

Derivatisation of boryl substituted titanium half-sandwich complexes – Molecular structures of $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4)\text{B}(\text{NiPr}_2)\text{N}(\text{H})t\text{Bu}\}\text{Cl}_2(\text{NMe}_2)]$ and $[\{\text{TiCl}_2(\mu\text{-}\{\text{OB}(\text{NHMe}_2)\text{-}\eta^5\text{-C}_5\text{H}_4\})\}_2\text{-}\mu\text{-O}]$

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Received 28 July 2005; received in revised form 4 October 2005; accepted 4 October 2005

Available online 14 November 2005

Abstract

The half-sandwich complex $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4)\text{B}(\text{NiPr}_2)\text{N}(\text{H})i\text{Pr}\}(\text{NMe}_2)_3]$ (**6**) was prepared from $(\eta^1\text{-C}_5\text{H}_5)\text{B}(\text{NiPr}_2)\text{N}(\text{H})i\text{Pr}$ (**5**) and $[\text{Ti}(\text{NMe}_2)_4]$ with cleavage of one equivalent of HNMe_2 and further converted into the corresponding constrained geometry complex $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4)\text{B}(\text{NiPr}_2)\text{N}i\text{Pr}\}(\text{NMe}_2)_2]$ (**7**) by elimination of a second equivalent of HNMe_2 . Reaction of the half-sandwich complexes $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4)\text{B}(\text{NiPr}_2)\text{N}(\text{H})\text{R}\}(\text{NMe}_2)_3]$ ($\text{R} = i\text{Pr}, t\text{Bu}$) with excess Me_3SiCl yielded the corresponding dichloro complexes $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4)\text{B}(\text{NiPr}_2)\text{N}(\text{H})\text{R}\}\text{Cl}_2(\text{NMe}_2)]$ ($\text{R} = t\text{Bu}$ (**10**), $i\text{Pr}$ (**11**)). The intermediate species $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4)\text{B}(\text{NiPr}_2)\text{N}(\text{H})i\text{Pr}\}\text{Cl}(\text{NMe}_2)_2]$ (**9**) could also be spectroscopically characterised. Partial hydrolysis of **10** and **11**, respectively, resulted in formation of $[\{\text{TiCl}_2(\mu\text{-}\{\text{OB}(\text{NHMe}_2)\text{-}\eta^5\text{-C}_5\text{H}_4\})\}_2\text{-}\mu\text{-O}]$ (**12**). The molecular structures of **10** and **12** have been determined by X-ray crystallographic analyses. Complex **10**, when activated with MAO, was found to be a highly active styrene polymerisation catalyst while being inactive towards the polymerisation of ethylene.

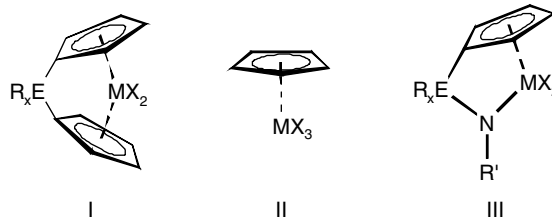
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Keywords: Boron; Constrained geometry complex; Half-sandwich complex; Linked cyclopentadienyl-amido ligand; Titanium

1. Introduction

Cyclopentadienyl complexes of Group 4 transition metals have received extensive research interest through their application as olefin polymerisation catalysts, usually in the presence of co-catalysts [1]. Metallocenes, especially *ansa*-metallocenes (**I**) with a bridging moiety between the two cyclopentadienyl fragments, are widely used for the polymerisation of ethylene and propylene [2]. Non-chelating half-sandwich complexes (**II**) bearing only one cyclopentadienyl moiety are commonly used for the polymerisation of styrene and its derivatives [3]. Complexes bearing linked cyclopentadienyl-amido ligands in a chelat-

ing fashion (**III**), often referred to as constrained geometry complexes (CGCs), facilitate the copolymerisation of ethylene with a number of other olefins, including ω -vinyl-macromonomers and styrene derivatives, giving access to unique polymer architectures [4].



In complexes of the type **I** and **III**, the identity of the bridging moiety is known to have a crucial effect on the

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steric and electronic situation and consequently on their reactivity [5,6]. Borane based bridging moieties were anticipated to be particularly advantageous for several reasons [7]: (i) the small size of the boron atom should result in an acute Cp(centroid)–M–Cp(centroid) resp. Cp(centroid)–M–N angle, a feature that was previously associated with high polymerisation activity, (ii) the small size of the boron atom should also positively affect the rigidity of the ligand and hence improve stereocontrol, e.g., in propylene polymerisation and (iii) the close proximity of the potentially Lewis-acidic boron centre and the catalytically active transition metal centre may improve the catalytic performance. Consequently, we and others reported on the synthesis and catalytic performance of various boron-bridged *ansa*-metallocenes [8–10] and CGCs [11].

The boron-bridged CGCs **1a–c** and **2** were prepared by reacting suitable ligand precursors of the type $(\eta^5\text{-C}_5\text{H}_5)\text{B}(\text{NR}_2)\text{N}(\text{H})\text{Ph}$, which incorporate a NHPh moiety, with $[\text{M}(\text{NMe}_2)_4]$ (M = Ti, Zr, Hf) with elimination of two equivalents of HNMe_2 [11]. On the other hand, reaction of the related ligand precursors $(\eta^5\text{-C}_5\text{H}_5)\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{R}$ (R = Cy, *t*Bu) bearing alkyl substituted NHR groups resulted only in the deprotonation of the cyclopentadienyl moiety and formation of the half-sandwich complexes

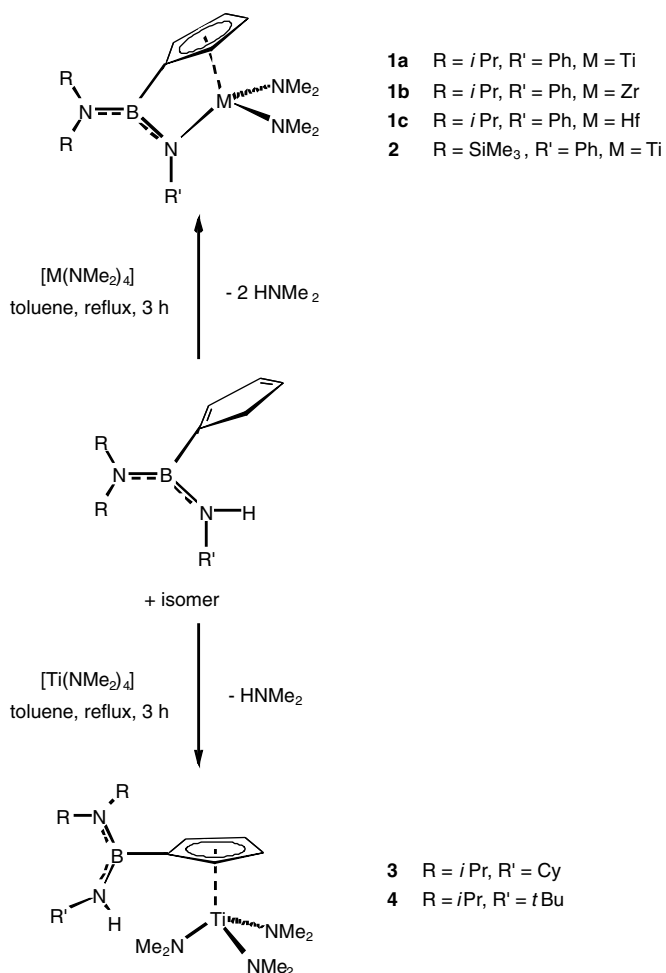
$[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4)\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{R}\}(\text{NMe}_2)_3]$ (R = Cy (**3**), *t*Bu (**4**)) (Scheme 1) [11b].

In the present paper, we report on further aspects of the chemistry of such half-sandwich complexes incorporating a pendent boryl group.

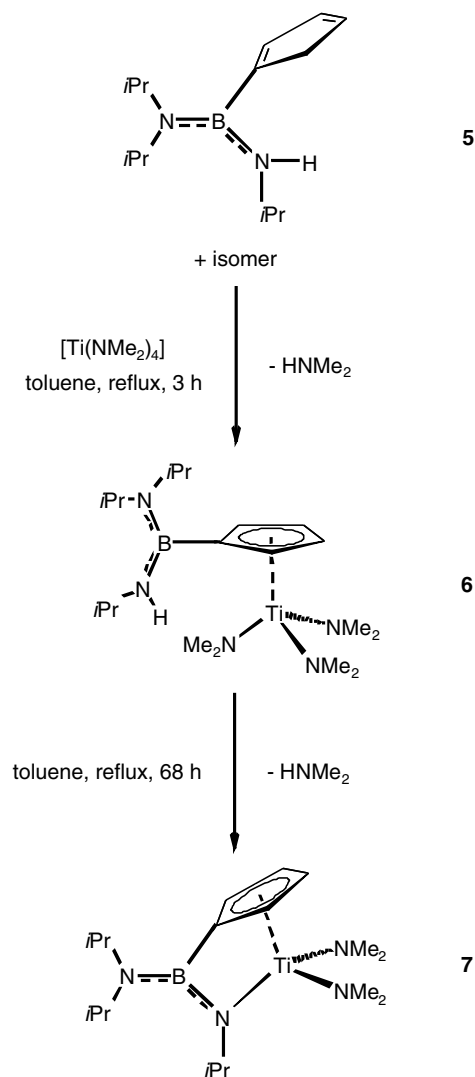
2. Results and discussion

2.1. Synthesis and spectroscopic characterisation

Following the literature procedure [11b], $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4)\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})i\text{Pr}\}(\text{NMe}_2)_3]$ (**6**) was prepared by treating $(\eta^1\text{-C}_5\text{H}_5)\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})i\text{Pr}$ (**5**) with $[\text{Ti}(\text{NMe}_2)_4]$ in refluxing toluene for 3 h (Scheme 2). The ^1H NMR spectrum of **6** displays a characteristic pair of pseudo-triplets corresponding to the titanium coordinated substituted Cp moiety as well as typical resonances for the $\text{N}i\text{Pr}_2$ moiety. Furthermore, resonances corresponding to the alkyl part of the $\text{N}Hi\text{Pr}$ fragment were observed, but the NH resonance was not visible in the spectrum due to line



Scheme 1.



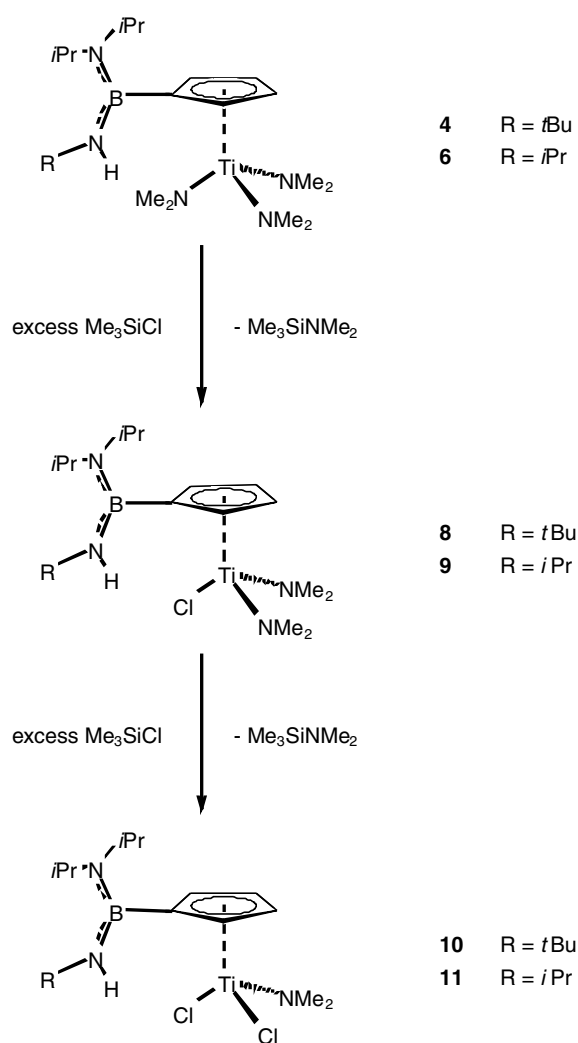
Scheme 2.

broadening induced by quadrupolar coupling to the neighbouring ^{14}N nucleus [12]. However, the integration of the sharp resonances corresponding to the NMe_2 groups at the titanium centre in relation to the integration of the other signals strongly support the non-chelating formulation of the compounds. Further evidence is provided by the IR spectrum of **6** that shows a characteristic NH stretching band at 3441 cm^{-1} . The ^{11}B NMR spectrum of **6** is unremarkable and the observed chemical shift closely resembles that determined for the ligand precursor **5**. Likewise, the ^{13}C NMR spectrum of **6** meets the expectations. Only the resonance corresponding to the *ipso*-C of the Cp ring could not be detected due to quadrupolar ^{13}C – ^{11}B coupling [13].

Thorough inspection of the ^1H NMR spectrum of **6** revealed the presence of trace amounts of a second compound **7** with a titanium coordinated substituted Cp moiety, as indicated by a second set of two pseudo-triplets. Consequently, we heated a sample of **6** in toluene to reflux for 68 h and monitored the reaction progress by frequent ^1H NMR spectroscopic analyses. The reaction proceeded rather cleanly with steady consumption of **6** and concomitant formation of **7**. Based on multinuclear 1D and 2D NMR spectroscopy, we identified **7** as the new CGC $[\text{Ti}\{\eta^5\text{-}\eta^1\text{-}(\text{C}_5\text{H}_4)\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{R}\}(\text{NMe}_2)_2]$ that is formed from **6** by elimination of one equivalent of HNMe_2 and concurrent ring closure (Scheme 2). ^1H and ^{13}C NMR spectra display all the expected signals apart from the BC resonance. The proposed formulation of **7** is supported by the integral ratio of the NMe_2 resonance to the other signals in the ^1H NMR spectrum that indicates the presence of two NMe_2 groups per boron bridged CGC ligand in the molecule. The ^{11}B NMR chemical shift of $\delta = 29.1$ resembles again the values observed for the corresponding ligand precursor as well as for the starting material **6**. Compound **7** is the first boron-bridged CGC incorporating an alkylamido moiety in the chelating ligand.

In contrast, prolonged heating of **4** in toluene does not yield the corresponding CGC but results in uncontrolled decomposition of the starting material.

Substitution of the NMe_2 groups on titanium in **4** and **6** was attempted by reaction with excess Me_3SiCl with the aim to prepare the corresponding half-sandwich complexes $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{R}\}\text{Cl}_3]$ ($\text{R} = i\text{Pr}, t\text{Bu}$). A similar substitution reaction was reported to convert $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7)(\text{NMe}_2)_3]$ into $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}_3]$ ($\text{C}_9\text{H}_7 = \text{indenyl}$) [14]. The trichloro derivatives appeared to be interesting synthetic targets as they may further react to the corresponding CGCs with elimination of HCl . However, Me_3SiCl even in large excess was found to substitute only two of the three NMe_2 groups in the respective starting materials **4** and **6** to give $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{R}\}\text{Cl}_2(\text{NMe}_2)]$ ($\text{R} = t\text{Bu}$ (**10**), $i\text{Pr}$ (**11**)) (Scheme 3). In the case of the reaction of **6** with excess Me_3SiCl the almost pure mono-chlorinated intermediate $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})i\text{Pr}\}\text{Cl}_2(\text{NMe}_2)]$ (**9**) could be isolated and characterised after 16 h, while conversion to the

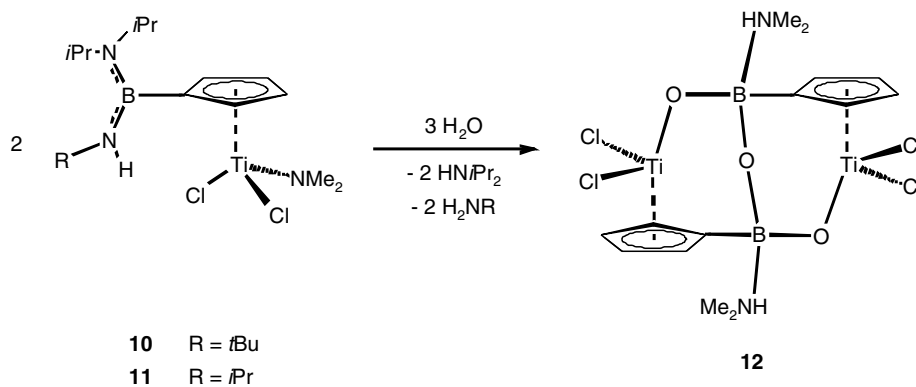


Scheme 3.

dichlorinated species **11** needed a significantly longer reaction time (64 h). Apparently, the substitution of one NMe_2 group by a chloride significantly reduces the reaction rate for further substitution. The exchange of another NMe_2 group by chloride then reduces the reaction rate further so that the third substitution step is practically not observed.

Complexes **9–11** were analysed by multinuclear 1D and 2D NMR spectroscopy and the latter two as well by IR spectroscopy. Furthermore, an X-ray structure determination of **10** was obtained confirming the assumed constitution (vide infra). ^1H , ^{11}B , ^{13}C NMR and IR spectra were unobtrusive and closely resemble the spectra of the respective starting materials **4** and **6**. The NMe_2 groups of **9–11** give rise to only one signal in the respective ^1H and ^{13}C NMR spectra at ambient temperature.

In order to test for the stability of $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{R}\}\text{Cl}_2(\text{NMe}_2)]$ ($\text{R} = t\text{Bu}$ (**10**), $i\text{Pr}$ (**11**)), corresponding solutions in dichloromethane were exposed to the atmosphere. In both cases, small yellow crystals formed within weeks and were subsequently identified by



Scheme 4.

X-ray diffraction methods as $[\{\text{TiCl}_2(\mu\text{-}\{\text{OB}(\text{NHMe}_2)\text{-}\eta^5\text{-C}_5\text{H}_4\})\}_2\text{-}\mu\text{-O}]$ (**12**) (vide infra). Presumably, this product is formed by partial hydrolysis of the respective starting materials (Scheme 4).

The course of the hydrolysis reaction, however, remains unclear at this stage. Noteworthy is the stability of the Ti–Cl bonds under the applied conditions and the migration of the protonated NMe₂ fragment from the titanium centre to boron, while two other B–N bonds per boron centre are cleaved in the course of the reaction. Characterisation of **12** by means of solution NMR spectroscopy failed due to its poor solubility in common NMR solvents that may be ascribed to a certain polarity of the compound (each boron centre carries a negative formal charge and each nitrogen centres carries a positive formal charge).

2.2. X-ray structure determination of complexes **10** and **12**

Single crystals of **10** were obtained by recrystallisation from hexane at 4 °C. Compound **10** crystallises in the monoclinic space group *C*2/*c* and adopts *C*₁ symmetry in

the crystal (Fig. 1). Selected bond lengths and angles are listed in Table 1.

As expected for a compound of the general formula (CpR)TiCl₂(X), the titanium centre is placed in a pseudo-tetrahedral environment with the coordination sphere being defined by the π -coordinated substituted cyclopentadienyl ligand, two chlorides and the N-donor of the dimethylamido ligand. Overall, the structure resembles very much those of previously reported related compounds $[(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{TiCl}_2(\text{NH}t\text{Bu})]$ (R, R' = H, Me) [15,16], $[(\eta^5\text{-C}_5\text{R}_5)\text{TiCl}_2(\text{N}i\text{Pr}_2)]$ (R = H, Me) [17], and $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\{\text{N}(\text{SiMe}_3)_2\}]$ [18].

The structure is well-behaved except for the disorder in the N(2)-bound *tert*-butyl group. The C₅ ring moiety is coplanar to within 0.008 Å. The boryl substituent is bent out of the C₅ ring plane away from the titanium centre as indicated by a dip angle α^* ($\alpha^* = 180^\circ - \alpha$, with α being the angle Cp(centroid)–C_{ipso}–B) of 10.5°. Both the B and N(1) atoms adopt trigonal planar geometries and the B–N(1) and B–N(2) distances of 1.432(3) and 1.427(3) Å, respectively, indicate some degree of π -interaction along this linkage. C–C bond lengths in the C₅ ring range from 1.395 to 1.433 Å. This asymmetry is as well reflected in the disposition of the titanium centre such that the distance to the boryl substituted carbon atom C(1) with 2.400(2) Å is distinctly longer than the distances to C(2)–C(5) in the range of 2.339–2.362 Å. The Ti–Cp(centroid) distance of 2.033 Å is noticeably longer than the corresponding

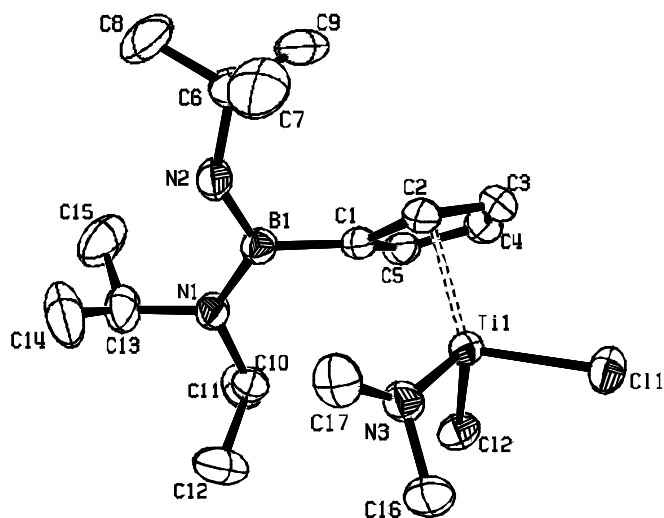


Fig. 1. ORTEP representation of the molecular structure of complex **10**. Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for complex **10**

Ti(1)–N(3)	1.867(2)	N(3)–Ti(1)–Cl(1)	101.66(6)
Ti(1)–Cl(1)	2.3015(8)	N(3)–Ti(1)–Cl(2)	107.67(8)
Ti(1)–Cl(2)	2.3034(9)	Cl(1)–Ti(1)–Cl(2)	101.45(3)
Ti(1)–C(1)	2.400(2)	C(1)–B(1)–N(1)	122.02(19)
Ti(1)–C(2)	2.339(2)	C(1)–B(1)–N(2)	118.80(19)
Ti(1)–C(3)	2.350(3)	N(1)–B(1)–N(2)	119.18(19)
Ti(1)–C(4)	2.352(3)	C(16)–N(3)–Ti(1)	108.66(19)
Ti(1)–C(5)	2.363(2)	C(17)–N(3)–Ti(1)	140.64(18)
B(1)–N(1)	1.432(3)	C(16)–N(3)–C(17)	110.6(2)
B(1)–N(2)	1.427(3)		
B(1)–C(1)	1.605(3)		

distances in boron-bridged constrained geometry titanium dichloride complexes **1a** (1.989 and 1.995 Å, respectively, for two crystallographically independent molecules) and **2** (1.992 Å) [11b], but comparable to those in $[(\eta^5\text{-C}_5\text{H}_5)\text{-TiCl}_2(\text{NH}t\text{Bu})]$ (2.032 Å) [15] and $[(\eta^5\text{-C}_5\text{H}_5)\text{-TiCl}_2(\text{NiPr}_2)]$ (2.035 Å) [17]. The relative disposition of the bulky boryl substituent on the C₅ ring and the NMe₂ group as the sterically most demanding η^1 -substituent on titanium can be described by the N(3)–Ti–Cp(centroid)–B torsion of 38.0° and is most likely enforced by crystal packing forces. The trigonal planar geometry of the N(3) atom on titanium (sum of angles of respective substituents 359.9°) and the short N(3)–Ti distance of 1.867(2) Å indicate significant π -interaction despite the observation of only one resonance in the ¹H NMR spectrum at ambient temperature for the NMe₂ group (vide supra). However, variable temperature NMR investigations on related complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{-TiCl}_2(\text{NMe}_2)]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{-TiCl}_2(\text{NH}t\text{Bu})]$ indicated virtually free rotation about the Ti–N vector in solution that is facilitated by two orthogonal sets of π -acceptor orbitals on titanium [15]. The NMe₂ moiety adopts a virtually orthogonal position with respect to the C₅ ring plane (torsion angle between respective planes: 86.8°) and is bent away from the C₅ ring as is illustrated by the angles Ti–N(3)–C(17) and Ti–N(3)–C(16) of 140.64(18)° and 108.66(19)°, respectively. A similar arrangement was observed in $[(\eta^5\text{-C}_5\text{H}_5)\text{-TiCl}_2(\text{NiPr}_2)]$ where it was accompanied by a β -agostic interaction involving the methine C–H bond of an *isopropyl* group and the metal centre with a Ti···H distance of ca. 2.25 Å [17]. However, in the present case, the minimum Ti···H distance is ca. 2.55 Å, so that the somewhat peculiar disposition of the NMe₂ substituent appears to be an outcome of steric repulsion rather than of agostic interaction.

Single crystals of **12** were obtained by precipitation from the reaction mixture in dichloromethane at ambient temperature. Compound **12** crystallises in the monoclinic space group *C2/c* and adopts *C*₂ symmetry in the crystal with the *C*₂ axis piercing O(1) (Fig. 2). Selected bond lengths and angles are listed in Table 2.

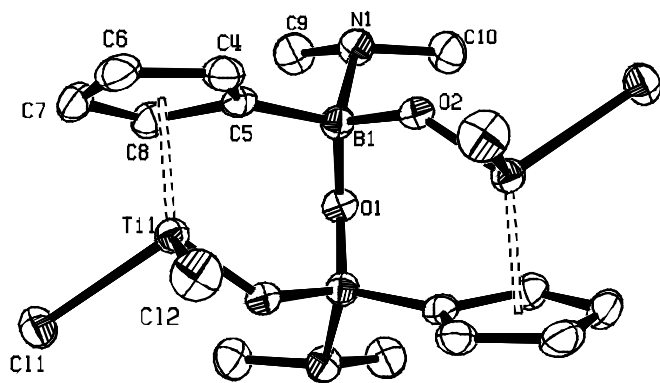


Fig. 2. ORTEP representation of the molecular structure of complex **12**. Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for complex **12**

Ti(1)–O(2)	1.7473(13)	O(2)–Ti(1)–Cl(2)	103.24(5)
Ti(1)–Cl(2)	2.2791(6)	O(2)–Ti(1)–Cl(1)	101.70(5)
Ti(1)–Cl(1)	2.2969(6)	Cl(2)–Ti(1)–Cl(1)	102.54(2)
O(1)–B(1)	1.428(2)	B(1)–O(1)–B(1')	116.7(2)
O(2)–B(1)	1.486(3)	B(1)–O(2)–Ti(1)	145.24(12)
B(1)–N(1)	1.621(3)	O(1)–B(1)–O(2)	112.44(15)
C(5)–B(1')	1.618(3)	O(1)–B(1)–C(5')	114.25(16)
N(1)–C(9)	1.488(3)	O(2)–B(1)–C(5')	108.02(16)
N(1)–C(10)	1.491(3)	O(1)–B(1)–N(1)	105.63(16)
		O(2)–B(1)–N(1)	105.38(16)
		C(5')–B(1)–N(1)	110.77(15)

The coordination around the titanium atom is that of a pseudo-three-legged piano-stool as is commonly found in titanium half-sandwich complexes of the type CpTiCl₂(X). Two of these titanium half-sandwich fragments are bridged by –B–O– units in such a way, that the Cp ring of one fragment is substituted by a boron atom that is connected via an oxygen atom to the other titanium centre. The respective boron atoms of the two linkages are in turn connected via another oxygen bridge. The boron centres are both tetra-coordinated, carrying NMe₂H groups as the fourth substituent. The molecule is overall neutral, with the boron centres being formally negatively charged, while the nitrogen atoms carry positive formal charges.

The molecular structure of **12** in some way resembles that of the dimeric silicon-oxo-bridged complex $[\text{TiCl}_2(\mu\text{-OSiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)]_2$, however, the latter exhibits *C*_i symmetry due to a different relative disposition of the silyl moieties compared to the borate groups [19]. This difference is the outcome of a higher degree of freedom in the silicon-oxo-bridged compound, where the silyl groups are rotated in a position that ensures minimum interaction, i.e., with the methyl substituents *exo* to the cyclic core (–Cp–Si–O–Ti–Cp'–Si'–O'–Ti'–) of the molecule. On the contrary, in the boron-oxo-bridged complex, one of the substituents on boron, i.e., O(2) of the central B(1)–O(2)–B(1') linkage, is positioned *endo* to the cyclic core (–Cp–B–O(1)–Ti–Cp'–B'–O(1')–Ti'–) of the molecule and enforces the observed conformation.

The Cp moiety is essentially planar with a r.m.s. deviation of 0.0065 Å of the respective atoms from the plane. The Ti–Cp(centroid) distance of 2.009 Å is slightly longer than in boron-bridged titanium dichloride CGCs **1a** (1.989 and 1.995 Å for two crystallographically independent molecules, respectively) and **2** (1.992 Å) [11b], but significantly shorter than that of unbridged half-sandwich complex **10** (2.033 Å) or the related complex $[\text{TiCl}_2(\mu\text{-OSiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)]_2$ (2.026 Å) [19]. The titanium centres are slightly displaced from a position directly underneath the respective C₅ ring centroids such that the Ti–Cp(centroid) vectors subtend angles of 1.9° to the normals to the ring planes. The boron atoms are with 6.1° slightly bent out of the C₅ ring plane towards the titanium centre. The *C*_{ipso}–B distances with 1.618(3) Å are longer than those in

Table 3
Polymerisation of styrene with [CpTiCl₃]/MAO and **10**/MAO

Entry	Catalyst	Yield (g)	<i>M_w</i>	<i>M_w</i> / <i>M_n</i>
1	[CpTiCl ₃]	2.16	7500	2.5
2	10	2.63	35000	2.0

Polymerisation conditions: solvent = toluene, *T_p* = 50 °C, [Ti] = 2.0 × 10⁻⁴ mol L⁻¹, [Al] = 0.10 mol L⁻¹, [styrene] = 1.74 mol L⁻¹, activation period before injection of styrene = 15 min, reaction time = 60 min.

boron-bridged CGCs **1a** (1.602(6) and 1.605(6) Å for two crystallographically independent molecules, respectively) and **2** (1.595(5) Å) [11b] and unbridged boryl substituted half-sandwich complex **10** (1.605(3) Å) and reflect the different degree of hybridisation of the involved boron centres. The B(1)–O(2)–B(1') linkage is with 116.76(19)° substantially more bent than the B(1)–O(1)–Ti(1) moiety with 145.22(11)°, indicating some degree of π-interaction between O(1) and Ti(1) (maximum π-interaction in a Ti–O bond corresponds to angles of 180° with regard to the two substituents on oxygen [19a]). This assumption is further supported by the relative short Ti(1)–O(1) distance of 1.7472(12) Å and an elongation of the B–O bond length in the B–O–Ti unit relative to the B–O–B unit (1.487(2) and 1.427(2) Å respectively). Both the Ti(1)–O(1) distance and B(1)–O(1)–Ti(1) angle resemble very much the corresponding values found in the C₃-bridged cyclopentadienyl alkoxy complex [Ti{η⁵:η¹-(C₅Me₄)(CH₂)₃O}Cl₂] [20].

2.3. Polymerisation activity of compound **10**

Preliminary investigations have been performed to establish the capability of systems based on complex **10** to catalyse the polymerisation of ethylene and styrene, respectively. The system **10**/MAO (Al to Ti ratio 4500:1) was found to be inactive towards the polymerisation of ethylene. Conversely, the system **10**/MAO (Al to Ti ratio 500:1) exhibited a catalytic activity towards the homopolymerisation of styrene that is comparable to that of the benchmark system [CpTiCl₃]/MAO under equivalent reaction conditions (Table 3).

3. Conclusions

The synthesis of the first boron-bridged CGC [Ti{(η⁵-C₅H₄)B(NiPr₂)NiPr}(NMe₂)₂] (**7**) incorporating an alkylamido moiety was achieved by prolonged heating of the non-bridged precursor [Ti{(η⁵-C₅H₄)B(NiPr₂)N(H)*i*Pr}(NMe₂)₃] (**6**). This reaction is, however, not generally applicable, as was demonstrated by the decomposition of [Ti{(η⁵-C₅H₄)B(NiPr₂)N(H)*t*Bu}(NMe₂)₃] (**4**) under identical reaction conditions. The half-sandwich complexes [Ti{(η⁵-C₅H₄)B(NiPr₂)N(H)R}(NMe₂)₃] (**4**, **6**) may be converted to their dichloro derivatives (**10**, **11**) by treatment with excess Me₃SiCl. Partial hydrolysis of **10** and **11**, respectively, yielded the mutual bimetallic product **12** via a yet unidentified reaction pathway. Complex **10** exhibits a high activity in the catalysis of the styrene homopolymer-

isation when activated with MAO and is currently subject of further investigations.

4. Experimental

4.1. General methods

All manipulations were performed under a dry atmosphere of argon using standard Schlenk line and dry box techniques. Solvents were dried utilising an M. Braun Solvent Purification System and stored under argon over molecular sieves. Deuterated solvents were degassed, dried and stored over molecular sieves. Styrene was distilled twice from CaH₂ prior to use. (η¹-C₅H₅)B(NiPr₂)Cl [21], [Ti(NMe₂)₄] [22], [Ti{(η⁵-C₅H₄)B(NiPr₂)N(H)*t*Bu}(NMe₂)₃] (**4**) [11b] and [CpTiCl₃] [23] were prepared by previously published methods. Lithium *isopropyl* amide was synthesised by deprotonation of *isopropyl* amine with butyl lithium. MAO as a 10 wt% solution in toluene was purchased from Crompton, Bergkamen, Germany, and used as supplied. Me₃SiCl was obtained from commercial sources and used without further purification.

¹H NMR spectra were recorded on either a Bruker 200 Avance spectrometer or a Bruker 400 Avance spectrometer. ¹³C-{¹H} NMR spectra were recorded on either a Bruker DRX 300 spectrometer or a Bruker 400 Avance spectrometer. ¹¹B-{¹H} NMR spectra were recorded on a Bruker 200 Avance spectrometer. All chemical shifts are reported in ppm. Chemical shifts for ¹H and ¹³C-{¹H} NMR spectra were referenced to internal solvent resonances and are reported relative to SiMe₄. Assignments were made from the analysis of ¹H,¹³C-HMQC-COSY NMR experiments. Chemical shifts for ¹¹B-{¹H} NMR spectra were referenced to BF₃ · OEt₂ as an external standard. IR spectroscopy was conducted on CH₂Cl₂ solutions and performed on a Bruker Vector 22 FT-IR spectrometer. Mass spectra were recorded on a Thermo Finnigan Trio 1000 mass spectrometer. Mass spectra of complexes **7**–**12** showed only signals of the ligands and, hence, are of no analytical value.

4.2. Synthesis of (η¹-C₅H₅)B(NiPr₂)N(H)*i*Pr (**5**)

In analogy to a literature procedure [21], a freshly prepared solution of lithium *isopropyl* amide (1.10 g, 17.0 mmol) in toluene (30 mL) was added dropwise to a solution of (η¹-C₅H₅)B(NiPr₂)Cl (3.09 g, 17.0 mmol) in hexane (40 mL) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and was subsequently stirred for 16 h. LiCl that was precipitated was filtered off, solvents were removed in vacuo at ambient temperature and the residue was distilled in vacuo over a short path at elevated temperature. Pure **5** (1.56 g, 6.7 mmol, 39%) as a mixture of two constitutional isomers (ratio 5:4) was obtained in the form of a white crystalline solid (melting point 35 °C). ¹H NMR

(200 MHz, benzene- D_6): [major isomer]: $\delta = 0.98$ (d, $^3J_{H-H} = 6.4$ Hz, 6H, Me_{NH_iPr}), 1.09 (d, $^3J_{H-H} = 6.9$ Hz, 12H, Me_{NiPr_2}), 3.09 (m, 2H, CH_2), 3.11 (m, 1H, CH_{NH_iPr}), 3.34 (m, 2H, CH_{NiPr_2}), 6.50–6.70 (m, 3H, CH_{Cp}), NH resonance not observed; [minor isomer]: $\delta = 1.03$ (d, $^3J_{H-H} = 6.4$ Hz, 6H, Me_{NH_iPr}), 1.14 (d, $^3J_{H-H} = 6.9$ Hz, 12H, Me_{NiPr_2}), 2.91 (m, 2H, CH_2), 3.31 (m, 1H, CH_{NH_iPr}), 3.44 (m, 2H, CH_{NiPr_2}), 6.40–6.50 (m, 2H, CH_{Cp}), 6.76–6.89 (m, 1H, CH_{Cp}), NH resonance not observed. ^{13}C NMR (101 MHz, benzene- D_6): [major isomer]: $\delta = 23.3$ (Me_{NiPr_2}), 27.5 (Me_{NH_iPr}), 44.7 (CH_{NiPr_2}), 46.3 (br, CH_{NH_iPr}), 46.5 (CH_{2Cp}), 133.6 (CH_{Cp}), 133.8 (CH_{Cp}), 134.9 (CH_{Cp}), BC resonance not observed; [minor isomer]: $\delta = 23.4$ (Me_{NiPr_2}), 27.5 (Me_{NH_iPr}), 43.2 (CH_{2Cp}), 44.6 (CH_{NiPr_2}), 46.3 (br, CH_{NH_iPr}), 132.3 (CH_{Cp}), 135.5 (CH_{Cp}), 137.4 (CH_{Cp}), BC resonance not observed. ^{11}B NMR (64 MHz, benzene- D_6): [isomer mixture]: $\delta = 29.6$. MS (EI^+) m/z (%): 234 (20) [M^+], 219 (100) [$M^+ - Me$], 134 (20) [$M^+ - NiPr_2$], 86 (88) [$C_6H_{14}^+$]. IR 3439 w $\nu(NH)$.

4.3. Synthesis of $[Ti\{\eta^5-C_5H_4\}B(NiPr_2)N(H)iPr\}(NMe_2)_3]$ (**6**)

Compound **5** (1.56 g, 6.67 mmol) was dissolved in toluene (30 mL) and neat $[Ti(NMe_2)_4]$ (1.50 g, 6.67 mmol) was added by syringe at 0 °C. The resulting yellow solution was allowed to warm to ambient temperature and no colour change was observed. The reaction mixture was then heated to 70 °C during which the colour changed slowly to light orange. Upon subsequent reflux for 3 h the mixture further darkened in colour. After cooling to ambient temperature, all volatiles were removed in vacuo to yield **6** (2.50 g, 6.06 mmol, 91%) in the form of a dark red oil. 1H NMR (200 MHz, benzene- D_6): $\delta = 1.10$ (d, $^3J_{H-H} = 6.3$ Hz, 6H, Me_{iPr}), 1.16 (d, $^3J_{H-H} = 6.8$ Hz, 12H, Me_{iPr}), 3.18 (s, 18H, NMe_2), 3.53–3.75 (m, 3H, CH_{iPr}), 5.96 (pt, 2H, CH_{Cp}), 6.42 (pt, 2H, CH_{Cp}), NH resonance not observed. ^{13}C NMR (101 MHz, benzene- D_6): $\delta = 23.8$ (Me_{iPr}), 28.0 (Me_{iPr}), 44.2 (CH_{iPr}), 46.4 (br, CH_{iPr}), 50.4 (NMe_2), 111.2 (CH_{Cp}), 120.0 (CH_{Cp}), BC resonance not observed. ^{11}B NMR (64 MHz, benzene- D_6): $\delta = 28.8$. MS (EI^+) m/z (%): 369 (7) [$M^+ - NMe_2$], 323 (6) [$M^+ - 2HNMe_2$], 234 (13) [$(C_5H_5)B(NiPr_2)N(H)iPr^+$], 219 (55) [$(C_5H_5)B(NiPr_2)N(H)iPr^+ - Me$], 86 (100) [iPr_2^+]. IR 3441 w $\nu(NH)$.

4.4. Synthesis of $[Ti\{\eta^5-\eta^1-(C_5H_4)B(NiPr_2)NiPr\}(NMe_2)_2]$ (**7**)

Complex **6** (0.25 g, 0.60 mmol) was dissolved in toluene (20 mL). The resulting red solution was refluxed and reaction progress was monitored by 1H NMR spectroscopy. After 20 h, conversion was ca. 35% according to integral ratios. After 68 h, the conversion was virtually complete and only negligible traces of by-products were detected. All volatiles were removed in vacuo to yield **7** (0.18 g,

0.49 mmol, 82%) as a red oil. Separation of the reaction components by recrystallisation from different solvents at various temperatures was unsuccessful. 1H NMR (200 MHz, benzene- D_6): $\delta = 1.31$ (d, $^3J_{H-H} = 6.3$ Hz, 6H, Me_{TiNiPr}), 1.36 (d, $^3J_{H-H} = 6.8$ Hz, 12H, Me_{NiPr_2}), 2.99 (s, 12H, NMe_2), 3.59 (m, $^3J_{H-H} = 6.8$ Hz, 2H, CH_{NiPr_2}), 4.07 (m, $^3J_{H-H} = 6.3$ Hz, 2H, CH_{TiNiPr}), 5.78 (pt, 2H, CH_{Cp}), 6.17 (pt, 2H, CH_{Cp}). ^{13}C NMR (75 MHz, benzene- D_6): $\delta = 25.1$ (Me_{NiPr_2}), 27.4 (Me_{TiNiPr}), 46.5 (CH_{NiPr_2}), 48.8 (NMe_2), 53.3 (CH_{TiNiPr}), 114.9 (CH_{Cp}), 119.6 (CH_{Cp}), BC resonance not observed. ^{11}B NMR (64 MHz, benzene- D_6): $\delta = 29.1$.

4.5. Synthesis of $[Ti\{\eta^5-C_5H_4\}B(NiPr_2)N(H)iPr\}Cl(NMe_2)_2]$ (**9**)

Compound **6** (0.27 g, 0.65 mmol) was dissolved in hexane (10 mL) and neat Me_3SiCl (0.72 g, 6.5 mmol, 10 equivalents) was added. The red mixture was stirred for 16 h at ambient temperature. 1H NMR spectroscopy on a dried sample revealed almost full conversion to the mono-chlorinated product **9**. All volatiles were consequently removed in vacuo to give **9** (0.26 g, 0.64 mmol, 98%) in virtually quantitative yield as a red oil that was slightly contaminated by the corresponding dichloro complex **11**. 1H NMR (400 MHz, benzene- D_6): $\delta = 1.07$ (d, $^3J_{H-H} = 6.3$ Hz, 6H, Me_{NH_iPr}), 1.15 (d, $^3J_{H-H} = 6.8$ Hz, 12H, Me_{NiPr_2}), 3.16 (s, 12H, NMe_2), 3.58 (m, 3H, CH_{iPr}), 5.95 (pt, 2H, CH_{Cp}), 6.47 (pt, 2H, CH_{Cp}), NH resonance not observed. ^{13}C NMR (101 MHz, benzene- D_6): $\delta = 23.6$ (Me_{NiPr_2}), 27.7 (Me_{NH_iPr}), 44.5 (CH_{NH_iPr}), 46.6 (br, CH_{NiPr_2}), 48.9 (NMe_2), 113.9 (CH_{Cp}), 121.8 (CH_{Cp}), BC resonance not observed. ^{11}B NMR (64 MHz, benzene- D_6): $\delta = 28.9$.

4.6. Synthesis of $[Ti\{\eta^5-C_5H_4\}B(NiPr_2)N(H)tBu\}Cl_2(NMe_2)_2]$ (**10**)

$[Ti\{\eta^5-C_5H_4\}B(NiPr_2)N(H)tBu\}(NMe_2)_3]$ (**4**) (0.83 g, 1.95 mmol) was dissolved in hexane (20 mL) to give a bright orange solution. Neat Me_3SiCl (2.11 g, 19.5 mmol, 10 equivalents) was added and the resulting mixture was stirred at ambient temperature for 6 h. 1H NMR spectroscopy on a small aliquot dried in vacuo indicated almost full conversion to the dichloro complex **10**. All volatiles were subsequently removed in vacuo to afford a red oil. Recrystallisation from hexane at 4 °C afforded bright red crystals of **10** in almost quantitative yield (0.74 g, 1.80 mmol, 92%). 1H NMR (200 MHz, benzene- D_6): $\delta = 1.01$ (s, 9H, Me_{tBu}), 1.07 (d, $^3J_{H-H} = 6.8$ Hz, 12H, Me_{iPr}), 3.06 (br s, 1H, NH), 3.29 (m, $^3J_{H-H} = 6.8$ Hz, 2H, CH_{iPr}), 3.49 (s, 6H, NMe_2), 6.30 (pt, 2H, CH_{Cp}), 6.59 (pt, 2H, CH_{Cp}). ^{13}C NMR (101 MHz, benzene- D_6): $\delta = 23.4$ (Me_{iPr}), 34.0 (Me_{tBu}), 47.2 (br, CH_{iPr}), 49.7 (*quaternary* C_{tBu}), 52.8 (NMe_2), 120.3 (CH_{Cp}), 125.5 (CH_{Cp}), BC resonance not observed. ^{11}B NMR (64 MHz, benzene- D_6): $\delta = 28.2$. IR 3450 w $\nu(NH)$.

4.7. Synthesis of $[Ti\{\eta^5-C_5H_4\}B(NiPr_2)N(H)iPr\}-Cl_2(NMe_2)]$ (**11**)

Complex **8** (0.20 g, 0.49 mmol) was dissolved in hexane (10 mL) and neat Me_3SiCl (0.72 g, 6.5 mmol, 13 equivalents) was added. The resulting red solution was stirred for 48 h at ambient temperature. 1H NMR spectroscopy on a dried sample indicated full conversion to the dichlorinated product **11**. Consequently, all volatiles were removed in vacuo to yield **11** (0.18 g, 0.46 mmol, 93%) in the form of a red oil. 1H NMR (400 MHz, benzene- D_6): $\delta = 1.08$ (d, $^3J_{H-H} = 6.3$ Hz, 6H, Me_{NHIPr}), 1.16 (d, $^3J_{H-H} = 6.8$, 12H, Me_{NiPr_2}), 3.41 (m, $^3J_{H-H} = 6.3$ Hz, 1H, CH_{NHIPr}), 3.45 (m, $^3J_{H-H} = 6.8$ Hz, 2H, CH_{NiPr_2}), 3.63 (s, 6H, NMe_2), 6.47 (pt, 2H, CH_{CP}), 6.64 (pt, 2H, CH_{CP}), NH resonance not observed. ^{13}C NMR (101 MHz, benzene- D_6): $\delta = 23.3$ (Me_{NiPr_2}), 27.4 (Me_{NHIPr}), 44.5 (CH_{NHIPr}), 46.7 (br, CH_{NiPr_2}), 52.6 (NMe_2), 120.6 (CH_{CP}), 124.9 (CH_{CP}), BC resonance not observed. ^{11}B NMR (64 MHz, benzene- D_6): $\delta = 27.8$. IR 3438 w $\nu(NH)$.

4.8. Formation of $[TiCl_2(\mu-\{OB(NHMe_2)-\eta^5-C_5H_4\})_2-\mu-O]$ (**12**) by partial hydrolysis of $[Ti\{\eta^5-C_5H_4\}-B(NiPr_2)N(H)R\}Cl_2(NMe_2)]$ ($R = tBu$ (**10**), iPr (**11**))

An unsealed GC–MS vial containing a solution of **10** in dichloromethane was allowed to stand for 4 weeks at ambient temperature. During this period, yellow crystals formed which were identified as $[TiCl_2(\mu-\{OB(NHMe_2)-\eta^5-$

$C_5H_4\})_2-\mu-O]$ (**12**) by X-ray diffraction experiments. Characterisation by multinuclear NMR spectroscopy was not possible due to poor solubility in common NMR solvents. Under the same conditions **11** hydrolyses to form the same complex **12**, as determined by X-ray diffraction methods.

4.9. X-ray structure determination of compounds **10** and **12**

Crystals of **10** and **12**, respectively, were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fibre and then transferred into the cold nitrogen gas stream of the diffractometer. **10**: Stoe IPDS image plate system (analytical absorption correction applied), **12**: Bruker SMART APEX with CCD area detector (absorption correction applied, based on comparison of redundant and equivalent reflections, SADABS) [24]. Data analysis was performed with XPREP [25]. In each case the structure was solved via direct methods and refined with the SHELX software package [26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealised positions and were included in structure factor calculations. The crystallographic data, parameters of the X-ray experiments and refinements for compounds **10** and **12** are listed in Table 4.

4.10. Styrene polymerisation

Styrene polymerisation experiments were performed in 100 mL Schlenk bottles following a modified literature procedure [27]. Specific amounts of toluene, a stock

Table 4
Summary of the crystal data and details of data collection and refinement for compounds **10** and **12**

Data	10	12
Empirical formula	$C_{17}H_{34}BCl_2N_3Ti$	$C_{14}H_{22}B_2Cl_4N_2O_3Ti_2$
Formula weight ($g\ mol^{-1}$)	410.08	525.56
Temperature (K)	193(2)	193(2)
Radiation, λ (Å)	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Unit cell dimensions		
a (Å)	24.325(5)	17.3081(13)
b (Å)	17.761(4)	8.9766(7)
c (Å)	12.096(2)	14.7711(11)
α (°)	90	90
β (°)	119.27(3)	112.5990(10)
γ (°)	90	90
Volume (Å ³)	4558.7(16)	2118.7(3)
Z	8	4
Calculated density ($Mg\ m^{-3}$)	1.195	1.648
Absorption coefficient (mm^{-1})	0.614	1.276
$F(000)$	1744	1064
θ Range for data collection (°)	2.29–27.38	2.55–26.09
Reflections collected	25618	15783
Independent reflections (R_{int})	4912 (0.0526)	2086 (0.0218)
Maximum/minimum transmission	0.8664/0.7984	0.89/0.7282
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4912/30/244	2086/0/167
Goodness-of-fit on F^2	1.023	1.120
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0339$, $wR_2 = 0.0838$	$R_1 = 0.0254$, $wR_2 = 0.0668$
R indices (all data)	$R_1 = 0.0432$, $wR_2 = 0.0881$	$R_1 = 0.0264$, $wR_2 = 0.0676$
Minimum/maximum residual electron density ($e\ \text{Å}^{-3}$)	0.259/−0.390	0.350/−0.204

solution of the catalyst precursor in toluene and MAO in toluene (total volume 40 mL, amount of catalyst precursor 10 μ mol) were added to a Schlenk bottle. The reaction vessel was placed in an oil bath that was pre-heated to 50 °C. After a 15 min introductory period, styrene (10.0 mL, giving a 1.74 M styrene solution in toluene) was added by syringe to start the polymerisation reaction. The reaction mixture was stirred at 50 °C for 1 h. The polymerisation reaction was stopped by addition of acidified methanol (50 mL, 10 vol% hydrochloric acid). All volatiles were removed in vacuo and the residue was dried to completion at elevated temperature. Gel permeation chromatography (GPC) of recovered polymer samples was performed RAPRA Technology, Shropshire, UK following a standardised protocol.

5. Supplementary data

Crystallographic data for the structures reported have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 279470 (**10**) and 279469 (**12**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax (int code): +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>].

Acknowledgements

This work was supported by BMBF, DFG, EPSRC, R. Soc. F.M.B. thanks the Fonds der Chemischen Industrie for a doctoral scholarship. Steve Holding (RAPRA Technology Ltd., UK) is acknowledged for performing polymer analyses.

References

- [1] Y. Imanishi, N. Naga, *Prog. Polym. Sci.* 26 (2001) 1147.
- [2] (a) R.L. Haltermann, *Chem. Rev.* 92 (1992) 965; (b) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, *Angew. Chem.* 107 (1995) 1255; *Angew. Chem., Int. Ed.* 34 (1995) 1143; (c) M. Bochmann, *J. Chem. Soc., Dalton Trans.* (1996) 255; (d) W. Kaminsky, *J. Chem. Soc., Dalton Trans.* (1998) 1413; (e) C. Janiak, in: A. Togni, R.L. Haltermann (Eds.), *Metallocenes*, vol. 2, Wiley-VCH, Weinheim, 1998, p. 547; (f) G.G. Hlatky, *Coord. Chem. Rev.* 181 (1999) 243; (g) H.G. Alt, A. Köppl, *Chem. Rev.* 100 (2000) 1205; (h) G.W. Coates, *Chem. Rev.* 100 (2000) 1223; (i) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* 100 (2000) 1253; (j) G.G. Hlatky, *Chem. Rev.* 100 (2000) 1347; (k) N.E. Grimmer, N.J. Coville, *S. Afr. J. Chem.* 54 (2001) 118.
- [3] J. Schellenberg, N. Tomotsu, *Prog. Polym. Sci.* 27 (2002) 1925.
- [4] (a) A.L. McKnight, R.M. Waymouth, *Chem. Rev.* 98 (1998) 2587; (b) J. Okuda, T. Eberle, in: A. Togni, R.L. Haltermann (Eds.), *Metallocenes*, vol. 1, Wiley-VCH, Weinheim, 1998, p. 415; (c) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem.* 111 (1999) 448; *Angew. Chem., Int. Ed.* 38 (1999) 428; (d) S. Chum, W.J. Kruper, M.J. Guest, *Adv. Mater.* 12 (2000) 1759; (e) V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283.
- [5] (a) P.J. Shapiro, *Coord. Chem. Rev.* 231 (2002) 67; (b) C.E. Zachmanoglou, A. Docrat, B.M. Bridgewater, G. Parkin, C.G. Brandow, J.E. Bercaw, C.N. Jardine, M. Lyall, J.C. Green, J.B. Keister, *J. Am. Chem. Soc.* 124 (2002) 9525.
- [6] (a) J.C. Stevens, *Stud. Surf. Sci. Catal.* 89 (1994) 277; (b) A.A. Trifonov, T.P. Spaniol, J. Okuda, *Organometallics* 20 (2001) 4869.
- [7] For reviews on boron-bridged Group 4 metallocenes and related compounds see: (a) P.J. Shapiro, *Eur. J. Inorg. Chem.* (2001) 321; (b) H. Braunschweig, F.M. Breitling, E. Gullo, M. Kraft, *J. Organomet. Chem.* 680 (2003) 31; (c) S. Aldridge, C. Bresner, *Coord. Chem. Rev.* 244 (2003) 71.
- [8] (a) D.S. Stelck, P.J. Shapiro, N. Basicke, *Organometallics* 16 (1997) 4546; (b) M.T. Reetz, M. Willuhn, C. Psiorz, R. Goddard, *Chem. Commun.* (1999) 1105.
- [9] (a) H. Braunschweig, C. von Koblinski, R. Wang, *Eur. J. Inorg. Chem.* (1999) 69; (b) H. Braunschweig, C. von Koblinski, M. Mamuti, U. Englert, R. Wang, *Eur. J. Inorg. Chem.* (1999) 1899; (c) H. Braunschweig, M.O. Kristen, C. von Koblinski, *Eur. Pat. Appl.* 2000, EP-1140955; (d) H. Braunschweig, M. Kraft, K. Radacki, S. Stellwag, *Eur. J. Inorg. Chem.* (2005) 2754; (e) H. Braunschweig, M. Kraft, K. Radacki, S. Stellwag, *Z. Anorg. Allg. Chem.* 690 (2005) 5000.
- [10] (a) A.J. Ashe III, X. Fang, J.W. Kampf, *Organometallics* 18 (1999) 2288; (b) A.J. Ashe III, X. Fang, A. Hokky, J.W. Kampf, *Organometallics* 23 (2004) 2197.
- [11] (a) H. Braunschweig, C. von Koblinski, U. Englert, *Chem. Commun.* (2000) 1049; (b) H. Braunschweig, F.M. Breitling, C. von Koblinski, A.J.P. White, D.J. Williams, *Dalton Trans.* (2004) 938; (c) H. Braunschweig, F.M. Breitling, K. Radacki, F. Seeler, *J. Organomet. Chem.* (accepted for publication).
- [12] F.A. Bovey, L. Jelinski, P.A. Mirau, *Nuclear Magnetic Resonance Spectroscopy*, second ed., Academic Press, San Diego, 1988.
- [13] B. Wrackmeyer, *Prog. NMR Spectrosc.* 12 (1979) 227.
- [14] J.R. Ascenso, C.G. de Azevedo, M.J. Correia, A.R. Dias, M.T. Duarte, J.L.F. da Silva, P.T. Gomes, F. Lourenço, A.M. Martins, S.S. Rodrigues, *J. Organomet. Chem.* 632 (2001) 58.
- [15] D.M. Giolando, K. Kirschbaum, L.J. Graves, U. Bolle, *Inorg. Chem.* 31 (1992) 3887.
- [16] Y. Bai, M. Noltemeyer, H.W. Roesky, *Z. Naturforsch. B: Chem. Sci.* 46 (1991) 1357.
- [17] R.M. Pupi, J.N. Coalter, J.L. Petersen, *J. Organomet. Chem.* 497 (1995) 17.
- [18] Y. Bai, H.W. Roesky, M. Noltemeyer, *Z. Anorg. Allg. Chem.* 595 (1991) 21.
- [19] (a) S. Ciruelos, T. Cuenca, P. Gómez-Sal, A. Manzanero, P. Royo, *Organometallics* 14 (1995) 177; (b) A.V. Churakov, D.A. Lemenovskii, L.G. Kuz'mina, *J. Organomet. Chem.* 489 (1995) C81.
- [20] R. Fandos, A. Meetsma, J.H. Teuben, *Organometallics* 10 (1991) 59.
- [21] H. Braunschweig, F.M. Breitling, M. Homberger, C. von Koblinski, A.J.P. White, D.J. Williams, *Z. Anorg. Allg. Chem.* 629 (2003) 2244.
- [22] D.C. Bradley, I.M. Thomas, *J. Chem. Soc.* (1960) 3857.
- [23] A.M. Cardoso, R.J.H. Clark, S. Moorhouse, *J. Chem. Soc., Dalton Trans.* (1980) 1156.
- [24] G. Sheldrick, *SADABS ver. 2.10*, Area Detector Absorption Correction Program, 2002.
- [25] XPREP ver. 6.10, Part of the SHELXTL Crystal Structure Determination Package, Bruker Advanced X-ray Solutions Inc., Madison, 1997–2001.
- [26] G. Sheldrick, *SHELXS-97: structure solution and SHELXL-97: structure refinement programs*, 1997.
- [27] B. Huang, K. Cao, B.-G. Li, S. Zhu, *J. Appl. Polym. Sci.* 94 (2004) 1449.