Synthesis and structure of the first boron-bridged constrained geometry complexes†

Holger Braunschweig,* Carsten von Koblinski and Ulli Englert

Institut für Anorganische Chemie der Technischen Hochschule, RWTH Aachen, Templergraben 55, D-52056 Aachen, Germany. E-mail: holger.braunschweig@ac.rwth.aachen.de

Received (in Basel, Switzerland) 21st December 1999, Accepted 3rd May 2000
Published on the Web 25th May 2000

In the course of investigations on new Ziegler–Natta-analogous catalyst systems, the first 'constrained geometry' complexes of titanium with a bridging boron atom have been conveniently obtained by a high yield synthesis and were structurally characterized.

Since 1990[1] 'constrained geometry' complexes as catalysts for olefin polymerization have attracted considerable interest, since they show some distinct advantages in comparison to metallocene-based Ziegler–Natta type catalysts,[2] such as formation of copolymers and an increased stability towards MAO even under thermally harsh reaction conditions.[1d]‡ Very recently it was shown by us[3] and others [4] that [1]borametallocenophanes of group 4 elements are easily accessible, highly active catalysts for the polymerization of ethene and propene.

In order to combine the properties of the small and Lewis acidic bridging boron atom with the advantages of constrained geometry catalysts we prepared the compounds $[\{\eta^5:\eta^1\text{-}C_5H_4B(NPr^i{}_2)NPh\}TiX_2]$ (X = NMe_2, **1**; X = Cl, **2**).

Similarly to the synthesis of the corresponding [1]boratitanocenophanes $[\{(\eta^5\text{-}C_5H_4)_2BNR_2\}Ti(NMe_2)_2]$,[3a] complex **1** is obtained in a convenient three-step synthesis according to Scheme 1 as an orange, crystalline material in 80% yield. Subsequent treatment of **1** with an excess of Me_3SiCl gave the corresponding dichloro complex **2** in almost quantitative yield as a yellow solid. The structures of **1** and **2** in solution were derived from the multinuclear NMR data.§ In the ^1H NMR spectra both compounds show the expected two pseudo-triplets for the cyclopentadienyl protons forming an AA′BB′ spin system. Double sets of signals for the isopropyl groups in the ^1H and ^{13}C NMR spectra indicate a hindered rotation with respect to the boron–nitrogen double bond in **1** and **2**. The ^{11}B NMR spectra show signals at δ 27.8 (**1**) and 28.4 (**2**), in the expected range for aryl(diamino)boranes.

Suitable single crystals of **1** (Fig. 1) for an X-ray structural analysis¶ were obtained from hexane at -30 °C. The compound crystallises in the triclinic space group $P\bar{1}$ and the molecule adopts C_1 symmetry in the crystal. Both atoms B and N2 are trigonal planar, and the planes C20–N2–C23 and N1–B–C1 are almost coplanar with a dihedral angle of 2.2(3)°. The B–N distances of 1.428(3) Å (B–N1) and 1.409(3) Å (B–N2) are in the expected range for B–N double bonds, and the Ti–N distances were found to be *ca.* 1.91 Å for N3 and N4, respectively, while the Ti–N1 distance is markedly longer at 2.020(2) Å.

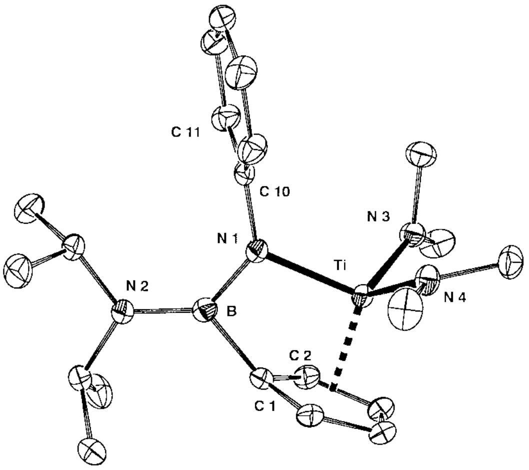
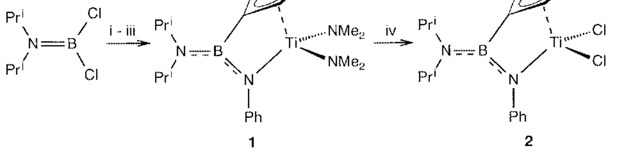


Fig. 1 Molecular structure of **1**. Selected distances (Å) and angles (°): B–N(1) 1.428(3), B–N(2) 1.409(3), Ti–N(1) 2.020(2), Ti–N(3) 1.9045(19), Ti–N(4) 1.913(2), N(3)–Ti–N(4) 103.44(9), N(1)–B–N(2) 131.0(2), C(1)–B–N(1) 103.57(18). Thermal ellipsoids are drawn at the 30% probability level.



Scheme 1 *Reagents and conditions*: i, hexane, 0 °C, $Na(C_5H_5)$; ii, toluene, 0 to 25 °C, Li(NPhH); iii, toluene, -78 to 40 °C, $[Ti(NMe_2)_4]$, 78%; iv, hexane, 0 °C, Me_3SiCl, 98%.

Preliminary polymerisation experiments showed compound **2** to be an effective catalyst for the polymerisation of ethene in the presence of MAO. In a typical experiment polyethylene with a molecular weight of *ca.* 470 000 was obtained with an activity of 500 kg polymer (mol cat h)$^{-1}$. As to be expected,[5] complex **1** showed a considerably lower activity towards the polymerisation of olefins. Further investigations of the catalytic properties of compound **2** and related complexes for ethene/styrene-copolymerisation are in progress.

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG Ludwigshafen.

Notes and references

‡ For a recent review on non-metallocene catalysts see ref. 1(*f*).

§ *Spectroscopic data*: **1**: ^1H NMR (499.658 MHz, CD_2Cl_2): δ 0.90 (br, 6H, $CHCH_3$), 1.45 (br, 6H, $CHCH_3$), 2.97 (s, 12H, NMe_2), 3.31 (br, 2H, $CHCH_3$), 5.94 (m, 2H, C_5H_4), 6.44 (m, 2H, C_5H_4), 6.73 (m, 2H, C_6H_5), 6.83 (m, 1H, C_6H_5), 7.14 (m, 2H, C_6H_5). ^{11}B NMR (160.310 MHz, CD_2Cl_2): δ 27.76. ^{13}C NMR (125.639 MHz, CD_2Cl_2): δ 21.36 (br), 27.01 (br), 44.62 (br), 46.11 (br), 47.90 (NMe_2), 120.95 (C_5H_4), 124.00 (C_5H_4), 115.81, 119.99, 128.16, 155.48. MS (EI) (*m/z*, %): 402 (M^+, 45), 387 ($M^+ - Me$, 5), 358 ($M^+ - NMe_2$, 65), 314 ($M^+ - 2NMe_2$, 100), 93 ($C_6H_5NH_2{}^+$, 95), 64 ($C_5H_4{}^+$, 45). Correct elemental analysis.

2: ^1H NMR (499.658 MHz. CD_2Cl_2): δ 0.90 (d, 6H, ^3J 6.71 Hz, $CHCH_3$), 1.54 (d, 6H, ^3J 6.71 Hz, $CHCH_3$), 3.14 (m, 1H, ^3J 6.71 Hz, $CHCH_3$), 3.41 (m, 1H, ^3J 6.71 Hz, $CHCH_3$), 6.44 (m, 2H, C_5H_4), 7.08 (m, 2H, C_5H_4), 6.91 (m, 2H, C_6H_5), 7.14 (m, 1H, C_6H_5), 7.38 (m 2H, C_6H_5). ^{11}B NMR (160.310 MHz, CD_2Cl_2): δ 28.29. ^{13}C NMR (125.639 MHz, CD_2Cl_2): δ 21.40, 27.72, 45.20, 47.28, 122.52 (C_5H_4), 125.71 (C_5H_4), 124.32, 127.21, 129.62, 152.39. MS (EI) (*m/z*, %): 384 (M^+, 15), 369 ($M^+ - Me$, 30), 348 ($M^+ -$

---

† Electronic supplementary information (ESI) available: experimental and polymerisation studies. See http://www.rsc.org/suppdata/cc/b0/b000380h/

DOI: 10.1039/b000380h

Cl, 50), 333 ($M^+ - Cl - Me$, 20), 318 ($M^+ - Cl - 2Me$, 20], 93 ($C_6H_5NH_2^+$, 70), 64 ($C_5H_4^+$, 25). Correct elemental analysis.

¶ *X-Ray structure determination* of **1**: ENRAF-Nonius CAD4 diffractometer, Mo-Kα radiation, incident beam graphite monochromator (λ = 0.71073 Å), T = 213 K, orange platelet of approximate dimensions 0.70 × 0.60 × 0.15 mm directly mounted in dry air flux (Whatman 75-52).

Crystal data: triclinic, space group $P\bar{1}$, a = 9.464(6), b = 9.754(4), c = 13.596 Å, α = 101.94(2), β = 102.32(4), γ = 103.37(4)°, V = 1149 Å^3, Z = 2, D_c = 1.17 g cm^{-3}, μ = 3.8 cm^{-1}. 4351 reflections, 4068 independent, θ_{max} = 26°, solution with direct methods (SHELXS97),[6] refinement on F^2 (SHELXL97),[8] 252 variables, $wR2$ (all data) = 0.1162, $R1$ [for 3347 data with $I > 2\sigma(I)$] = 0.0444, max./min. electron density from final difference Fourier map, 0.437 and −0.200 e Å^{-3}.

CCDC 182/1628. See http://www.rsc.org/suppdata/cc/b0/b000380h/ for crystallographic files in .cif format.

1 (*a*) P. J. Shapiro, E. E. Bunel, W. P. Schaefer and J. E. Bercaw, *Organometallics*, 1990, **9**, 867; (*b*) J. Okuda, *Chem. Ber.*, 1990, **123**, 1649; (*c*) T. Eberle, T. P. Spaniol and J. Okuda, *Eur. J. Inorg. Chem.*, 1998, 237; (*d*) A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587 and references therein; (*e*) L. Duda, G. Erker, R. Fröhlich and F. Zippel, *Eur. J. Inorg. Chem.*, 1998, 1153; (*f*) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem.*, 1999, **111**, 448; *Angew. Chem., Int. Ed.*, 1999, **38**, 4228.

2 W. Kaminski, *J. Chem. Soc., Dalton Trans.*, 1998, 1413 and references therein.

3 (*a*) H. Braunschweig, C. von Koblinski and R. Wang, *Eur. J. Inorg. Chem.*, 1999, 69; (*b*) H. Braunschweig, C. von Koblinski and M. O. Kristen, Patentschrift, O.Z.0050/49643, 1998, submitted; H. Braunschweig, C. von Koblinski, M. Mamuti, U. Englert and R. Wang, *Eur. J. Inorg. Chem.*, 1999, 1899.

4 A. J. Ashe, III, X. Fang and J. W. Kampf, *Organometallics*, 1999, **18**, 2288; M. T. Reetz, M. Willuhn, C. Psiorz and R. Goddard, *Chem. Commun.*, 1999, 1105.

5 Y. Chen and T. J. Marks, *Organometallics*, 1997, **16**, 3649.

6 G. M. Sheldrick, SHELXL97: Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.