

## Synthesis and Structure of a Linked-Bis(amidate) Ligand and Some Complexes with Titanium

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### Introduction

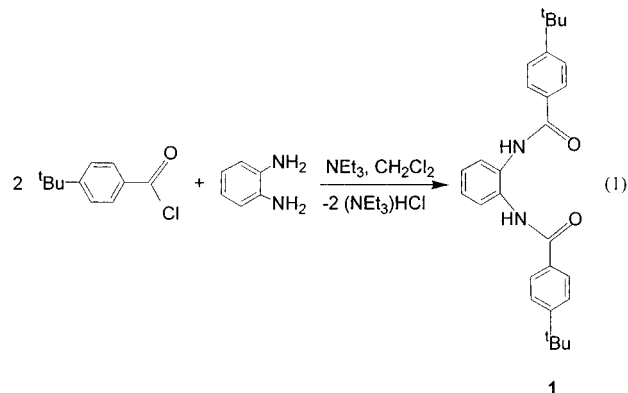
The development of new ligands that are capable of supporting novel reactivity is one of the cornerstones of organotransition metal chemistry. Since the discovery of group 4 metallocene catalyst systems, there has been increasing interest in well-defined transition-metal complexes that contain ligands other than cyclopentadienyl.<sup>1–3</sup> Nitrogen-based ligands have been actively studied in this regard, and we ourselves have been particularly interested in the synthesis and reaction chemistry of amidinates for group 3–5 metals.<sup>4–9</sup> In contrast to the wealth of information now available for these systems, the related *amidate* ligands are virtually unknown in transition-metal chemistry. Although titanium amidates have been invoked as intermediates in numerous catalytic cycles,<sup>10,11</sup> the number of well-defined group 4  $\eta^2$ -amide complexes remains low, and those reported are generally the result of isocyanate insertion into a metal–alkyl bond.<sup>12</sup>

Our goal here was to investigate the utility of  $\eta^2$ -amides as supporting ligands for early transition metals; additionally, we sought to link two of these ligands together in a constrained manner analogous to *ansa*-cyclopentadienyls.<sup>8,13</sup> These compounds may represent an attractive alternative to traditional salen complexes and/or Schiff base complexes utilizing a dianionic  $N_2O_2$  coordination sphere for use in the polymerization of olefins,<sup>14–18</sup> or asymmetric catalysis.<sup>19,20</sup> Here we report the

synthesis of a new linked bis-amidate ligand and a series of titanium complexes supported by this ligand system.

### Results and Discussion

The linked-amidate ligand **1** is easily prepared in high yield by the reaction of *p*-<sup>t</sup>Bu-benzoyl chloride with phenylenediamine in the presence of triethylamine in refluxing  $CH_2Cl_2$  (eq 1).<sup>13,21</sup>



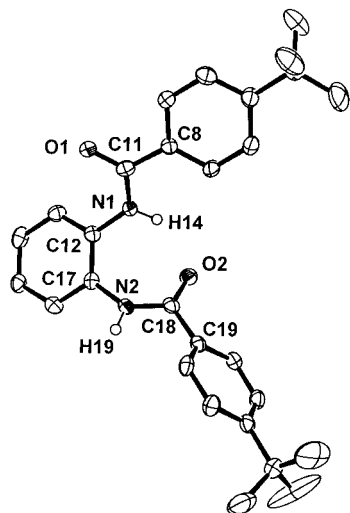
The *p*-<sup>t</sup>Bu group aids in solubility and provides a convenient spectroscopic handle within the ligand framework. Compound **1** is isolated as an air-stable white solid, which is soluble in solvents such as diethyl ether, benzene, toluene, or tetrahydrofuran. The <sup>1</sup>H NMR spectrum is indicative of a  $C_s$ -symmetric species in solution; additionally, the IR spectrum shows characteristic NH stretches from 3270 to 3240  $cm^{-1}$  along with strong absorbances around 1650  $cm^{-1}$  due to  $\nu_{C=O}$ . Cooling a saturated diethyl ether solution of **1** to  $-30\text{ }^\circ C$  resulted in colorless crystals that were suitable for X-ray diffraction.

An ORTEP view of the molecular structure of  $(NO)_2H_2$  (**1**) is shown in Figure 1; bond lengths and angles are given in Table 1. Complete details of the crystallographic analyses of compounds **1** and **3** are given in Table 3. The X-ray analysis shows a monomeric compound with two amides bound to a rigid phenylene spacer. All hydrogen atoms were found and refined. There is an intramolecular hydrogen bond between H14 on N1 and O2 on the other amide group (1.99 Å), with an angle of 142.3°. This interaction results in the two amide groups facing in opposing directions in relation to the phenylene backbone. No intermolecular contacts were noted. The C–N and C=O bond lengths of the two amide groups are similar to each other and are unremarkable.

$(NO)_2H_2$  (**1**) is readily deprotonated with  $LiN(SiMe_3)_2$  (2 equiv) in cold THF to yield the dilithio salt,  $(NO)_2Li_2(THF)_x$  (**2**) (Scheme 1). The product is insoluble in hydrocarbon and aromatic solvents, with only limited solubility in THF. The <sup>1</sup>H NMR spectrum of **2** suggests a  $C_s$ -symmetric structure in solution as found for the starting amide. The NH proton resonance of **1** (10.23 ppm) is absent in the spectrum of compound **2**, and peaks corresponding to coordinated THF are present. Integration suggests approximately one THF molecule per lithium atom, although this number decreases upon prolonged exposure to vacuum; microanalytical data are consistent with an unsolvated compound. We have been unable to obtain X-ray quality crystals of **2**, although the low solubility and high

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**Figure 1.** ORTEP view of  $(\text{NO})_2\text{H}_2$  (**1**) drawn with 50% probability ellipsoids.

**Table 1.** Selected Bond Distances (Å) and Angles (deg) for  $(\text{NO})_2\text{H}_2$  (**1**)

C11–O1	1.238(4)	C18–O2	1.232(4)
C11–N1	1.355(5)	C18–N2	1.356(5)
N1–H14	0.89(4)	N2–H19	0.87(4)
O1–C11–C8	120.0(3)	O2–C18–C19	122.4(4)
O1–C11–N1	122.7(4)	O2–C18–N2	132.2(4)
C8–C11–N1	117.3(3)	C19–C18–N2	114.4(3)
C11–N1–C12	124.0(3)	C18–N2–C17	127.3(3)

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for  $[(\text{NO})_2\text{Ti}(\text{NMe}_2)_2]_2$  (**3**)

Ti1–N1	2.22(8)	Ti2–N2	2.23(2)
Ti1–N3	2.23(1)	Ti2–N4	2.22(2)
Ti1–N5	1.88(2)	Ti2–N7	1.88(2)
Ti1–N6	1.90(2)	Ti2–N8	1.87(2)
Ti1–O1	2.05(1)	Ti2–O2	2.01(1)
Ti1–O3	2.01(1)	Ti2–O4	2.02(1)
O1–C77	1.35(2)	O2–C78	1.33(2)
N1–C77	1.22(2)	N2–C78	1.32(2)
O3–C79	1.27(2)	O4–C80	1.29(2)
N3–C79	1.32(2)	N4–C80	1.31(2)
N1–Ti1–N3	87.2(6)	N2–Ti2–N4	84.6(6)
N1–Ti1–N5	93.5(7)	N2–Ti2–N7	94.0(7)
N1–Ti1–N6	150.4(8)	N2–Ti2–N8	153.7(7)
N1–Ti1–O1	61.1(6)	N2–Ti2–O2	61.7(6)
N1–Ti1–O3	97.4(6)	N2–Ti2–O4	98.2(6)
N3–Ti1–N5	155.1(7)	N4–Ti2–N7	152.2(7)
N3–Ti1–N6	92.5(7)	N4–Ti2–N8	93.0(7)
N3–Ti1–O1	95.1(5)	N4–Ti2–O2	98.6(6)
N3–Ti1–O3	61.8(5)	N4–Ti2–O4	61.8(6)
N5–Ti1–N6	98.8(8)	N7–Ti2–N8	99.9(8)
N5–Ti1–O1	107.1(6)	N7–Ti2–O2	105.2(7)
N5–Ti1–O3	93.4(7)	N7–Ti2–O4	91.0(7)
N6–Ti1–O1	89.5(7)	N8–Ti2–O2	93.0(7)
N6–Ti1–O3	108.6(7)	N8–Ti2–O4	103.8(6)
O1–Ti1–O3	150.4(6)	O2–Ti2–O4	154.4(6)
O1–C77–N1	115(2)	O3–C79–N3	115(2)
O2–C78–N2	112(2)	O4–C80–N4	115(2)

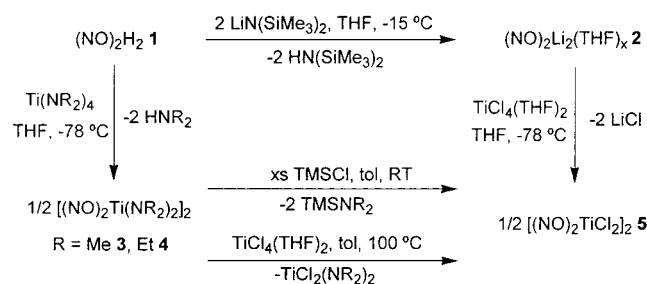
melting point of this compound suggest a polymeric structure in the solid state.

$(\text{NO})_2\text{H}_2$  (**1**) also reacts with the homoleptic titanium amides  $\text{Ti}(\text{NR}_2)_4$  ( $\text{R} = \text{Me}, \text{Et}$ ) to directly generate the titanium complexes  $[(\text{NO})_2\text{Ti}(\text{NMe}_2)_2]_2$  (**3**) and  $[(\text{NO})_2\text{Ti}(\text{NEt}_2)_2]_2$  (**4**) (Scheme 1). The amine elimination reactions were carried out in cold THF, yielding deep red solutions of **3** and **4**. Both titanium complexes are soluble in diethyl ether, benzene, toluene, and THF but only slightly soluble in pentane. Com-

**Table 3.** Crystallographic Data

compd	$(\text{NO})_2\text{H}_2$ ( <b>1</b> )	$[(\text{NO})_2\text{Ti}(\text{NMe}_2)_2]_2(\text{Et}_2\text{O})_2$ ( <b>3</b> )
formula	$\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_2$	$\text{C}_{72}\text{H}_{104}\text{N}_8\text{O}_6\text{Ti}_2$
fw	428.57	1273.46
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
$a$ , Å	12.5782(4)	13.899(1)
$b$ , Å	14.5619(4)	28.319(1)
$c$ , Å	13.7768(4)	18.516(1)
$\beta$ , °	100.902(1)	101.330(2)
$V$ , Å <sup>3</sup>	2477.85(19)	7145.9(8)
$Z$	4	4
total reflns	11548	19397
indep reflns	4305	5779
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	0.72	2.78
$R_{\text{int}}$	0.06	0.16
$R$	0.055	0.072
$R_w$	0.055	0.069
$T$ , °C	-143	-93

**Scheme 1**



pounds **3** and **4** exhibit highly symmetric <sup>1</sup>H NMR spectra as found for **1** and **2**. Cooling a saturated diethyl ether solution of **3** to -30 °C resulted in deep red crystals that were amenable to X-ray diffraction.

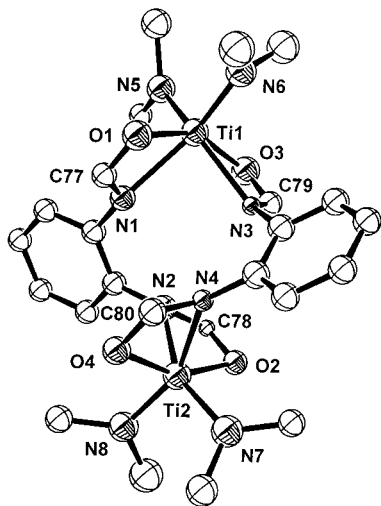
The molecular structure of compound **3** can be found in Figure 2. Selected bond distances and angles are presented in Table 2. The compound cocrystallizes with two molecules of diethyl ether, which do not interact with the metal centers and are omitted for the sake of clarity. As seen in Figure 2, compound **3** is dimeric in the solid state. Each dianionic ligand binds two titanium centers, with each of the two amidate groups binding different metal centers. The titanium atoms are ligated by two amidate groups and two NMe<sub>2</sub> units, generating an octahedral geometry. The steric constraints of the ligand result in some distortion from an idealized geometry; for example, the trans O–Ti–O linkages exhibit angles of 150.4(6)° and 154.4(6)°. The dimeric nature of **3** also results in a cis orientation of the two NMe<sub>2</sub> groups, which may have favorable implications with regard to the use of these complexes as olefin polymerization catalysts.<sup>15,16,22,23</sup> A similar orientation of NMe<sub>2</sub> groups has been reported for unlinked bis(salicylaldiminato) and β-diketiminato complexes of zirconium.<sup>17,24</sup> The Ti–N(amidate) bonds are longer than the Ti–N(amido) bond lengths (~2.22 Å vs ~1.88 Å) due to the delocalized nature of the amidate double bond. The Ti–N(amido) bond lengths (1.87(2)–1.90(2) Å) are similar to those reported for  $\text{Ti}(\text{NMe}_2)_3\text{Cl}$  (1.866(4) Å);<sup>25</sup> additionally, the Ti–N(amidate) bonds are comparable to those found in previously reported titanium–salen complexes.<sup>26–29</sup>

$[(\text{NO})_2\text{Ti}(\text{NMe}_2)_2]_2$  (**3**) and  $[(\text{NO})_2\text{Ti}(\text{NEt}_2)_2]_2$  (**4**) react with excess  $\text{Me}_3\text{SiCl}$  in toluene to yield the dichloride  $(\text{NO})_2\text{TiCl}_2$

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**Figure 2.** ORTEP view of  $[(\text{NO})_2\text{Ti}(\text{NMe}_2)_2]_2$  (**3**) drawn with 50% probability ellipsoids. Amidate aryl groups have been omitted for clarity.

(**5**) (Scheme 1). Compound **5** may also be synthesized via a disproportionation reaction between  $[(\text{NO})_2\text{Ti}(\text{NMe}_2)_2]$  (**3**) and 1 equiv of  $\text{TiCl}_4(\text{THF})_2$  in refluxing toluene. In both cases,  $(\text{NO})_2\text{TiCl}_2$  (**5**) was isolated as a pentane soluble red/brown solid. Attempts to prepare compound **5** by salt metathesis between the dilithio salt **2** and  $\text{TiCl}_4(\text{THF})_2$  were partially successful; although the dichloride was also formed by this route, we were unable to separate the product from other ligand-containing impurities formed in the reaction. Notable in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **5** are the absence of resonances corresponding to  $\text{NR}_2$  groups and a doubling of all of the ligand peaks, in contrast to that found for compounds **1–4**. This suggests an asymmetric solution structure, as a result of either aggregation or a rigid monomeric structure. A similar asymmetry has been noted for a series of monomeric Schiff base complexes of titanium.<sup>23</sup> The extremely high solubility of **5** has prevented us thus far from obtaining X-ray quality crystals of this compound.

Preliminary screening of some of the compounds reported here (bis-amido **3** and dichloro **5**) indicates that these systems exhibit only modest activities for polymerization of ethylene (1 atm) when activated with methylalumoxane (500 equiv).

## Conclusions

The synthesis of a new ligand system in which two amides are coupled via a rigid phenylene spacer is readily accomplished in a high-yield, single-step reaction. This reaction should be easily extended to incorporate a chiral spacer into the ligand backbone, i.e., *trans*-1,2-diaminocyclohexane or (1*S*,2*S*)-1,2-diphenylethylenediamine, resulting in a new class of  $C_2$ -symmetric ligands. This report also illustrates that the amidate ligand is a suitable spectator ligand for titanium, providing the metal center with an  $\text{N}_2\text{O}_2$  coordination sphere similar to that found in the more well-studied salen, bis(salicylaldiminato), and  $\beta$ -diketiminate systems. Bis-amido complex **3**

and the dichloro compound **5** exhibit only modest activities as ethylene polymerization catalysts in the presence of MAO (500 equiv).

## Experimental Section

**General Considerations.** Standard Schlenk-line and glovebox techniques were used unless stated otherwise. Pentane, diethyl ether, toluene, tetrahydrofuran, and methylene chloride were purified by passage through a column of activated alumina and degassed with argon.  $\text{C}_6\text{D}_6$  was vacuum transferred from sodium/benzophenone. *p*-*T*-butylbenzoyl chloride was purchased from Aldrich and used as received. Phenylenediamine was purchased from Aldrich and recrystallized from benzene prior to use. Triethylamine was purchased from Aldrich and distilled over Na. Chlorotrimethylsilane was purchased from Strem and distilled over  $\text{CaH}_2$  prior to use.  $\text{LiN}(\text{SiMe}_3)_2$ ,<sup>30</sup>  $\text{Ti}(\text{NMe}_2)_4$ ,<sup>31</sup>  $\text{Ti}(\text{NET}_2)_4$ ,<sup>31</sup> and  $\text{TiCl}_4(\text{THF})_2$ <sup>32</sup> were prepared according to literature procedures. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected.  $^1\text{H}$  NMR spectra were recorded at ambient temperature; chemical shifts are given relative to  $\text{C}_6\text{D}_5\text{H}$  (7.15 ppm) or  $\text{CD}_2\text{HCN}$  (1.94 ppm).  $^{13}\text{C}$  NMR chemical shifts are given relative to  $\text{C}_6\text{D}_6$  (128.39 ppm). IR samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses were determined at the College of Chemistry, University of California, Berkeley. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

**$(\text{NO})_2\text{H}_2$  (**1**).** This reaction was performed without the exclusion of air. A three-neck round-bottomed flask equipped with a reflux condenser and a dropping funnel was charged with 4-*tert*-butylbenzoyl chloride (14.1 g, 71.7 mmol), triethylamine (7.25 g, 71.7 mmol) and 250 mL of  $\text{CH}_2\text{Cl}_2$ . A methylene chloride solution (50 mL) of phenylenediamine (3.88 g, 35.9 mmol) was added to the dropping funnel and added dropwise to the benzoyl chloride/triethylamine solution at 0 °C over a period of 15 min. This resulted in a cloudy yellow slurry. The mixture was heated to reflux for 12 h. The clear yellow solution was then cooled to room temperature and the solvent removed under vacuum. The yellow solid was then extracted with water (3  $\times$  300 mL) and filtered to yield a white solid. The solid was dried under vacuum at 100 °C to remove residual water (13.5 g, 88% yield). Cooling a saturated diethyl ether solution to  $-30$  °C resulted in small colorless blocks suitable for X-ray diffraction. Mp: 235–238 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  10.23 (br s, 2H, NH), 8.37 and 7.31 (AB dd, 8H, amidate phenyl,  $^3J_{\text{H-H}} = 8.5$  Hz), 7.52 and 6.51 (AB dd, 4H, backbone phenyl,  $^3J_{\text{H-H}} = 8.0$  Hz), 1.14 (s, 18H, *tert*-butyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  166.5, 155.5 and 130.7 (tertiary phenyl), 127.6, 125.9, 125.8, and 125.6 (phenyl CH), 35.0 ( $\text{CMe}_3$ ), 31.2 ( $\text{CMe}_3$ ), amidate carbon not observed. IR ( $\text{cm}^{-1}$ ): 3269 (w), 3243 (w), 1649 (m), 1609 (m), 1598 (m), 1529 (m), 1506 (m), 1365 (m), 1320 (m), 1308 (m), 1270 (w), 759 (w). Anal. Calcd for  $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_2$ : C, 78.47; H, 7.53; N, 6.54. Found: C, 78.39; H, 7.54; N, 6.44.

**$(\text{NO})_2\text{Li}_2(\text{THF})_x$  (**2**).** To a THF solution of **1** (1.00 g, 2.33 mmol) maintained at  $-78$  °C was slowly added a THF solution of  $\text{LiN}(\text{SiMe}_3)_2$  (780 mg, 4.66 mmol) via cannula, generating a yellow solution. After stirring overnight, the solvent was removed in vacuo and the resulting white powder washed with pentane to remove  $\text{HN}(\text{SiMe}_3)_2$  (1.01 g, 85% yield). Mp:  $>350$  °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 300 MHz):  $\delta$  7.99 and 7.45 (AB dd, 8H, amidate phenyl,  $^3J_{\text{H-H}} = 8.0$  Hz), 7.90 and 6.91 (AB m, 4H, backbone phenyl), 1.33 (s, 18H, *tert*-butyl). The solubility of compound **2** was too low to obtain a suitable  $^{13}\text{C}$  NMR spectrum. IR ( $\text{cm}^{-1}$ ): 1654 (s), 1596 (s), 1576 (s), 1520 (s), 1504 (s), 1263 (m), 1102 (w), 1044 (m), 1016 (m), 904 (w), 852 (w), 794 (m), 776 (m), 754 (m), 709 (m). Anal. Calcd for  $\text{C}_{28}\text{H}_{30}\text{Li}_2\text{N}_2\text{O}_2$ : C, 76.36; H, 6.87; N, 6.36. Found: C, 76.05; H, 7.08; N, 6.02.

**$(\text{NO})_2\text{Ti}(\text{NMe}_2)_2$  (**3**) and  $(\text{NO})_2\text{Ti}(\text{NET}_2)_2$  (**4**).** For **3**: A pentane solution of  $\text{Ti}(\text{NMe}_2)_4$  (520 mg, 2.33 mmol) was added to a THF

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solution of **1** (1.00 g, 2.33 mmol) maintained at  $-78$  °C. The homogeneous red solution was stirred overnight and allowed to warm to room temperature. The solvent was then removed under vacuum, and the orange solid was washed with pentane. The solid was then dissolved in a minimum amount of diethyl ether and cooled to  $-30$  °C, resulting in small red blocks (435 mg, 33% yield). Compound **4** was prepared in a similar manner from **1** and  $\text{Ti}(\text{NEt}_2)_4$ .

**Data for 3.** Mp: 180–182 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  7.65 and 6.97 (AB dd, 8H, amidate phenyl,  $^3J_{\text{H-H}} = 8.5$  Hz), 6.69 and 6.54 (AB m, 4H, backbone phenyl), 3.62 (s, 12H,  $\text{NCH}_3$ ), 1.09 (s, 18H, *tert*-butyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  172.5, 153.4 and 143.4 (tertiary phenyl), 131.6, 127.0, 124.9, and 124.2 (phenyl CH), 46.8 ( $\text{NCH}_3$ ), 35.0 ( $\text{CMe}_3$ ), 31.5 ( $\text{CMe}_3$ ), amidate carbon not observed. IR ( $\text{cm}^{-1}$ ): 1608 (s), 1576 (s), 1542 (s), 1505 (s), 1412 (s), 1266 (s), 1194 (s), 1108 (m), 1018 (m), 957 (m), 937 (m), 843 (m), 800 (m), 716 (m), 695 (m), 654 (m). Anal. Calcd for  $\text{C}_{32}\text{H}_{42}\text{N}_4\text{O}_2\text{Ti}(\text{Et}_2\text{O})_2$ : C, 67.91; H, 8.23; N, 8.80. Found: C, 67.05; H, 7.57; N, 9.45.

**Data for 4.** Mp: 216–218 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  7.59 and 6.96 (AB dd, 8H, amidate phenyl,  $^3J_{\text{H-H}} = 8.5$  Hz), 6.72 and 6.67 (AB m, 4H, backbone phenyl), 4.71 and 3.15 (m, 8H,  $\text{NCH}_2\text{CH}_3$ ,  $^3J_{\text{H-H}} = 6.7$  Hz), 1.35 (t, 12H,  $\text{NCH}_2\text{CH}_3$ ,  $^3J_{\text{H-H}} = 6.7$  Hz), 1.12 (s, 18H, *tert*-butyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  172.3, 153.2 and 143.4 (tertiary phenyl), 131.5, 126.7, 124.9, and 124.3 (phenyl CH), 48.3 ( $\text{NCH}_2\text{CH}_3$ ), 35.0 ( $\text{CMe}_3$ ), 31.6 ( $\text{CMe}_3$ ), 15.4 ( $\text{NCH}_2\text{CH}_3$ ), amidate carbon not observed. IR ( $\text{cm}^{-1}$ ): 1610 (m), 1575 (m), 1543 (m), 1505 (m), 1411 (m), 1268 (w), 1187 (w), 999 (w), 930 (w), 884 (m), 842 (m), 786 (m), 753 (w), 716 (w), 694 (w). Anal. Calcd for  $\text{C}_{36}\text{H}_{50}\text{N}_4\text{O}_2\text{Ti}$ : C, 69.89; H, 8.15; N, 9.06. Found: C, 69.66; H, 8.25; N, 8.93.

**(NO)<sub>2</sub>TiCl<sub>2</sub> (5).** **Method A.**  $\text{Me}_3\text{SiCl}$  (7.6 mL, 60.0 mmol) was added to a toluene solution of **4** (3.70 g, 6.00 mmol) via syringe, causing the solution to darken. The solution was stirred at room temperature for 24 h, after which time the volatiles were removed under vacuum. The remaining oily solid was extracted with pentane, forming a dark red solution and a red solid. The pentane layer was filtered away from the insoluble material, and the solvent was removed to yield a red solid (2.80 g, 86% yield). Compound **5** may also be generated starting with the dimethylamido derivative **3**.

**Method B.** Compound **3** (563 mg, 1.00 mmol) and  $\text{TiCl}_4(\text{THF})_2$  (334 mg, 1.00 mmol) were combined in a Schlenk tube. Toluene was added, and the contents were heated to 100 °C for 24 h, forming a dark brown solution and some insoluble material. The reaction mixture was then cooled to room temperature. The reaction mixture was filtered,

and the solvent was removed under vacuum to yield a dark red/brown solid (393 mg, 72% yield).

**Method C.** A THF solution of  $\text{TiCl}_4(\text{THF})_2$  (195 mg, 0.585 mmol) was added via cannula to a THF solution of the dilithio salt **3** (300 mg, 0.585 mmol) at  $-78$  °C. The resultant dark red solution was left to stir overnight and warm to room temperature. The solvent was removed under vacuum, and the residue was extracted with toluene, forming a red solution over a white precipitate. The reaction mixture was filtered to remove  $\text{LiCl}$ , and the solvent was removed to yield a red solid. The product could not be fully separated from other ligand-containing impurities (160 mg, 50% yield (estimated)). Mp: 135–138 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  8.04, 7.54, 7.17, and 7.03 (AB dd, 4H, backbone phenyl,  $^3J_{\text{H-H}} = 6.0$  Hz), 7.72, 7.46, 7.00, and 6.92 (AB dd, 8H, amidate phenyl,  $^3J_{\text{H-H}} = 8.6$  Hz), 1.04 and 0.99 (s, 18H, *tert*-butyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  169.1, 158.1, 154.2, 152.9, 143.0, 135.0, 130.2, and 127.5 (tertiary phenyl), 130.7, 128.9, 125.6, 125.2, 124.3, 124.1, 120.0, and 113.0 (phenyl CH), 35.2 and 34.7 ( $\text{CMe}_3$ ), 31.0 and 30.9 ( $\text{CMe}_3$ ). IR ( $\text{cm}^{-1}$ ): 1702 (s), 1605 (s), 1334 (s), 1288 (s), 1264 (s), 1230 (m), 1193 (m), 1148 (m), 1017 (m), 930 (m), 907 (m), 837 (s), 762 (m), 735 (s). Independently prepared samples of **5** consistently analyzed low in carbon. Anal. Calcd for  $\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{N}_2\text{O}_2\text{Ti}$ : C, 61.67; H, 5.55; N, 5.14. Found: C, 55.90; H, 6.28; N, 5.13. (See Supporting Information for a copy of  $^1\text{H}$  NMR spectrum.)

**General Procedures for X-ray Crystallography.** Pertinent details for the individual compounds can be found in Table 3. For compound **1**, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. For compound **3**, only a low-quality data set was obtained; thus only the titanium atoms were refined anisotropically. The aromatic rings were treated as rigid groups, and all hydrogen atoms were assigned idealized positions and were included in structure factor calculations, but were not refined.

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**Supporting Information Available:** Tables of positional and thermal parameters and bond distances and angles for compounds **1** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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