 3.56 (sept, *J* = 6.9 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.15 (sept, *J* = 6.9 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.25 (sept, *J* = 6.0 Hz, 1 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 5.86 (s, 2 H, $\mathrm{C}H\mathrm{N}$), 6.80−7.80 (m, 21 H, $\mathrm{Ph}H$), 8.06 (s, 1 H, $\mathrm{C}H\mathrm{{=}NAr}$) ppm. ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$): δ 23.9, 24.5, 26.4, 26.5, 26.6, 26.8, 28.5, 28.8, 69.8 ($C\mathrm{HN}$), 76.8($\mathrm{O}C\mathrm{H(CH_3)_2}$), 123.5, 123.8, 123.9, 124.0, 124.3, 124.9, 125.9, 126.6, 127.5, 127.7, 127.9, 128.2, 128.5, 128.8, 129.0, 129.2, 129.4, 130.0, 131.8, 134.2, 138.2, 162.4, 176.7 ($C\mathrm{H{=}NAr}$) ppm. Anal. Calcd for $\mathrm{C_{56}H_{65}N_3OTi}$: C, 79.69; H, 7.76; N, 4.98. Found: C, 79.68; H, 7.75; N, 4.96.

X-ray Structure Determinations of 2a, 2b, 2e, and 3a. Single crystals of **2a**, **2b**, **2e**, and **3a** suitable for X-ray structural analysis were obtained from the mixture of $\mathrm{CH_2Cl_2}$/hexane. The data were collected on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) for **2e** and **3a** at 184.5K and on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) for **2a** and **2b** at 293 K. Details of the crystal data, data collection, and structure refinements are summarized in Table 1. The structures were solved by direct methods[20] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized position. All calculations were performed using *SHELXTL*[21] crystallographic software packages.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) *SHELXTL*; PC Siemens Analytical X-ray Instruments: Madison, WI, 1993.

(21) Sheldrick, G. M. *SHELXTL Structure Determination Programs*, version 5.0; PC Siemens Analytical Systems: Madison, WI, 1994.