

# Synthesis and Structure of the First [1]Boratitanocenophanes

Holger Braunschweig,<sup>\*,[a]</sup> Carsten von Koblinski,<sup>[a]</sup> and Ruimin Wang<sup>[a]</sup>

**Keywords:** Boron / Titanium / Metallocenophanes / [1]Boratitanocenophanes

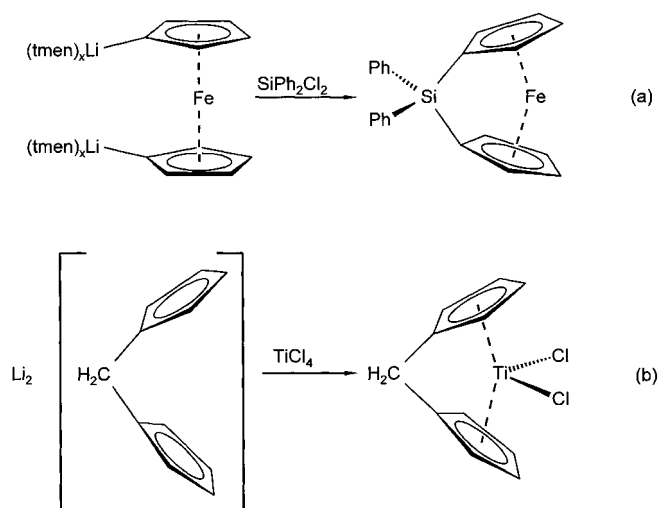
This paper presents two methods for the synthesis of the first [1]boratitanocenophanes. The novel bis(cyclopentadienyl)borane  $[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_5)_2]$ , the dilithio salt  $\text{Li}_2[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_4)_2]$  (**1**) of which was characterized by multinuclear NMR methods, was prepared in situ, and served as starting material for several [1]boratitanocenophanes.  $[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**) was obtained in high yield by a convenient one-pot synthesis starting from **1** and  $[\text{TiCl}_3(\text{thf})_3]$ , followed by oxidation with  $\text{PbCl}_2$ . The highly reactive  $[(\text{Me}_2\text{N})_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**3**) was obtained by the

reaction of  $[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_5)_2]$ , prepared in situ, with  $\text{Ti}(\text{NMe}_2)_4$  and converted into the chloro derivatives  $[(\text{Me}_2\text{N})\text{CITi}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**4**) and  $[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**) by treatment with one or two equivalents of a suitable diaminochloroborane. All [1]boratitanocenophanes were characterized in solution by multinuclear NMR spectroscopy, and in addition the structure of **2** in the crystalline state was determined by a single-crystal X-ray study.

## Introduction

[1]Metallocenophanes have been known for almost 30 years, and since then these compounds have attracted considerable interest due to their versatile chemistry. The first example of a [1]ferrocenophane was obtained by the reaction of dilithioferrocene-tmen (tmen = tetramethylethylenediamine) with  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$  (Equation 1a).<sup>[1]</sup> Due to the high ring strain of such complexes, which depends on the covalent radius of the bridging atom, [1]ferrocenophanes undergo thermal or radiation-induced ring-opening polymerization<sup>[2a,b]</sup> yielding high molecular weight polyferrocenes.<sup>[3a–d]</sup> Corresponding [1]metallocenophanes of early transition-metal complexes were obtained, for example, by the reaction of  $\text{Li}_2[\text{H}_2\text{C}(\text{C}_5\text{H}_4)_2]$  with  $\text{TiCl}_4$  (Equation 1b).<sup>[4]</sup> Such metallocenophanes especially of titanium and zirconium have already proven to be highly active Ziegler–Natta-type catalysts for the olefin polymerization.<sup>[5]</sup>

We have started to investigate the synthesis and properties of [1]borametallocenophanes, since we expect a particularly interesting reactivity of such compounds. On one hand, the incorporation of the small boron atom into the bridge of a [1]ferrocenophane leads to highly strained, and thus very reactive molecules. That was already demonstrated in the case of  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$ , which exhibits the highest tilt angle of  $32.4(2)^\circ$  recorded for a [1]ferrocenophane to date.<sup>[6]</sup> On the other hand catalytic processes with metallocenophanes of early transition metals could be accelerated by a Lewis acidic atom such as boron in the bridge. Very recently, the first [1]borazirconocenophane was synthesized and structurally characterized.<sup>[7]</sup> This compound, however, exhibits  $\text{SMe}_2$  as a boron-coordinated base, thus cancelling the Lewis acidity of the bridging boron atom. A [1]borazirconocenophane with a three-fold



coordinated boron atom was reported in 1996,<sup>[8]</sup> the structure of this product in the crystal, however, is not known.

Dilithiometallocenes, which serve as starting materials for the synthesis of [1]metallocenophanes according to Equation 1a, are only available in the case of iron and ruthenium. In order to achieve a method for the preparation of various [1]borametallocenophanes we aimed at the synthesis of bis(cyclopentadienyl)boranes as versatile ligands. In contrast to the well-developed chemistry of cyclopentadienylboranes<sup>[9a–f]</sup> the knowledge of bis(cyclopentadienyl)boranes is restricted to a few examples of the type  $(\text{C}_5\text{H}_4\text{R})_2\text{BPh}$  ( $\text{R} = \text{SiMe}_3, \text{SnMe}_3$ ).<sup>[8][10]</sup> Due to decomposition during distillation these products could not be isolated in pure form. Related compounds, however, with four-coordinate boron atoms include the lithium borate  $\text{Li}(\text{OEt})_4[(\text{C}_5\text{H}_5)_2\text{B}(\text{C}_6\text{F}_5)_2]$ <sup>[11]</sup> and the borane–pyridine adduct  $(\text{C}_5\text{H}_5)_2\text{PhBNC}_5\text{H}_5$ .<sup>[12]</sup>

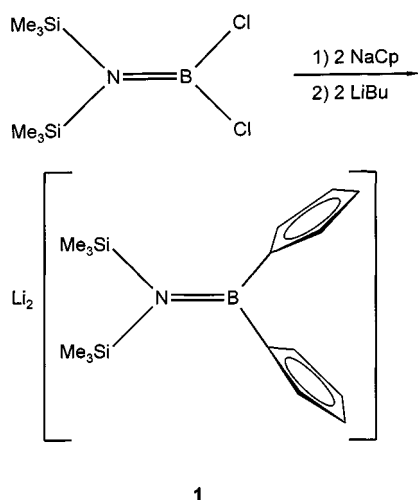
In the present paper we report the high-yield synthesis and spectroscopic characterization of the dilithiated bis(cyclopentadienyl)borane  $\text{Li}_2[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_4)_2]$  and its re-

<sup>[a]</sup> Institut für Anorganische Chemie der Technischen Hochschule, Templergraben 55, D-52056 Aachen, Germany  
E-mail: holger.braunschweig@ac.rwth-aachen.de

action with  $[\text{TiCl}_3(\text{thf})_3]$  giving the first [1]boratitanocenophane. An alternative route for the synthesis of such compounds starting from  $[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_5)_2]$  is also described.

## Results and Discussion

The reaction of  $(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_5)_2$  with a slight excess of  $\text{NaC}_5\text{H}_5$  in hexane followed by filtration and treatment of the hexane filtrate with 2 equivalents of  $\text{LiBu}$  afforded  $\text{Li}_2[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_4)_2]$  (**1**) in almost quantitative yield as a white pyrophoric solid (Equation 2).

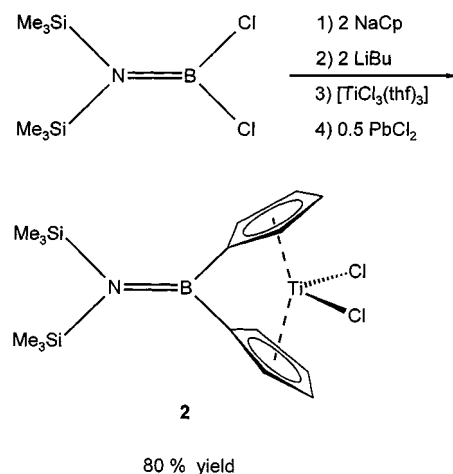


The structure of **1** in solution derives from the NMR spectra showing the expected signal patterns for the mono-substituted cyclopentadienyl rings and an  $^{11}\text{B}$ -NMR signal at  $\delta = 46.6$ , characteristic for an aminodiarylborane. This compound proved to be highly reactive and shows considerable signs of decomposition in  $\text{thf}$  solution, and even in the solid state at ambient temperature. Hence, for subsequent syntheses we found it convenient not to store the ligand, but rather to prepare it in situ.

According to Equation 3, the [1]boratitanocenophane  $[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**) was obtained in a four-step one-pot synthesis. The dilithio salt **1**, which was obtained as a hexane slurry by the method described above, was treated with an equimolar amount of  $[\text{TiCl}_3(\text{thf})_3]$  at  $-100^\circ\text{C}$  and the intermediate  $\text{Ti}^{\text{III}}$  species was subsequently oxidized with  $\text{PbCl}_2$  according to a known procedure.<sup>[13]</sup>

Complex **2** was obtained as dark red crystals from  $\text{CH}_2\text{Cl}_2$  in 80% yield. The compound was found to be very soluble in halogenated solvents, such as  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ , and less soluble in aromatic solvents such as benzene or mesitylene. Solutions of **2** are very sensitive to air and moisture, and an instant colour change from dark red to light green indicates decomposition.

The constitution of **2** in solution is deduced from NMR spectra. The  $^1\text{H}$ -NMR spectra show the expected two pseudo triplets at  $\delta = 5.53$ , and 7.05 for the cyclopentadienyl protons forming an  $\text{AA}'\text{BB}'$  spin system, and the



$^{11}\text{B}$ -NMR signal at  $\delta = 46.6$  matches that of the uncoordinated ligand.

Suitable single crystals for an X-ray structure analysis were obtained by recrystallization from benzene at  $7^\circ\text{C}$  (Figure 1). In the solid state the molecule exhibits a slight deviation from the ideal  $C_{2v}$  symmetry, which is assumed for its structure in solution. This is demonstrated, for example, by the twisting of the  $\text{Si1}-\text{N}-\text{Si2}$  plane with respect to the  $\text{Cp}_1-\text{Ti}-\text{Cp}_2$  ( $\text{Cp}_c$  = ring centroid) plane; the corresponding dihedral angle was determined to be  $11.5^\circ$ . The comparison of the present structure with that of  $[\text{Cp}_2\text{TiCl}_2]$  shows some characteristic differences, due to the albeit small strain of **2**.<sup>[14]</sup> The tilt angle between the two cyclopentadienyl rings as well as the  $\text{Cl1}-\text{Ti}-\text{Cl2}$  angle is larger by about  $3^\circ$ , while the  $\text{Cp}_1-\text{Ti}-\text{Cp}_2$  angle decreases by almost  $13^\circ$  with respect to the corresponding values found for  $[\text{Cp}_2\text{TiCl}_2]$ . While the cyclopentadienyl rings are staggered in the latter molecule, they adopt an eclipsed conformation in the present case. The boron–nitrogen distance was found to be 138(1) pm, thus being in the expected range for a B–N double bond.

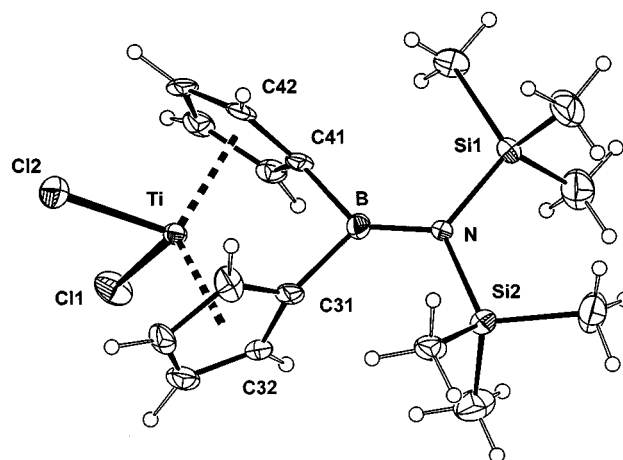
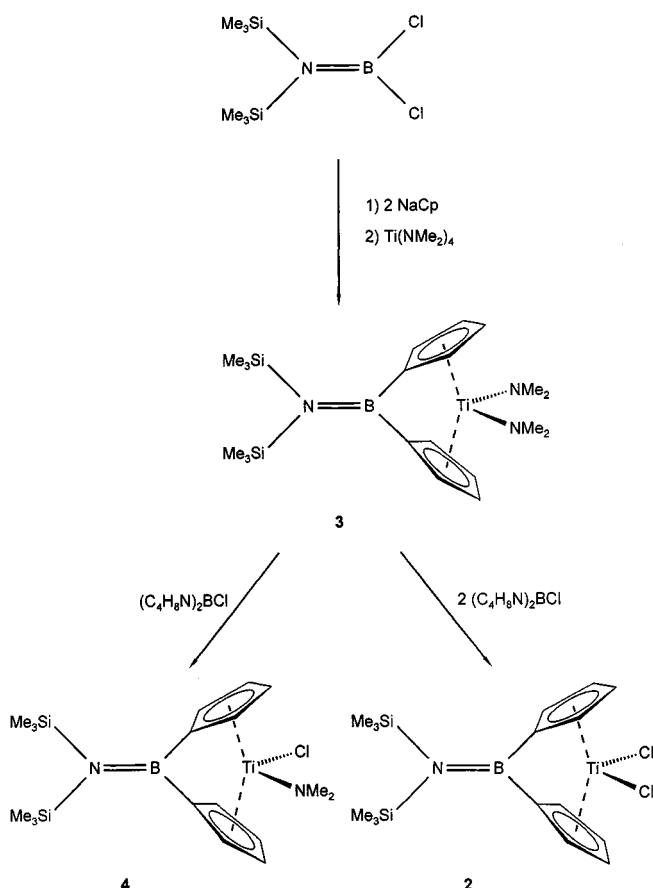


Figure 1. Structure of **2** in the crystal (ellipsoids at 30% probability); selected distances [pm] and angles  $^\circ$ :  $\text{Ti}-\text{Cl1}$  233.1(2),  $\text{Ti}-\text{Cl2}$  233.9(2),  $\text{B}-\text{N}$  138(1);  $\text{Cl1}-\text{Ti}-\text{Cl2}$  97.45(9),  $\text{C31}-\text{B}-\text{C41}$  98.3(6),  $\text{C41}-\text{B}-\text{N}$  132.8(6),  $\text{C31}-\text{B}-\text{N}$  128.6(6)

All attempts to obtain **2** directly from  $\text{Li}_2[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_4)_2]$  (**1**) and  $\text{TiCl}_4$  or  $[\text{TiCl}_4(\text{thf})_2]$  resulted in mixtures of several products, which could not be separated.

The reaction of  $[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_5)_2]$  prepared in situ with  $\text{Ti}(\text{NMe}_2)_4$ , however, proved to be a suitable method for the direct preparation of a corresponding  $\text{Ti}^{\text{IV}}$  species.  $[(\text{Me}_2\text{N})_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**3**) was obtained as a dark red solid in yields of about 30% with formation of two equivalents of  $\text{HNMe}_2$  (Equation 4). Due to the labile  $\text{NMe}_2$  ligands **3** shows an even greater tendency to decompose compared to  $[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**), and hence, cannot be stored at ambient temperature even in the solid state.



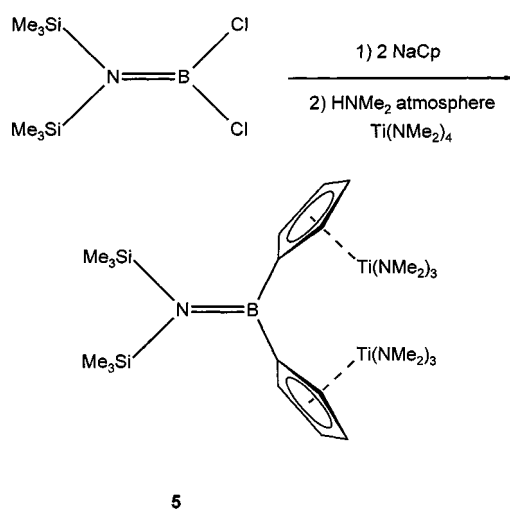
By treating this compound in situ with one or two equivalents of a chloroborane of moderate reactivity such as  $(\text{C}_4\text{H}_8\text{N})_2\text{BCl}$ , however, it may be converted into the more stable chloro derivatives  $[(\text{Me}_2\text{N})\text{ClTi}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**4**) and  $[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**), respectively (Equation 3), which were isolated in yields of about 40% and 15%.

These reactions occurred with substitution of the titanium-bound  $\text{NMe}_2$  groups and formation of the corresponding triaminoborane  $(\text{C}_4\text{H}_8\text{N})_2\text{BNMe}_2$ , which was characterized by  $^{11}\text{B}$ -NMR spectroscopy from the reaction mixture ( $\delta = 26.0$ ). The use of diaminochloroboranes proved to be crucial for this synthesis, since the more reactive aminodichloroboranes always led to decomposition of **3**.

Due to its lower symmetry,  $[(\text{Me}_2\text{N})\text{ClTi}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**4**) shows four signals for the cyclopentadienyl

groups in the  $^1\text{H}$ -NMR spectra at  $\delta = 5.08, 5.29, 6.62$ , and  $6.83$ . Furthermore, the spectroscopic findings for **3** and **4**, such as the  $^{11}\text{B}$ -NMR signals at  $\delta = 46.9$ , and  $46.4$ , are comparable to those of **2**, thus proving their structure in solution.

The instability of **3** is obviously due to the cleavage of the  $\text{NMe}_2$  ligands, and hence we attempted to synthesize this compound under an atmosphere of  $\text{HNMe}_2$ . The reaction of  $\text{Ti}(\text{NMe}_2)_4$  with one equivalent of  $[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_5)_2]$  under a constant flow of dimethylamine, however, resulted in the formation of the dinuclear half sandwich complex **5** (Equation 5), which was isolated in yields of about 45% as a red brown solid. The structure of **5** in solution was deduced from the NMR spectra, resembling those of the related chloro derivative  $[(\text{Cl}_3\text{Ti})_2\{(\text{C}_5\text{H}_4)_2\text{BPh}\}]$ , which was also characterized in the crystalline state.<sup>[10]</sup>



## Conclusion

The synthesis and characterization of the first [1]boratitanocenophanes was achieved by two different methods starting from the novel bis(cyclopentadienyl)borane  $[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_5)_2]$ .

The highly reactive bis(dimethylamido) complex  $[(\text{Me}_2\text{N})_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**3**) was achieved directly from the reaction of this ligand with  $\text{Ti}(\text{NMe}_2)_4$ , whereas the corresponding dichloro derivative  $[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**) was obtained by a convenient one-pot synthesis in high yield starting from the dilithiated ligand  $\text{Li}_2[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_4)_2]$  (**1**), and  $[\text{TiCl}_3(\text{thf})_3]$  followed by oxidation of the intermediate  $\text{Ti}^{\text{III}}$  species with  $\text{PbCl}_2$ . The latter complex was chosen as a representative example for X-ray structure analysis. Compound **3** served as starting material for the preparation of  $[(\text{Me}_2\text{N})\text{ClTi}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**4**) and  $[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**) by substitution of the  $\text{NMe}_2$  group with a suitable diaminochloroborane.

[1]Metalocenophanes of group-4 elements containing a Lewis acidic atom such as boron in the bridge should serve

as effective catalysts for Ziegler–Natta-type olefin polymerizations. Our further work will focus on the utilization of the convenient synthetic method being described in this paper and especially on the investigation of the catalytic properties of such compounds. Preliminary experiments already proved **2** and **4** to be suitable catalysts for the polymerization of ethene.

## Experimental Section

All manipulations were carried out under dry nitrogen with common Schlenk techniques. Solvents and reagents were dried by standard procedures, distilled, and stored under nitrogen over molecular sieves.  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$ ,<sup>[15]</sup>  $\text{NaC}_5\text{H}_5$ ,<sup>[16]</sup>  $\text{Ti}(\text{NMe}_2)_4$ ,<sup>[17]</sup>  $[\text{TiCl}_3(\text{thf})_3]$ ,<sup>[18]</sup> and  $(\text{C}_4\text{H}_8\text{N})_2\text{BCl}$ <sup>[19]</sup> were synthesized according to literature procedures. NMR: Varian Unity 500 at 499.843 MHz ( $^1\text{H}$ , internal standard TMS), 150.364 MHz ( $^{13}\text{C}$ ,  $\text{BF}_3 \cdot \text{OEt}_2$  in  $\text{C}_6\text{D}_6$  as external standard), 125.639 MHz ( $^{13}\text{C}\{^1\text{H}\}$ , APT, internal standard TMS); all NMR spectra were recorded in  $\text{CD}_2\text{Cl}_2$  as solvent unless otherwise stated. Mass spectra were recorded with a Finnigan MAT 95 (70 eV) and elemental analyses (C, H, N) were obtained from a Carlo-Erba elemental analyzer, model 1106.

**$\text{Li}_2[(\text{Me}_3\text{Si})_2\text{NB}(\text{C}_5\text{H}_4)_2]$  (**1**):** 8.23 g (93.54 mmol)  $\text{NaC}_5\text{H}_5$  was suspended in 100 mL of hexane and a solution of 11.13 g (46.05 mmol) of  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$  in 20 mL of hexane was added dropwise at ambient temperature. After stirring for 2 h, the reaction mixture was cooled to  $0^\circ\text{C}$  and 57.6 mL (92.10 mmol) of a 1.6 M BuLi solution was added dropwise. A white precipitate formed immediately. The reaction mixture was allowed to warm up to ambient temperature and after stirring for 1 h, all volatiles were removed in high vacuum, and the solid residue was extracted with 150 mL of hexane overnight. The mixture was filtered and the solid dried in vacuo to give **1** as a white, pyrophoric solid in yields of 98% (14.13 g). –  $^1\text{H}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta$  = 0.01 [s, 18 H,  $\text{Si}(\text{CH}_3)_3$ ], 5.83 (m, 4 H,  $\text{C}_5\text{H}_4$ ), 6.45 (m, 4 H,  $\text{C}_5\text{H}_4$ ). –  $^{11}\text{B}$  NMR:  $\delta$  = 46.6 (s). –  $^{13}\text{C}$  NMR:  $\delta$  = 4.31 [s,  $\text{Si}(\text{CH}_3)_3$ ], 103.16, 106.63, 116.63 ( $\text{C}_5\text{H}_4$ ).

**$[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**) (Method A):** As described for **1** 3.20 g (13.24 mmol) of  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$  was treated with 2.39 g (27.17 mmol) of  $\text{NaC}_5\text{H}_5$  and to the obtained filtrate was added 16.6 mL (26.48 mmol) of 1.6 M BuLi in hexane. The light yellow suspension was stirred at ambient temperature for 2 h, cooled to  $-100^\circ\text{C}$ , and 4.90 g (13.24 mmol) of  $[\text{TiCl}_3(\text{thf})_3]$  and 20 mL of thf were added. The mixture was allowed to come to ambient temperature, and the colour changed from light brown to dark violet. The suspension was stirred for 3 h and then treated with 1.84 g (6.62 mmol) of  $\text{PbCl}_2$ . After stirring for 16 h, all volatile materials were removed in high vacuum. The remaining solid was extracted with 50 mL of  $\text{CH}_2\text{Cl}_2$  and filtered. **2** was recovered from the filtrate at  $-30^\circ\text{C}$  as a dark red solid (4.43 g, 80%). –  $^1\text{H}$  NMR:  $\delta$  = 0.08 [s, 18 H,  $\text{Si}(\text{CH}_3)_3$ ], 5.53 (m, 4 H,  $\text{C}_5\text{H}_4$ ), 7.05 (m, 4 H,  $\text{C}_5\text{H}_4$ ). –  $^{11}\text{B}$  NMR:  $\delta$  = 46.6 (s). –  $^{13}\text{C}$  NMR:  $\delta$  = 4.89 [ $\text{Si}(\text{CH}_3)_3$ ], 114.85, 133.44 ( $\text{C}_5\text{H}_4$ ). – MS;  $m/z$  (%): 417 (35) [ $\text{M}^+$ ], 402 (15) [ $\text{M}^+ - \text{Me}$ ], 382 (25) [ $\text{M}^+ - \text{Cl}$ ]. –  $\text{C}_{16}\text{H}_{26}\text{BCl}_2\text{NSi}_2\text{Ti}$  (418.18): calcd. C 45.96, H 6.27, N 3.35; found C 46.56, H 7.05, N 2.87.

**$[(\text{Me}_2\text{N})_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**3**):** As described for **1** 2.08 g (8.60 mmol) of  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$  was treated with 1.51 g (17.20 mmol) of  $\text{NaC}_5\text{H}_5$ . The obtained filtrate was cooled to  $-30^\circ\text{C}$ , and a solution of 1.93 g (8.60 mmol) of  $\text{Ti}(\text{NMe}_2)_4$  in 5 mL of hexane was added dropwise. The mixture was allowed to warm up to ambient temperature, and the colour changed from yellow to dark red. After stirring for 1 h, all volatiles were removed in high vacuum,

and the remaining solid was suspended in 10 mL of hexane. After filtration and removal of all volatiles under high vacuum, compound **3** was obtained as a dark red solid (1.05 g, 28%). –  $^1\text{H}$  NMR:  $\delta$  = 0.09 (s, 18 H,  $\text{Si}(\text{CH}_3)_3$ ), 3.14 (s, 12 H,  $\text{N}(\text{CH}_3)_2$ ), 5.42 (m, 4 H,  $\text{C}_5\text{H}_4$ ), 6.73 (m, 4 H,  $\text{C}_5\text{H}_4$ ). –  $^{11}\text{B}$  NMR:  $\delta$  = 46.9 (s). –  $^{13}\text{C}$  NMR:  $\delta$  = 4.89 [ $\text{Si}(\text{CH}_3)_3$ ], 51.11 [ $\text{N}(\text{CH}_3)_2$ ], 112.73, 131.66 ( $\text{C}_5\text{H}_4$ ). –  $\text{C}_{20}\text{H}_{38}\text{BN}_3\text{Si}_2\text{Ti}$  (435.43): calcd. C 55.17, H 8.80, N 9.65; found C 55.62, H 8.22, N 9.59.

**$[(\text{Me}_2\text{N})\text{CITi}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**4**):** As described for **1** 1.09 g (4.50 mmol) of  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$  was treated with 0.88 g (10.00 mmol) of  $\text{NaC}_5\text{H}_5$ . The obtained filtrate was cooled to  $-30^\circ\text{C}$ , and a solution of 1.01 g (4.50 mmol) of  $\text{Ti}(\text{NMe}_2)_4$  in 5 mL of hexane was added dropwise. The mixture was allowed to warm up to ambient temperature, and treated with 0.84 g (4.50 mmol) of  $(\text{C}_4\text{H}_8\text{N})_2\text{BCl}$ . After stirring for 1 h, all volatiles were removed in high vacuum, and the remaining solid was suspended in 20 mL of hexane, filtered and stored at  $-30^\circ\text{C}$  to yield 0.79 g (41%) of compound **4** as a dark red crystalline solid. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.28 (s, 18 H,  $\text{Si}(\text{CH}_3)_3$ ), 3.26 (s, 6 H,  $\text{N}(\text{CH}_3)_2$ ), 5.08 (m, 2 H,  $\text{C}_5\text{H}_4$ ), 5.29 (m, 2 H,  $\text{C}_5\text{H}_4$ ), 6.62 (m, 2 H,  $\text{C}_5\text{H}_4$ ), 6.83 (m, 2 H,  $\text{C}_5\text{H}_4$ ). –  $^{11}\text{B}$  NMR:  $\delta$  = 46.4 (s). –  $^{13}\text{C}$  NMR:  $\delta$  = 7.53 [ $\text{Si}(\text{CH}_3)_3$ ], 57.54 [ $\text{N}(\text{CH}_3)_2$ ], 115.73, 117.57, 126.93, 128.54 ( $\text{C}_5\text{H}_4$ ). –  $\text{C}_{18}\text{H}_{32}\text{BClN}_2\text{Si}_2\text{Ti}$  (426.80): calcd. C 50.66, H 7.56, N 6.56; found C 50.23, H 7.59, N 6.39.

**$[\text{Cl}_2\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**2**) (Method B):** As described for **4** 1.45 g (6.00 mmol) of  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$  was treated with 1.08 g (12.30 mmol) of  $\text{NaC}_5\text{H}_5$ , and to the obtained filtrate was added a solution of 1.34 g (6.00 mmol) of  $\text{Ti}(\text{NMe}_2)_4$  in 5 mL of hexane. The resulting mixture was subsequently treated with 2.24 g (12.00 mmol) of  $(\text{C}_4\text{H}_8\text{N})_2\text{BCl}$  to yield 0.38 g (15%) of **2** as a dark red crystalline solid.

**$[(\text{Me}_2\text{N})_3\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{BN}(\text{SiMe}_3)_2\}]$  (**5**):** As described for **1** 1.31 g (5.40 mmol) of  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$  was treated with 0.97 g (11.00 mmol) of  $\text{NaC}_5\text{H}_5$ . The obtained filtrate was cooled to  $-30^\circ\text{C}$ , and a solution of 1.21 g (5.40 mmol) of  $\text{Ti}(\text{NMe}_2)_4$  in 5 mL of hexane was added dropwise under a constant stream of  $\text{HNMe}_2$ . After warming up to ambient temperature, the dark red solution was stirred for 1 h and then stored under an atmosphere of  $\text{HNMe}_2$  at  $-30^\circ\text{C}$ . After 3 d, compound **5** was isolated as a red brown solid (1.60 g, 45%). –  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.28 [s, 18 H,  $\text{Si}(\text{CH}_3)_3$ ], 3.18 [s, 36 H,  $\text{N}(\text{CH}_3)_2$ ], 6.14 (m, 4 H,  $\text{C}_5\text{H}_4$ ), 6.78 (m, 4 H,  $\text{C}_5\text{H}_4$ ). –  $^{11}\text{B}$  NMR:  $\delta$  = 46.9 (s). –  $^{13}\text{C}$  NMR:  $\delta$  = 5.79 [ $\text{Si}(\text{CH}_3)_3$ ], 50.35 [ $\text{N}(\text{CH}_3)_2$ ], 113.03, 121.65 ( $\text{C}_5\text{H}_4$ ). – MS:  $m/z$  (%) = 615 (5) [ $\text{M}^+ - \text{N}(\text{CH}_3)_2$ ], 571 (50) [ $\text{M}^+ - 2 \text{N}(\text{CH}_3)_2$ ], 527 (50) [ $\text{M}^+ - 3 \text{N}(\text{CH}_3)_2$ ], 347 (100) [ $\{(\text{CH}_3)_3\text{Si}_2\text{NBCp}_2\text{Ti}\}$ ]. –  $\text{C}_{28}\text{H}_{62}\text{BN}_7\text{Si}_2\text{Ti}_2$  (659.64): calcd. C 50.98, H 9.47, N 14.86; found C 50.56, H 9.36, N 14.77.

**X-ray Structure Determination of **2**:**  $\text{C}_{16}\text{H}_{26}\text{BCl}_2\text{NSi}_2\text{Ti}$ , ENRAF-Nonius CAD4; Mo- $K_\alpha$  radiation ( $\lambda$  = 0.71073 Å, graphite monochromator); data collection with  $\omega$  scan at 203 K. Dark red platelet,  $0.06 \times 0.24 \times 0.65$  mm, monoclinic space group  $C2/c$  (No. 15),  $M$  = 418.18 g mol $^{-1}$ , unit cell dimensions  $a$  = 28.493(8) Å,  $b$  = 10.540(4) Å,  $c$  = 15.103(5) Å,  $\beta$  = 112.71(3)°,  $V$  = 4184(5) Å $^3$ ,  $Z$  = 8,  $\rho_{\text{calcd.}}$  = 1.33 g cm $^{-3}$ ,  $\mu(\text{Mo-}K_\alpha)$  = 7.73 cm $^{-1}$ ; 5040 reflections were collected in the scan range  $2^\circ < \Theta < 25^\circ$ ; after Lorentz and polarization corrections, an empirical absorption correction based on azimuthal scans<sup>[20]</sup> (min. trans. 0.766, max. trans. 1.000) was applied before averaging symmetry-related intensity data. Since the crystal was not stable, intensity data were corrected for the resulting decay on the basis of three regularly measured check reflections. 2510 independent observations with  $I > \sigma(I)$  in structure solution by direct methods<sup>[21]</sup> and refinement with the



SDP program system<sup>[22]</sup> for 208 variables; all non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were included in riding geometry with fixed isotropic displacement parameters [ $C-H = 0.98 \text{ \AA}$ ,  $U_{iso}(H) = 1.30 U_{eq}(C)$ ]. Convergence at  $R = 0.092$ ,  $R_w = 0.076$ ,  $w^{-1} = \sigma^2(F_o)$ , GOF = 1.324. Max. residual electron density  $0.722 \text{ e \AA}^{-3}$ . Further details on the crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk) on quoting the depository number CCDC-102132.

## Acknowledgments

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

- [1] A. G. Osborne, R. H. Whiteley, *J. Organomet. Chem.* **1975**, *101*, C27–C28.
- [2] [2a] D. Foucher, R. Ziembinski, R. Petersen, J. Pudelski, M. Edwards, Y. Ni, J. Massey, C. R. Jaeger, G. J. Vancso, I. Manners, *Macromolecules* **1994**, *27*, 3992–3999. – [2b] J. Rasburn, D. A. Foucher, W. F. Reynolds, I. Manners, G. J. Vancso, *J. Chem. Soc., Chem. Commun.* **1998**, 843–844.
- [3] [3a] W. Finckh, B.-Z. Tang, D. A. Foucher, D. B. Zamble, R. Ziembinski, A. Lough, I. Manners, *Organometallics* **1993**, *12*, 823–829. – [3b] P. Gomez-Elipse, P. M. MacDonald, I. Manners, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 762–764. – [3c] K. H. Pannell, H. K. Sharma, *Organometallics* **1997**, *16*, 3077–3079. – [3d] T. J. Peckham, J. A. Massey, M. Edwards, I. Manners, D. Foucher, *Macromolecules* **1996**, *29*, 2396–2403.
- [4] T. J. Katz, N. Acton, *Tetrahedron* **1970**, *28*, 2497–2499.
- [5] W. Kaminski, *J. Chem. Soc., Dalton Trans.* **1998**, 1413–1418 and references herein.
- [6] H. Braunschweig, R. Dirk, M. Müller, P. Nguyen, R. Resendes, D. P. Gates, I. Manners, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2338–2340.
- [7] D. S. Stelck, P. J. Shapiro, N. Basickes, *Organometallics* **1997**, *16*, 4546–4550.
- [8] K. Rufanov, E. Avtomonov, N. Kazennova, V. Kotov, A. Khvorost, D. Lemenovskii, J. Lorberth, *J. Organomet. Chem.* **1997**, *536–537*, 361–373.
- [9] [9a] G. E. Herberich, A. Fischer, *Organometallics* **1996**, *15*, 58–67. – [9b] H. Grundke, P. I. Paetzold, *Chem. Ber.* **1971**, *104*, 1136–1146. – [9c] H. D. Johnson, T. W. Hartford, C. W. Spangler, *J. Chem. Soc., Chem. Commun.* **1978**, 242. – [9d] B. Boeke, Doctoral Dissertation, Technische Hochschule Aachen, Germany, **1975**. – [9e] B. M. Mikhailov, T. K. Baryshnikova, V. S. Bogdanov, *Dokl. Akad. Nauk SSSR* **1972**, *202*, 358; *Chem. Abstr.* **1972**, *76*, 140940. [9f] P. Jutzi, A. Seufert, *J. Organomet. Chem.* **1979**, *169*, 327.
- [10] S. A. Larkin, J. T. Golden, P. J. Shapiro, G. P. A. Yap, D. M. J. Foo, A. L. Rheingold, *Organometallics* **1996**, *15*, 2393–2398.
- [11] M. Bochmann, S. J. Lancaster, O. B. Robinson, *J. Chem. Soc., Chem. Commun.* **1995**, 2081.
- [12] K. A. Rufanov, V. V. Kotov, N. B. Kazennova, D. A. Lemenovskii, E. V. Avtomonov, J. Lorberth, *J. Organomet. Chem.* **1996**, *525*, 287–289.
- [13] J. Okuda, T. Eberle, T. P. Spaniol, *Chem. Ber.* **1997**, *130*, 209–215.
- [14] A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal, *Can. J. Chem.* **1975**, *53*, 1622–1629.
- [15] P. Geymayer, E. G. Rochow, U. Wannegat, *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 633.
- [16] K. Ziegler, H. Froitzheim-Kühlhorn, K. Hafner, *Chem. Ber.* **1956**, *89*, 434.
- [17] D. C. Bradley, I. M. Thomas, *J. Chem. Soc.* **1960**, 3857–3861.
- [18] L. E. Manzer, *Inorg. Synth.* **1982**, *21*, 135.
- [19] D. Loderer, H. Nöth, H. Pommerening, W. Rattay, H. Schick, *Chem. Ber.* **1994**, *127*, 1605–1611.
- [20] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr.* **1968**, *A24*, 351.
- [21] G. M. Sheldrick, *SHELXS86, Program for Structure Solution*, University of Göttingen, Germany, **1986**.
- [22] ENRAF-Nonius, *SDP Version 3.0*, Delft, The Netherlands, **1989**.

Received July 10, 1998  
[198227]