Conformationally Rigid Diamide Complexes: Synthesis and Structure of Titanium(IV) Alkyl Derivatives

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Titanium complexes bearing a pyridinediamide ligand [2,6-$(RNCH_2)_2NC_5H_3]^{2-}$ (R = 2,6-diisopropylphenyl (BDPP); R = 2,6-dimethylphenyl (BDMP)) have been synthesized. The dichloride complexes [2,6-$(RNCH_2)_2NC_5H_3]TiCl_2$ are prepared in high yield from {2,6-[$(Me_3Si)RNCH_2]_2NC_5H_3$} and $TiCl_4$ via the elimination of 2 equiv of $CiSiMe_3$. Mono(alkyl) and bis(alkyl) complexes are prepared from [2,6-$(RNCH_2)_2NC_5H_3]TiCl_2$ and various Grignard reagents. A single-crystal X-ray diffraction study of (BDMP)$TiBr(CH_2CMe_2Ph)\cdot C_6H_6$ (**8b**·C_6H_6) revealed a distorted square pyramid structure with the neophenyl group occupying the axial position.

Introduction

The organometallic chemistry of Ti(IV) has been dominated by complexes supported by the cyclopentadienyl ligand.[1] In contrast, the alkyl chemistry of Ti(IV) in non-Cp ligand environments remains relatively unexplored.[2−13] Amide complexes of titanium[14−22] have been shown to stabilize a number of reactive species including alkyl groups with β-hydrogens[23] and methylidene ligands.[24] Our interest in the steric and electronic effects of conformationally rigid ligands led us to explore the synthesis of bulky chelating diamide ancillaries,[25,26] in particular, amides which bear bulky 2,6-disubstituted aryl groups. Recently, we reported that chelating diamide complexes of the type [$RN(CH_2)_3NR$]$TiMe_2$ (R = 2,6-$^iPr_2C_6H_3$, 2,6-$Me_2C_6H_3$) are active catalyst precursors for the polymerization of α-olefins.[27] Hence, we became interested in investigating the ability of other diamide ligand systems to stabilize Ti(IV) alkyls. We report here the synthesis, structure, and characterization of alkyl complexes of titanium supported by a conformationally rigid diamide ligand.

Results and Discussion

We have reported[28] that the aminolysis reaction between the diamines 2,6-$(RHNCH_2)_2NC_5H_3$ (R = 2,6-$^iPr_2C_6H_3$, 2,6-$Me_2C_6H_3$) and $Zr(NMe_2)_4$ provides 2 equiv of $HNMe_2$ and the mixed amide complexes [2,6-$(RNCH_2)_2NC_5H_3]Zr(NMe_2)_2$ in greater than 90% yield. These mixed amide complexes serve as excellent precursors to dichloride derivatives. Surprisingly, no reaction occurs between the diamines 2,6-$(RHNCH_2)_2NC_5H_3$ and $Ti(NMe_2)_4$, even at elevated temperatures (110 °C). Therefore, an alternative route to pyridinediamide complexes of titanium was necessary.

The addition of 2 equiv of $LiNR(SiMe_3)$ (**a**, R = 2,6-$^iPr_2C_6H_3$;[29] **b**, R = 2,6-$Me_2C_6H_3$) to a dimethoxyethane (DME) solution of 2,6-bis(bromomethyl)pyridine[30] at −30 °C affords the white crystalline silylated diamines

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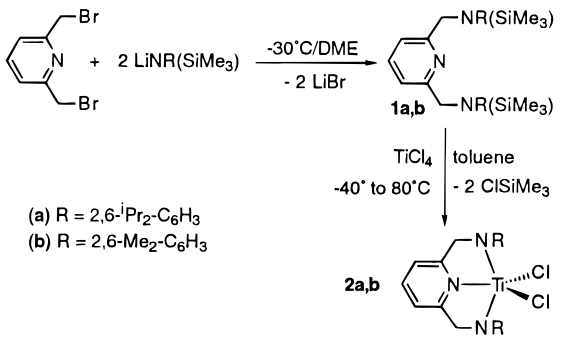
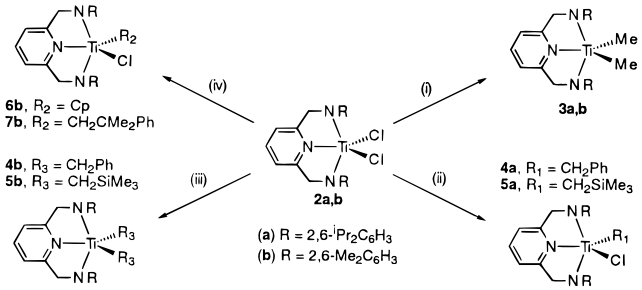
Scheme 1



Scheme 2. Alkylation of Compounds 2a,b[a]



[a] Reagents and conditions: (i) 2 equiv of MeMgBr, Et_2O, −78 °C; (ii) 1 equiv of $PhCH_2MgCl$ or $LiCH_2SiMe_3$, Et_2O, 22 °C; (iii) 2 equiv of $PhCH_2MgCl$ or $LiCH_2SiMe_3$, Et_2O, 22 °C; (iv) 1 equiv of NaCp·DME or $PhMe_2CCH_2MgCl$, Et_2O, −30 °C.

2,6-$[(Me_3Si)RNCH_2]_2NC_5H_3$ **(1a,b)** in moderate yield after workup (Scheme 1). Ligands **1a,b** can be prepared in about 40% yield on a scale of 2−5 g. The silylated ligand precursors react cleanly with $TiCl_4$ to give 2 equiv of $ClSiMe_3$ (confirmed by ^1H NMR spectroscopy) and the red dichloride complexes **(2a,b)** in >80% yield (Scheme 1). The dichlorides are insoluble in aliphatic hydrocarbons, slightly soluble in ether, and soluble in aromatic solvents and THF.

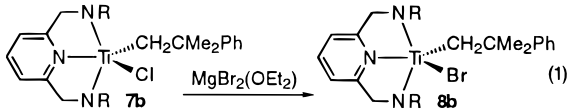
The proton NMR spectra of complexes **2a,b** are consist with a meridional coordination of the ligand as evidenced by the singlet observed for the methylene protons (CH_2N) of the ligand. Similar shifts are observed for the analogous zirconium dichloride derivatives $[2,6\text{-}(RNCH_2)_2NC_5H_3]ZrCl_2$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-$Me_2C_6H_3$).[28] In contrast, a facial coordination geometry is enforced by the pyridinediamide ligand in $[CH(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]TiBr_2$.[19] The isopropyl methyl groups of complex **2a** are diastereotopic, which we interpret as a consequence of restricted rotation about the N−C_{ipso} bond. We have no direct spectroscopic means of determining whether the same restricted rotation exists in the 2,6-dimethylphenyl-substituted derivative **2b**; however, modeling studies[31] and a structurally characterized halooalkyl derivative *(vide infra)* indicate that the barrier to rotation is likely high. The rigid coordination of the ligand and enforced location of the aryl groups creates a "pocket" opposite the pyridine and necessarily protects the metal above and below the N_3 plane.

With the aim of preparing titanium alkyl derivatives, the reaction of compounds **2a,b** with various alkylating reagents has been investigated (Scheme 2). The addition of 2 equiv of MeMgBr to ether suspensions of **2a,b** at −78 °C affords the dimethyl derivatives **3a,b** in good yield. Compounds **3a,b** are thermally sensitive in the absence of coordinating ligands; for example, they can be crystallized readily from ether or THF but decompose slowly in toluene or benzene. In contrast, the isoelectronic zirconium dimethyl derivatives $[2,6\text{-}(RNCH_2)_2\text{-}NC_5H_3]ZrMe_2$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-$Me_2C_6H_3$) are thermally stable.[28] Titanium dimethyl complexes bearing amide ligands are known to form methylidene species[24] via α-elimination, and we are examining this possible transformation.

The addition of 1 equiv of $PhCH_2MgCl$ or $LiCH_2SiMe_3$ to an ether suspension of **2a** at 22 °C yields the monoalkyl derivatives **4a** and **5a**, respectively, in high yield (Scheme 2). The proton NMR spectra of complexes **4a** and **5a** show characteristic AB quartet patterns for the methylene protons (CH_AH_BN) of the ligand indicating that there is asymmetry above and below the N_3 plane. In addition, two isopropyl methine and four isopropyl methyl resonances are observed which is in agreement with the C_s symmetry of the complexes and the restricted rotation of the N−C_{ipso} bond. The addition of excess alkylating reagent does not afford bis(alkyl) derivatives; evidently, the steric bulk of the 2,6-diisopropylphenyl-substituted ligand precludes formation of these species.

The alkylation chemistry of the dichloride complex **2b** clearly demonstrates the difference in steric bulk between the two ligand systems. The addition of 2 equiv of $PhCH_2MgCl$ or $LiCH_2SiMe_3$ to an ether suspension of **2b** at 22 °C yields the bis(alkyl) derivatives **4b** and **5b**, respectively, in high yield (Scheme 2). The C_{2v} symmetry of complexes **4b** and **5b** is supported by the observed singlet in the proton NMR for the methylene protons (CH_2N) of the ligand. The addition of 1 equiv of $PhCH_2MgCl$ or $LiCH_2SiMe_3$ at −78 °C affords a 50% yield (by ^1H NMR spectroscopy) of **4b** and **5b**.

The η^5-cyclopentadienyl derivative **6b** is obtained from the dichloride complex **2b** and 1 equiv of NaCp·DME in ether (Scheme 2). No reaction is observed between the bulkier dichloride compound **2a** and NaCp·DME. The proton NMR spectrum of **6b** reveals a C_s-symmetric complex as evidenced by a AB quartet pattern for the methylene protons (CH_AH_BN) of the ligand. In addition, the aryl methyl groups of **6b** are inequivalent suggesting that free rotation about the N−C_{ipso} bond is hindered by the presence of the Cp group. Surprisingly, the reaction of **2b** with 2 equiv of $PhMe_2CCH_2MgCl$ affords only the mono(alkyl) complex **7b** and not the expected bis(neophyl) derivative. Spectroscopic data are consistent with a C_s-symmetric complex and restricted rotation about the N−C_{ipso} bond of **7b** (no evidence of N−C_{ipso} bond rotation is observed to 80 °C). Although we have been unable to grow X-ray-quality crystals of complex **7b**, the bromide analogue **8b** does provide suitable crystals. The bromide complex **8b** was obtained from complex **7b** and excess $MgBr_2(OEt_2)$ in ether (eq 1).



The solid-state structure of **8b**·C_6H_6 was determined by X-ray crystallography (Table 1). The molecular

(31) Calculations were performed on an appropriate model using CAChe Scientific Inc. software.

Table 1. Summary of Crystallographic Data, Collection Parameters, and Refinement Parameters for Compound 8b·C_6H_6[a]

empirical formula	$C_{39}H_{44}BrN_3Ti$
fw	682.58
temp (*K*)	298(2)
wavelength (Å)	Mo Kα (0.710 73)
cryst system	monoclinic
space group	$P2_1/n$
a (Å)	14.892(2)
b (Å)	14.741(3)
c (Å)	16.080(3)
β (deg)	98.66(2)
V (Å^3)	3489.8(12)
Z	4
ρ(calc) (g/cm^{-3})	1.299
abs coeff (mm^{-1})	1.421
F(000)	1424
cryst dimens (mm)	0.29 × 0.24 × 0.15
θ range for data collcn (deg)	1.74−24.97
index ranges	$-1 \le h \le 17$, $-1 \le k \le 17$, $-19 \le l \le 18$
reflcns collcd	7094
indepdt reflcns	6115 [R(int) = 0.0323]
refinement method	full-matrix least squares on F^2
restraints/params	0/403
goodness of fit on F^2 (GooF)	1.059
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0706$, w$R2 = 0.1869$
R indices (all data)	$R1 = 0.1769$, w$R2 = 0.2404$
largest diff peak and hole (e Å^{-3})	0.585 and −1.037

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; w$R2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; GooF $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (where n is the number of reflections and p is the number of parameters refined).

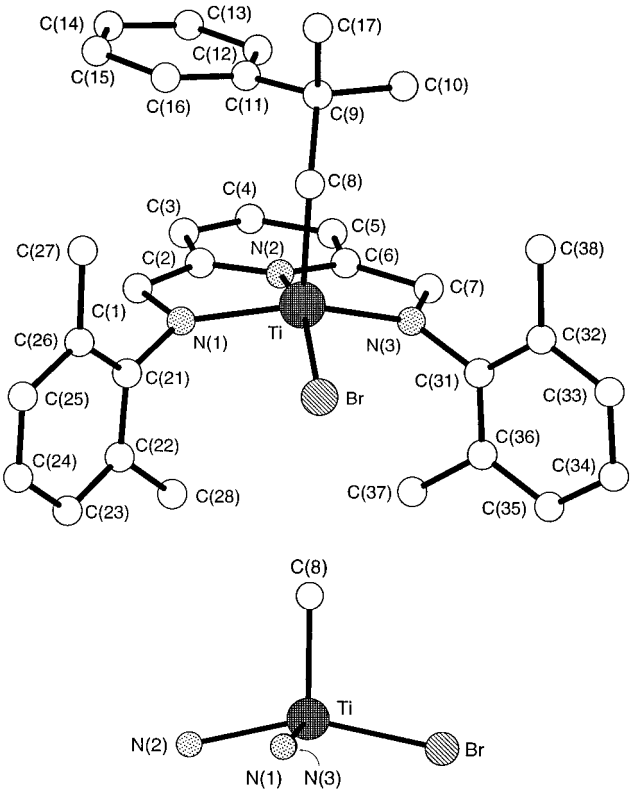


Figure 1. Top: Chem 3D drawing of the molecular structure of **8b**·C_6H_6. (The benzene molecule is not shown.) Bottom: Chem 3D drawing of the core **8b**·C_6H_6.

structure of complex **8b**·C_6H_6 can be found in Figure 1, and relevant bond distances and angles, in Table 2. The structure is best described as a distorted square pyramid with the neophyl carbon (C(8)) occupying the axial position (Figure 1). The titanium atom lies about 0.48 Å above the basal plane defined by the bromide, amides, and pyridine ligands. The Ti−amide distances (1.979(5) and 1.977(6) Å) are comparable to other titanium−amide complexes.[15,18,19,21−24,27] Each amide is nearly sp^2-hybridized as evidenced by the sum of the angles about each nitrogen (N(1) = 359.1° and N(3) = 359.3°). The rigid coordination of the ligand and enforced location of the aryl methyl groups (the aryl rings lie perpendicular to the plane of the ligand) necessarily protects the metal above and below the N_3 plane.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 8b·C_6H_6

Bond Distances			
Ti−Br	2.399(2)	Ti−N(1)	1.979(5)
Ti−N(2)	2.126(6)	Ti−N(3)	1.977(6)
Ti−C(8)	2.121(7)		
Bond Angles			
N(1)−Ti−N(3)	142.1(2)	Br−Ti−N(3)	100.3(2)
C(8)−Ti−Br	102.8(2)	Br−Ti−N(1)	98.1(2)
C(8)−Ti−N(2)	101.4(3)	Br−Ti−N(2)	155.8(2)
C(8)−Ti−N(1)	102.7(3)	C(8)−Ti−N(3)	105.1(3)

Conclusion

A high yield route to pyridinediamide complexes of titanium has been demonstrated. Restricted rotation about the N−C_{ipso} bond of the ligand and the availability of substituted anilines provides an opportunity to vary the sterics with little change to the electronic environment about the metal. Both mono(alkyl) and bis(alkyl) complexes are stabilized by these pyridinediamide ligand systems; however, the dimethyl derivatives are thermally unstable. On the basis of preliminary results, compounds **2a,b** show very low activities for the polymerization of ethylene when activated with methyl aluminoxane (MAO), presumably due to reduction to Ti(III). Successful preparation of Ti(III) derivatives via reduction of the mono(alkyl) complexes will be reported shortly.

Experimental Section

General Details. All experiments were performed under a dry dinitrogen atmosphere using standard Schlenk techniques or in an Innovative Technology Inc. glovebox. Solvents were distilled from sodium/benzophenone ketyl (DME, THF, hexanes, diethyl ether, benzene) or molten sodium (toluene) under argon and stored over activated 4 Å molecular sieves. $TiCl_4$ and MeMgBr were purchased from Aldrich and used as received. 2,6-Diisopropylaniline and 2,6-dimethylaniline were purchased from Aldrich and distilled under reduced pressure before use. LiNR(SiMe$_3$) (R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$) was prepared as noted in the literature.[29] A CH_2Cl_2 solution of 2,6-bis(bromomethyl)pyridine·HBr[30] was extracted with saturated $NaHCO_3$ to yield 2,6-bis(bromomethyl)pyridine. $MgBr_2(Et_2O)$ was made from Mg and $BrCH_2CH_2Br$ in ether. Me_3SiCH_2Li[32] and NaC_5H_5·DME[33] were prepared using previously reported syntheses. Proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in C_6D_6, unless otherwise noted, at approximately 22 °C on a Varian Gemini-300 spectrometer. The proton chemical shifts were referenced to internal C_6D_5H ($\delta = 7.15$ ppm), and the carbon resonances, to C_6D_6 ($\delta = 128.0$ ppm). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Ar = 2,6-

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diisopropylphenyl, Ar′ = 2,6-dimethylphenyl, $[2,6\text{-}(ArNCH_2)_2NC_5H_3]^{2-}$ = BDPP, and $[2,6\text{-}(Ar'NCH_2)_2NC_5H_3]^{2-}$ = BDMP.

2,6-[(Me$_3$Si)ArNCH$_2$]$_2$NC$_5$H$_3$ (1a). A DME (150 mL) solution of LiNR(SiMe$_3$) (8.820 g, 35.53 mmol) was added slowly to a DME (100 mL) solution of 2,6-bis(bromomethyl)pyridine (4.621 g, 17.44 mmol) at −30 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The solvent was removed in *vacuo* and the resulting solid extracted with hexanes (3 × 100 mL) and filtered through Celite. The volume of the filtrate was reduced to 50 mL and cooled to −30 °C for 12 h. White crystalline **1a** was isolated by filtration and dried under vacuum (4.530 g, 7.502 mmol, 44%): ^{1}H NMR δ 7.15 (t, 2H, Ar), 7.02 (d, 4H, Ar), 6.48 (t, 1H, py), 6.47 (d, 2H, py), 4.28 (s, 4H, NC*H*$_2$), 3.31 (sept, 4H, C*H*Me$_2$), 1.17 (d, 12H, CH*Me*$_2$), 0.90 (d, 12H, CH*Me*$_2$), 0.27 (s, 18H, Si*Me*$_3$); ^{13}C{^{1}H} NMR δ 159.88, 148.69, 143.40, 135.88, 126.30, 124.24, 122.28, 58.78, 27.94, 25.18, 1.06; MS (EI) *m*/*z* 601.423 (M$^+$), calcd for $C_{37}H_{59}N_3Si_2$ 601.424.

2,6-[(Me$_3$Si)Ar′NCH$_2$]$_2$NC$_5$H$_3$ (1b). The preparation of compound **1b** is identical to that for **1a**. LiNR(SiMe$_3$) (4.500 g, 23.30 mmol) and 2,6-bis(bromomethyl)pyridine (3.083 g, 11.73 mmol) gave white crystalline **1b** (2.389 g, 4.882 mmol, 42%): ^{1}H NMR δ 6.88−6.98 (t, 6H, Ar), 6.72 (t, 1H, py), 6.34 (d, 2H, py), 4.18 (s, 4H, NC*H*$_2$), 2.01 (S, 12H, Me), 0.23 (s, 18H, Si*Me*$_3$); ^{13}C{^{1}H} NMR δ 159.89, 146.32, 138.22, 135.54, 128.74, 125.09, 121.51, 56.50, 19.30, 0.87; MS (EI) *m*/*z* (M$^+$) 489.2997, calcd for $C_{29}H_{43}N_3Si_2$ 489.2995.

(BDPP)TiCl$_2$ (2a). A toluene solution of $TiCl_4$ (9.37 mL, 1.04 M, 9.752 mmol) was added in small portions to a toluene (100 mL) solution of **1a** (5.880 g, 9.737 mmol) at −40 °C. The solution immediately turned bright red, was warmed to room temperature, and heated to 80 °C for 12 h. The solution was filtered through Celite and the solvent removed in *vacuo*. The resulting solid was washed with cold hexanes (3 × 50 mL) to yield **2a** as a bright red powder (4.450 g, 7.747 mmol, 80%): ^{1}H NMR δ 7.14 (m, 6H, Ar), 6.75 (t, 1H, py), 6.27 (d, 2H, py), 4.87 (s, 4H, NC*H*$_2$), 3.75 (sept, 4H, C*H*Me$_2$), 1.53 (d, 12H, CH*Me*$_2$), 1.19 (d, 12H, CH*Me*$_2$); ^{13}C{^{1}H} NMR δ 161.58, 154.08, 142.83, 138.88, 124.80, 117.56, 103.30, 70.60, 28.58, 26.33, 25.12. Anal. Calcd for $C_{31}H_{41}N_3TiCl_2$: C, 64.81; H, 7.19; N, 7.31. Found: C, 64.35; H, 7.08; N, 6.95.

(BDMP)TiCl$_2$ (2b). The preparation of compound **2b** is identical to that for **2a**. $TiCl_4$ (2.35 mL, 1.04 M, 2.44 mmol) and **1b** (1.088 g, 2.223 mmol) gave **2b** as a red powder (0.839 g, 1.815 mmol, 82%): ^{1}H NMR δ 6.95−7.05 (m, 6H, Ar), 6.85 (t, 1H, py), 6.36 (d, 2H, py), 4.52 (s, 4H, NC*H*$_2$), 2.42 (S, 12H, Me); ^{1}H NMR (CD_2Cl_2) δ 8.09 (t, 1H, Py), 7.58 (d, 2H, py), 7.00−7.15 (m, 6H, Ar), 5.8 (s, 4H, NC*H*$_2$), 2.32 (S, 12H, Me); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 163.51, 154.50, 140.29, 133.54, 129.22, 126.91, 118.96, 69.13 (*C*H$_2$N), 19.48.

(BDPP)TiMe$_2$ (3a). To a diethyl ether (25 mL) suspension of **2a** (0.500 g, 0.870 mmol) was added 2.2 equiv of MeMgBr (0.58 mL, 3.0 M, 1.7 mmol) at −78 °C. The solution changed from orange to dark red within minutes and was stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a red-brown solution. The solvent was removed in vacuo, the solid dissolved in a minimum amount of diethyl ether, and the solution cooled to −30 °C for 12 h. Yellow crystalline **3a** was isolated by filtration and dried under vacuum (0.314 g, 0.461 mmol, 53%). The solid is thermally sensitive but can be stored at −40 °C to prevent decomposition: ^{1}H NMR δ 7.02 (m, 6H, Ar), 6.76 (t, 1H, py), 6.30 (d, 2H, py), 4.98 (s, 4H, NC*H*$_2$), 3.69 (sept, 4H, C*H*Me$_2$), 1.28 (d, 12H, CH*Me*$_2$), 1.11 (d, 12H, CH*Me*$_2$), 1.06 (s, 6H, Ti*Me*); ^{13}C{^{1}H} NMR δ 162.93, 145.41, 137.87, 129.29, 126.33, 124.51, 117.03, 68.33, 64.40 (Ti*C*H$_3$), 28.11, 28.04, 24.35.

(BDMP)TiMe$_2$ (3b). The preparation of compound **3b** is identical to that for **3a**. **2b** (0.100 g, 0.216 mmol) and 2.2 equiv of MeMgBr (0.2 mL, 2.40 M, 0.48 mmol) gave yellow crystalline **3b** (0.072 g, 0.171 mmol, 79%). The solid is thermally sensitive but can be stored at −40 °C to prevent decomposition: ^{1}H NMR δ 7.21 (d, 4H, Ar), 7.08 (t, 2H, Ar), 6.91 (t, 1H, py), 6.47 (d, 2H, py), 4.73 (s, 4H, NC*H*$_2$), 2.38 (s, 12H, Me), 1.08 (s, 6H, Ti*Me*); ^{13}C{^{1}H} NMR δ 163.49, 153.08, 137.50, 135.09, 129.09, 125.41, 117.13, 65.96, 62.28 (Ti*C*H$_3$), 18.62.

(BDPP)TiCl(CH$_2$Ph) (4a). To a diethyl ether (30 mL) suspension of **2a** (0.500 g, 0.870 mmol) was added 1 equiv of $PhCH_2MgCl$ (0.62 mL, 1.4 M, 0.87 mmol) at room temperature. The solution changed from orange to dark red within minutes and was stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a red-brown solution. The solvent was removed in vacuo, the solid dissolved in a minimum amount of hot hexanes, and the solution cooled to −40 °C for 12 h. Red crystalline **4a** was isolated by filtration and dried under vacuum (0.418 g, 0.663 mmol, 75%): ^{1}H NMR δ 7.30−6.80 (Ar and CH$_2$*Ph*), 6.69 (t, 1H, py), 6.54 (d, 2H, CH$_2$*Ph*), 6.19 (d, 2H, py), 4.92 (AB quartet, $^2J_{HH}$ = 22.7, 4H, NC*H*$_2$), 4.71 (sept, 2H, C*H*Me$_2$), 3.72 (s, 2H, C*H*$_2$Ph), 3.09 (sept, 2H, C*H*Me$_2$), 1.60 (d, 6H, CH*Me*$_2$), 1.52 (d, 6H, CH*Me*$_2$), 1.30 (d, 6H, CH*Me*$_2$), 1.06 (d, 6H, CH*Me*$_2$); ^{13}C{^{1}H} NMR δ 161.57, 154.84, 149.49, 143.83, 142.69, 138.27, 127.52, 126.66, 125.30, 124.52, 124.39, 121.81, 117.04, 79.89, 69.41, 28.87, 26.17, 25.79, 24.96, 24.81. Anal. Calcd for $C_{38}H_{45}N_3TiCl\cdot C_6H_{14}$: C, 73.78; H, 8.72; N, 5.87. Found: C, 73.98; H, 8.42; N, 5.90.

(BDPP)TiCl(CH$_2$SiMe$_3$) (5a). To a diethyl ether (30 mL) suspension of **2a** (0.500 g, 0.870 mmol) was added 1 equiv of $LiCH_2SiMe_3$ (0.082 g, 0.871 mmol) at room temperature. The solution changed from orange to yellow within minutes and was stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite. The solvent was removed in vacuo, the solid dissolved in a minimum amount of diethyl ether, and the solution cooled to −40 °C for 12 h. Yellow crystalline **5a** was isolated by filtration and dried under vacuum (0.430 g, 0.687) mmol, 79%): ^{1}H NMR δ 7.25−7.15 (Ar), 6.83 (t, 1H, py), 6.38 (d, 2H, py), 5.07 (AB quartet, $^2J_{HH}$ = 22.0, 4H, NC*H*$_2$), 4.39 (sept, 2H, C*H*Me$_2$), 3.25 (sept, 2H, C*H*Me$_2$), 2.89 (s, 2H, C*H*$_2$Si), 1.54 (d, 6H, CH*Me*$_2$), 1.45 (d, 6H, CH*Me*$_2$), 1.40 (d, 6H, CH*Me*$_2$), 1.11 (d, 6H, CH*Me*$_2$), −0.18 (s, 9H, Si*Me*$_3$); ^{13}C{^{1}H} NMR δ 162.76, 154.21, 143.74, 142.95, 138.62, 127.00, 126.52, 124.77, 124.35, 117.31, 83.70, 69.47, 38.83, 27.66, 26.81, 26.34, 25.28, 24.63, 2.34. Anal. Calcd for $C_{35}H_{52}N_3SiTiCl$: C, 67.13; H, 8.37; N, 5.71. Found: C, 67.08; H, 8.44; N, 5.79.

(BDMP)Ti(CH$_2$Ph)$_2$ (4b). To a diethyl ether (30 mL) suspension of **2b** (0.100 g, 0.216 mmol) was added 2.2 equiv of $PhCH_2MgCl$ (2.2 mL, 0.22 M, 0.48 mmol) at room temperature. The solution changed from orange to dark red within minutes and was stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a red-brown solution. The volume of the solvent was reduced (5 mL) and the solution cooled to −40 °C. Dark red crystalline **4b** was isolated by filtration (0.089 g, 0.124 mmol, 72%): ^{1}H NMR δ 7.17 (d, 4H, Ar), 7.05 (m, 2H, Ar), 6.88 (t, 4H, CH$_2$*Ph*), 6.77 (t, 1H, py), 6.62 (t, 2H, CH$_2$*Ph*), 6.60 (d, 4H, CH$_2$*Ph*), 6.25 (d, 2H, py), 4.59 (s, 4H, NC*H*$_2$), 2.62 (s, 4H, C*H*$_2$Ph), 2.46 (s, 12H, Me); ^{13}C{^{1}H} NMR δ 161.85, 156.88, 145.89, 137.83, 134.43, 129.26, 128.63, 125.49, 124.81, 122.31, 118.16, 116.83, 65.49, 19.92.

(BDMP)Ti(CH$_2$SiMe$_3$)$_2$ (5b). To a diethyl ether (30 mL) suspension of **2b** (0.100 g, 0.216 mmol) was added 2.2 equiv of $LiCH_2SiMe_3$ (0.045 g, 0.476 mmol) at −40 °C. The solution changed from orange to yellow within minutes and was stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite. The solvent was removed in vacuo, the solid dissolved in a minimum amount of hexanes, and the solution cooled to −40 °C for 12 h. Yellow crystalline **5b** was isolated by filtration and dried under vacuum (0.112 g, 0.198 mmol, 92%): ^{1}H NMR δ 7.17 (d, 4H, Ar), 7.03 (m, 2H, Ar), 6.89 (t, 1H, py), 6.45 (d, 2H, py), 4.76 (s, 4H, NC*H*$_2$), 2.52 (s, 12H, Me), 1.84 (s, 4H, C*H*$_2$Si), −0.19 (s, 18H, Si*Me*$_3$); ^{13}C{^{1}H} NMR δ

162.64, 156.36, 138.17, 134.07, 129.35, 125.29, 117.10, 83.16, 66.23, 19.62, 2.38.

(BDMP)TiCl(η^5-C_5H_5) (6b). To a diethyl ether (30 mL) suspension of **2b** (0.100 g, 0.216 mmol) was added 1.3 equiv of NaC_5H_5·DME (0.049 g, 0.275 mmol) at −40 °C. The solution changed from orange to yellow within minutes and was stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite. The solvent was removed in vacuo, the solid dissolved in a minimum amount of diethyl ether, and the solution cooled to −40 °C for 12 h. Orange crystalline **6b** was isolated by filtration and dried under vacuum (0.097 g, 0.197 mmol, 77%): ^{1}H NMR δ 7.17−7.00 (m, 7H, Ar and py), 6.50 (d, 2H, py), 6.02 (s, 5H, Cp), 4.47 (AB quartet, $^2J_{HH}$ = 21.83 Hz, 4H, NCH_2), 2.44 (s, 6H, Me), 1.80 (s, 6H, Me); ^{13}C{^{1}H} NMR δ 163.98, 159.76, 136.62, 133.44, 130.99, 129.29, 128.52, 124.53, 119.63 (Cp), 116.15, 69.26, 18.65.

(BDMP)TiCl(CH_2CMe_2Ph) (7b). To a diethyl ether (30 mL) suspension of **2b** (0.400 g, 0.865 mmol) was added 1.1 equiv of $PhMe_2CCH_2MgCl$ (1.09 mL, 0.867 M, 0.952 mmol) at −40 °C. The solution changed from orange to dark red within minutes and was stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite. The solvent was removed in vacuo, the solid dissolved in a minimum amount of a 20:1 mixture of THF/benzene, and the solution cooled to −40 °C for 12 h. Red crystalline **7b** was isolated by filtration and dried under vacuum (0.400 g, 0.627 mmol, 72%): ^{1}H NMR δ 7.19−6.98 (m, 11H, Ar and Ph), 6.89 (t, 1H, py), 6.39 (d, 2H, py), 4.59 (AB quartet, $^2J_{HH}$ = 21.98 Hz, 4H, NCH_2), 2.92 (s, 2H, CH_2CMe$_2$), 2.75 (s, 6H, Me), 2.10 (s, 6H, Me), 1.10 (s, 6H, CH$_2$CMe_2); ^{13}C{^{1}H} NMR δ 163.38, 157.73, 152.96, 138.26, 133.36, 132.50, 128.99, 128.87, 125.55, 125.42, 125.22, 117.35, 97.42, 66.33, 46.33, 32.05, 20.67, 18.50. Anal. Calcd for $C_{33}H_{38}N_3TiCl$·C_6H_6: C, 73.40; H, 6.95; N, 6.48. Found: C, 73.60; H, 7.26; N, 6.16.

(BDMP)TiBr(CH_2CMe_2Ph) (8b). To a diethyl ether (30 mL) solution of **7b** (0.400 g, 0.714 mmol) was added 10 equiv of $MgBr_2(Et_2O)$ (2.373 g, 7.14 mmol) at room temperature. The solution was stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite. The solvent was removed in vacuo, the solid dissolved in a minimum amount of a 20:1 mixture of THF/benzene, and the solution cooled to −40 °C for 12 h. Red crystalline **8b** was isolated by filtration and dried under vacuum (0.356 g, 0.522 mmol, 73%): ^{1}H NMR δ 7.19−6.98 (m, 11H, Ar and Ph), 6.86 (t, 1H, py), 6.36 (d, 2H, py), 4.59 (AB quartet, $^2J_{HH}$ = 21.98 Hz, 4H, NCH_2), 2.95 (s, 2H, CH_2CMe$_2$), 2.80 (s, 6H, Me), 2.03 (s, 6H, Me), 1.08 (S, 6H, CH$_2$CMe_2); ^{13}C{^{1}H} NMR δ 163.36, 158.33, 152.80, 138.22, 133.34, 132.51, 129.03, 128.88, 125.53, 125.51, 117.28, 102.03, 66.50, 46.89, 31.96, 20.78, 19.66. Anal. Calcd for $C_{33}H_{38}N_3TiBr$·C_6H_6: C, 68.62; H, 6.50; N, 6.16. Found: C, 68.61; H, 6.69; N, 5.76.

X-ray Crystallographic Analysis. A suitable crystal of **4b** was grown from a saturated THF/benzene solution at room temperature. Crystal data may be found in Table 1. Data were collected on a Enraf-Nonius CAD4F diffractometer using CAD4F software.[34] Intensity data were recorded in $\omega-2\theta$ scan mode at variable scan speeds within a maximum time per datum of 45 s. Moving background estimates were made at 25% scan extensions on each side. Standard reflections were monitored every 180 min of X-ray exposure time. Lorentz, polarization, and decay corrections were applied. Crystal faces were identified by optical goniometry, and a Gaussian absorption correction made to the data, which were averaged to yield 6115 unique data for structure solution and refinement. The structure was solved by a combination of SHELXS and difference Fourier syntheses using SHELXL-93 software.[35] Anisotropic thermal parameters were refined for all non-hydrogen atoms. All phenyl hydrogen atoms were located by difference Fourier methods, placed in calculated positions (C−H = 0.9 Å), and included in the structure factor calculations. The four methyl groups C(27), C(28), C(37), and C(38) showed disorder. The idealized tetrahedral groups were assigned 0.5 multiplicities. The benzene solvent molecule showed considerable thermal motion but refined well to an acceptable geometry.

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Supporting Information Available: Text describing X-ray procedures, tables of final crystallographic atomic coordinates, equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, and complete bond lengths and angles, and ORTEP diagrams for **8b**·C_6H_6 (11 pages). Ordering information is given on any current masthead page.

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