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# Titanium bis(alkylamido)phenylborane complexes

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Dedicated in honor of Professor Richard R. Schrock

#### Abstract

The bis(*tert*-butylamido)phenylborane ligand [<sup>t</sup>BuN-B<sup>Ph</sup>-N<sup>t</sup>Bu], may be delivered to titanium from its dilithio salt. Complexes containing a single chelating boradiamido ligand, [<sup>t</sup>BuN-B<sup>Ph</sup>-N<sup>t</sup>Bu]TiX<sub>2</sub>, (X = NMe<sub>2</sub> (1), Cl (2), Bn (3)), have been prepared and characterized by <sup>1</sup>H and <sup>11</sup>B NMR, and single crystal X-ray structure analysis (2,3).  $\bigcirc$  2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium complexes; Olefin polymerization; Borylamides; Suitemate

#### 1. Introduction

Non-metallocene early transition metal complexes provide entry to catalysts capable of effecting Ziegler– Natta polymerizations [1]. A successful design approach to such catalyst precursors involves the replacement of cyclopentadienyl ligands on titanium and zirconium dialkyls with chelating dianionic amido ligands [2–20]; these diamido-based pre-catalysts exhibit novel reactivity including the living polymerization of  $\alpha$ -olefins [21– 25]. Catalyst activity is profoundly affected by the nature of the ancillary groups on the amide nitrogen owing to perturbations of the ligand's electronic and steric properties.

One line of inquiry that has begun to be investigated is the direct attachment of Group 13 elements to the amide nitrogens. Schrock has utilized the N–B  $\pi$ -bonding character of borylamides to force the aryl groups on the terminal borane to assume a perpendicular orientation to the plane of the diamido ligand, thus significantly increasing the steric congestion about the metal center [26,27]. Alternatively, Patton has incorporated B–B and In into the diamide backbone to examine the effect of an electrophilic bridge on the activity of olefin

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polymerization [28,29]. Along these lines, the simplest structural ligand construct is offered by bis(amido)boranes, which situate a single boron atom between two amides.

The donor-acceptor-donor (N-B-N) motif of bis-(amido)borane ligands coincides with our recent interests in developing new reaction chemistry by controlling  $\pi$ -bonding within bidentate ligand frameworks. Our most recent studies have examined late transition metals bearing ligands with the inverse construct, an acceptordonor-acceptor (P-N-P) ligand motif [30-33]. The complementary donor-acceptor-donor construct of bis(amido)borane provides us the opportunity to develop new reaction chemistry for early transition metals. Accordingly, we have explored the chemistry of bis(alkvlamido)borane ligands with zirconium, hafnium and vanadium [34]. Our interests to elaborate further the coordination chemistry of bis(alkylamido)boranes and to participate in this festschrift issue in honor of our special colleague and friend led us to target titanium organometallic complexes of the ligand. Prior to the studies reported here, the only titanium compounds containing a bis(alkylamido)borane ligand were the bischelate,  $Ti[^{t}BuN-B^{Ph}-N^{t}Bu]_{2}$  where  $^{t}BuN-B^{Ph} N^{t}Bu = bis(tert-butylamido)phenylborane$  [35] and a binuclear titanium center bridged by bis(methylamido)phenylborane [36]. We now report the synthesis, spectroscopic characterization, and X-ray crystallo-

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graphic analysis of a family of titanium complexes containing a single chelating  ${}^{t}BuN-B^{Ph}-N{}^{t}Bu$  ligand.

## 2. Experimental

## 2.1. General procedures

All synthetic manipulations were carried out using modified Schlenk techniques under an atmosphere of  $N_2$ or within the confines of a Vacuum Atmosphere HE-553-2 glove box. Solvents for synthesis were of reagent grade or better and were dried according to standard methods [37]. Bis(*tert*-butylamino)phenylborane [38], N,N'-dilithiobis(*tert*-butylamino)phenylborane (PhB-(<sup>t</sup>BuNLi)<sub>2</sub>) [35] and dichlorobis(dimethylamido)titanium(IV) [39] were prepared by literature methods. All other materials were used as received.

# 2.2. $[^{t}BuN-B^{Ph}-N^{t}Bu]Ti(NMe_{2})_{2}$ (1)

Pentane (20 ml) solutions containing 1.75 g of TiCl<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> and 2.06 g of PhB(<sup>t</sup>BuNLi)<sub>2</sub> were frozen immediately upon the dissolution of the reactants. Upon thawing, the PhB(<sup>t</sup>BuNLi)<sub>2</sub> solution was added dropwise over 7 min to a partially thated  $TiCl_2(NMe_2)_2$ solution. The mixture was allowed to slowly warm to room temperature (r.t.). After stirring overnight, the solution was filtered through Celite to remove LiCl and a green titanium byproduct resulting from reduction of the Ti(IV) starting material. Solvent removal by vacuum evaporation afforded a red liquid, which was refiltered through fresh Celite. The filtrate was placed under vacuum for 12 h after which 1.365 g of an orange solid was collected (45.4% yield). <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 25 °C): δ 1.286 (s, 18H), 3.190 (s, 12H), 7.1–7.6 (m, 5H). <sup>11</sup>B NMR (96.205 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 29.961. Anal. Calc. for C<sub>18</sub>H<sub>35</sub>BN<sub>4</sub>Ti: C, 59.04; H, 9.63; N, 15.30. Found: C, 58.88; H, 9.53; N, 15.34%.

# 2.3. $\int BuN - B^{Ph} - N^{t}Bu / TiCl_{2}$ (2)

A 15-ml hexanes/chlorotrimethylsilane (TMSCl) (50:50) solution containing 560 mg of [<sup>t</sup>BuN-B<sup>Ph</sup>-N<sup>t</sup>Bu]Ti(NMe<sub>2</sub>)<sub>2</sub> was allowed to stir overnight. A bright orange precipitate was collected by filtration and the filtrate was concentrated to promote precipitate formation. The additional product was collected, combined with the first batch and the resulting total quantity of solid was washed with cold hexanes; 451 mg (90.5% yield) of the fluffy bright orange product was obtained. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.181 (s, 18H), 7.0–7.2 (m, 5H). <sup>11</sup>B NMR (96.205 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  30.485. *Anal*. Calc. for C<sub>14</sub>H<sub>23</sub>BCl<sub>2</sub>N<sub>2</sub>Ti: C, 48.19; H, 6.64; N, 8.03. Found: C, 48.26; H, 6.55; N, 7.90%.

2.4.  $\int BuN - B^{Ph} - N^{t}Bu / TiBn_{2}$  (3)

[<sup>t</sup>BuN–B<sup>Ph</sup>–N<sup>t</sup>Bu]TiCl<sub>2</sub> (100 mg) was dissolved in 10 ml of C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>. The solution was immediately frozen and then slowly warmed; 0.280 ml of BnMgCl (2.06 M in THF) was added dropwise to the partially thawed solution. The mixture was allowed to warm to r.t. After stirring overnight, solvent was removed in vacuo to yield an orange solid. Pentane (10 ml) was added, and the mixture was filtered through Celite to remove LiCl. Solvent was removed in vacuo to yield 121.4 mg of bright orange crystalline solid (92.4% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.166 (s, 18H), 2.149 (s, 4H), 6.8–7.5 (m, 15H). <sup>11</sup>B NMR (96.205 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  30.659. *Anal.* Calc. for C<sub>28</sub>H<sub>37</sub>BN<sub>2</sub>Ti: C, 73.06; H, 8.10; N, 6.09. Found: C, 72.84; H, 8.03; N, 5.96%.

#### 2.5. Reaction of 3 with $[Ph_3C][B(C_6F_5)_4]$ and 1-hexene

Separate solutions of  $C_6D_5Cl$  (0.3 ml) containing 10 mg of 3 and 20 mg of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] were frozen immediately upon dissolution of the reactants. Upon thawing, the two solutions were combined and stirred at -30 °C for 5 min. 1-Hexene (182 mg, 200 equiv.) was then added and the solution was allowed to react at -30 °C over the course of 3 h. Poly(1-hexene) was not observed by <sup>1</sup>H and <sup>13</sup>C NMR. The reaction was also performed at 0 and 25 °C; these too showed no poly(1-hexene) production.

## 2.6. Physical methods

<sup>1</sup>H NMR spectra were recorded on solutions at 25 °C within the magnetic fields of a Varian Unity 300 or Mercury 300 spectrometers, which were located in the Department of Chemistry Instrumentation Facility (DCIF) at MIT. Chemical shifts are reported using the standard  $\delta$  notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. <sup>11</sup>B NMR spectra were collected at the DCIF on a Varian Unity 300 spectrometer and referenced to an external BF<sub>3</sub>·OEt standard. Elemental analyses were performed at H. Kolbe Mikroanalytisches Laboratorium.

X-ray diffraction experiments were performed on single crystals grown from concd.  $C_5H_{12}$  or hexanes solutions at -35 °C. Crystals were removed from the supernatant liquid and transferred onto a microscope slide coated with Paratone N oil. Selected crystals were affixed to a glass fiber in wax and Paratone N oil and cooled to -90 °C. Data collection was performed by shining Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation onto crystals mounted onto a Siemens' three-circle goniometer equipped with a CCD detector. The data were processed and refined by using the program SAINT supplied by

Siemens Industrial Automation, Inc. The structures were solved by direct methods (G.M. Sheldrick, and Siemens Industrial Automation, Inc., SHELXTL-v6.10 (2000)) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Some details regarding the refined data and cell parameters are contained in Table 1. Selected bond distances and angles are supplied in Table 2.

#### 3. Results and discussion

Synthesis of titanium complexes containing a single bis(alkylamido)phenylborane ligand proved to be initially troubling. Attempts at transamination of Ti(NMe<sub>2</sub>)<sub>4</sub> with the diamine of the ligand were unsuccessful as was the reaction of PhB(<sup>t</sup>BuNLi)<sub>2</sub> with TiCl<sub>4</sub>. The latter reaction produces significant amounts of reduced titanium product and only small amounts of 1, which were inseparable from the other titanium byproducts. The initial target of a single chelate complex of  ${}^{t}BuN-B^{Ph}-N^{t}Bu$  was eventually obtained with the methods outlined in Scheme 1. Although the reaction of TiCl<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> with PhB(<sup>t</sup>BuNLi)<sub>2</sub> still shows significant reduction of the Ti(IV) reactant, 1 may be isolated in 45% yield. This orange compound proved to be a convenient synthon for the dichloride analog, 2, which may be cleanly converted to bisbenzyl complex 3 by using conventional Grignard chemistry.

The <sup>1</sup>H NMR spectra of 1-3 exhibit a pronounced singlet resonance in the region of 1.1-1.3 ppm that we ascribe to the *tert*-butyl groups of the diamide. All <sup>1</sup>H spectra also show multiplets at approximately 7 ppm

Table 1

Crystallographic data for  $[{}^tBuN-B^{Ph}-N{}^tBu]TiCl_2$  (2) and  $[{}^tBuN-B^{Ph}-N{}^tBu]TiBn_2$  (3)

	2	3
Formula	C14H23BCl2N2Ti	C <sub>28</sub> H <sub>37</sub> BN <sub>2</sub> Ti
Formula weight	348.95	460.31
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.895(2)	10.3234(8)
b (Å)	6.3282(10)	23.1906(19)
c (Å)	20.922(3)	11.7952(10)
α (°)	90	90
β(°)	98.471(2)	113.054(1)
γ (°)	90	90
V (Å <sup>3</sup> )	1688.6(5)	2598.3(4)
Ζ	4	4
Cryst. desc.	orange rod	orange block
$D_{\rm calc} ({\rm Mg}\;{\rm m}^{-3})$	1.373	1.177
Absorption coefficient $(mm^{-1})$	0.814	0.347
F(000)	728	984
$R_1$	0.0392	0.0362
$wR_2$	0.0965	0.0914
Goodness-of-fit	1.153	1.037

Table 2
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Selected bond	lengths (Å) and	l angles (°)	for [ <sup>t</sup> BuN-]	$B^{Ph}-N^{t}Bu]TiCl_{2}$
(2) and $\int^{t} BuN$	-B <sup>Ph</sup> -N <sup>t</sup> BulTiB	$n_2(3)$	-	

Compound 2			
Bond lengths			
Til-Cl1	2.5771(9)	Til-N1	1.852(2)
Til-Cl2	2.4482(9)	Til-N2	1.850(2)
Til-Cl1A <sup>a</sup>	2.4476(9)	N1-B1	1.471(4)
Til-Cl2A <sup>b</sup>	2.5565(8)	N2-B1	1.464(4)
Bond angles			
N1-Ti1-N2	80.67(10)	Cl1-Ti1-Cl1A	77.43(3)
N1-B1-N2	109.5(2)	Cl1-Ti1-Cl2A	81.45(3)
Til-N1-B1	84.80(17)	Cl2-Ti1-Cl1A	163.71(3)
Ti1-N2-B1	85.05(16)	Cl2-Ti1-Cl2A	77.92(3)
Cl1-Ti1-Cl2	90.67(3)	Cl1A-Ti1-Cl2A	89.21(3)
Compound 3			
Bond lengths			
Til-N1	1.8529(18)	Til-C23	2.458(2)
Til-N2	1.8578(17)	N1-B1	1.467(3)
Til-C15	2.155(2)	N2-B1	1.455(3)
Til-C22	2.158(2)		
Bond angles			
N1-Ti1-N2	79.97(8)	Ti1-C15-C16	115.38(14)
N1-B1-N2	109.34(19)	Ti1-C22-C23	83.47(14)
Ti1-N1-B1	85.22(13)	C15-Ti1-C22	127.91(9)
Til-N2-B1	85.36(13)		

Symmetry transformations used to generate equivalent atoms: a - x+1, -y, -z+1; b-x+1, -y+1, -z+1.



Scheme 1. (a) Toluene, frozen; (b) TMSCl hexanes; (c) BnMgCl, toluene, frozen.

corresponding to the phenyl protons, although this signal overlaps with that of benzene, thereby hindering any meaningful analysis of coupling to the other aryl protons and to boron . Sharp singlet resonances for the



Fig. 1. Solid state structure of  $\{\{^{t}BuN-B^{Ph}-N^{t}Bu\}$  (2), with thermal ellipsoids shown at the 50% probability level.

dimethylamido protons of **1** and the methylene protons of the benzyl group of **3** appear at 3.19 and 2.149 ppm, respectively. The <sup>11</sup>B NMR spectra of 1-3 show a single resonance in the region of 29.9–30.6 ppm.

Single-crystal X-ray structure analysis of 2 establishes that the dichloride compound is a polymer in the solid state (Fig. 1). Polymeric chains are propagated by chlorine atoms, which bridge adjacent [<sup>t</sup>BuN-B<sup>Ph</sup>-N<sup>t</sup>Bu]Ti subunits. The chelating diamide and four chlorines define a pseudo-octahedral geometry about the titanium. The coordination geometry resulting from  $^{t}BuN-B^{Ph}-N^{t}Bu$  chelation in 2 is characterized by an N-B-N angle of  $109.5(2)^{\circ}$  and a bite angle of 80.67(10)°. The N-B distances of 1.464(4) and 1.471(4) Å for 2 are similar to that of borazine, indicating significant double bond character [40]. This distance is consistent with that observed by Schrock for terminal borylamido complexes of Group 4 metals [26,27]. A trans-influence of the diamido ligand is demonstrated by the Ti-Cl bond lengths, which are approximately 0.1 Å longer when trans to a diamido nitrogen as opposed to those trans to another chlorine. Comparison of the trans-influence observed here with other amido ligands is precluded by a dearth of structurally similar complexes. The tert-butyl groups on the amide are directed away from the metal center as indicated by Ti-N-C angles of 147.12(18) and 146.68(19) $^{\circ}$ . The reduced steric congestion at Ti, resulting from the retracted tert-butyl groups, is manifested in the catenation of  $[{}^{t}BuN-B^{Ph}-$ 

 $N^{t}Bu]Ti$  subunits; hence the polymer chains of Fig. 1 are formed. A structural benchmark for **2** is provided by  $Ti[Me_2Si(^{t}BuN)_2]Cl_2$  in which the replacement of the BPh bridgehead of **2** by a SiMe<sub>2</sub> group gives rise to a more acute Ti-N-C angle of 136.1(5)° [41]. Interestingly, this bis(amido)silane compound is a monomer in the solid state.



Fig. 2. Solid state structure of  $[^{1}BuN-B^{Ph}-N^{t}Bu]TiBn_{2}$  (3) with thermal ellipsoids shown at the 50% probability level.

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A monomeric complex is formed when the chlorides of 2 are replaced with more bulky benzyl groups. Dibenzyl complex 3 exhibits the pseudo-tetrahedral coordination geometry shown in Fig. 2. The <sup>t</sup>BuN-B<sup>Ph</sup>-N<sup>t</sup>Bu ligand metrics are similar to those observed for 2. The notable aspect of this structure is the significant distortion of one of the benzyl ligands. The Ti- $C_{ipso}$  distance is 2.458(2) Å and a Ti- $C-C_{ipso}$  angle of  $83.47(14)^{\circ}$  is among the smallest observed for a titanium benzyl complex  $(81.9^{\circ} < \angle (Ti-C-C_{ipso}) <$  $139^{\circ}$  [42,43]). As a comparison, these metrical parameters surpass those observed for the largest distortion in TiBn<sub>4</sub> ( $\angle$ (Ti-C-C<sub>*ipso*</sub>) = 88(2)°, d(Ti-C<sub>*ipso*</sub>) = 2.61(3) Å) [44]. The Ti-C-C<sub>ipso</sub> small angle of 3 indicates a pronounced interaction between the titanium center and the  $\pi$ -system of the benzyl group, consistent with the ability of the boron bridgehead to mitigate the electron-donating ability of the amides. This distortion is consistent with a benzallylic interaction [45,46], which is confirmed by short Ti-C(24) and Ti-C(28) distances of 3.058(6) and 3.021(5) Å, respectively.

Preliminary studies have been undertaken to assess 3 as a precursor for Ziegler-Natta polymerization. Activation of **3** with  $[Ph_3C][B(C_6F_5)_4]$  followed by the addition of 200 equiv. of 1-hexene at room temperature and below showed no formation of poly(1-hexene). The lack of polymerization activity observed is most likely due to the insertion of a single olefin into the titaniumbenzyl bond. Coordination of the aryl ring of the resulting propyl phenyl group has been observed to inhibit polymerization of other Group 4 benzyl cations [9,47,48]. The extreme electrophilicity of the titanium center engendered by the presence of the boron bridgehead may also contribute to the lack of reactivity. This contention is in accordance with the inability of Schrock's titanium bis(borylamido) cation to polymerize ethylene owing to strong association of the counterion [26]. These two possibilities may be distinguished by the preparation of dialkyl congeners of **3**.

#### 4. Supplementary material

Table of X-ray crystallographic data for complexes 2 and 3 including a fully labeled thermal ellipsoid plot, final atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, and bond distances and angles. The materials are available from the authors on request.

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