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

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In the course of investigations on new Ziegler–Nattaanalogous 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 1990¹ 'constrained geometry' complexes as catalysts for olefin polymerization have attracted considerable interest, since they show some distinct advantages in comparison to metal-locene-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 us³ 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 $[\{\eta^5: \eta^1-C_5H_4B(NPr^i_2)NPh\}TiX_2]$ (X = NMe₂, 1; X = Cl, 2).

Similarly to the synthesis of the corresponding [1]boratitanocenophanes [$\{(\eta^5-C_5H_4)_2BNR_2\}$ Ti(NMe₂)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 Me₃SiCl 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 cyclopentadienlyl protons forming an AA'BB' spin system. Double sets of signals for the isopropyl groups in the ¹H and ¹³C NMR spectra indicate a hindered rotation with respect to the boron–nitrogen double bond in **1** and **2**. The ¹¹B 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 $P\overline{1}$ 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,



Scheme 1 Reagents and conditions: i, hexane, 0 °C, Na(C₅H₅); ii, toluene, 0 to 25 °C, Li(NPhH); iii, toluene, -78 to 40 °C, [Ti(NMe₂)₄], 78%; iv, hexane, 0 °C, Me₃SiCl, 98%.

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



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.

respectively, while the Ti–N1 distance is markedly longer at 2.020(2) Å.

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.

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Notes and references

‡ For a recent review on non-metallocene catalysts see ref. 1(*f*). § *Spectroscopic data*: 1: ¹H NMR (499.658 MHz, CD₂Cl₂): δ 0.90 (br, 6H, CHCH₃), 1.45 (br, 6H, CHCH₃), 2.97 (s, 12H, NMe₂), 3.31 (br, 2H, CHCH₃), 5.94 (m, 2H, C₅H₄), 6.44 (m, 2H, C₅H₄), 6.73 (m, 2H, C₆H₅), 6.83 (m, 1H, C₆H₅), 7.14 (m, 2H, C₆H₅). ¹¹B NMR (160.310 MHz, CD₂Cl₂): δ 27.76. ¹³C NMR (125.639 MHz, CD₂Cl₂): δ 21.36 (br), 27.01 (br), 44.62 (br), 46.11 (br), 47.90 (NMe₂), 120.95 (C₅H₄), 124.00 (C₅H₄), 115.81, 119.99, 128.16, 155.48. MS (EI) (*m*/*z*, %): 402 (M⁺, 45), 387 (M⁺ - Me, 5), 358 (M⁺ - NMe₂, 65), 314 (M⁺ - 2NMe₂, 100), 93 (C₆H₅NH₂⁺, 95), 64 (C₅H₄⁺, 45). Correct elemental analysis.

2: ¹H NMR (499.658 MHz. CD_2CI_2): $\delta 0.90$ (d, 6H, ³*J* 6.71 Hz, CHCH₃), 1.54 (d, 6H, ³*J* 6.71 Hz, CHCH₃), 3.14 (m, 1H, ³*J* 6.71 Hz, CHCH₃), 3.41 (m, 1H, ³*J* 6.71 Hz, CHCH₃), 6.44 (m, 2H, C₅H₄), 7.08 (m, 2H, C₅H₄), 6.91 (m, 2H, C₆H₅), 7.14 (m, 1H, C₆H₅), 7.38 (m 2H, C₆H₅). ¹¹B NMR (160.310 MHz, CD₂CI₂): $\delta 28.29$. ¹³C NMR (125.639 MHz, CD₂CI₂): $\delta 21.40$, 27.72, 45.20, 47.28, 122.52 (C₅H₄), 125.71 (C₅H₄), 124.32, 127.21, 129.62, 152.39. MS (EI) (*m*/*z*, %): 384 (M⁺, 15), 369 (M⁺ – Me, 30), 348 (M⁺ – Cl, 50), 333 (M⁺ - Cl - Me, 20), 318 (M⁺ - Cl - 2Me, 20], 93 (C₆H₅NH₂⁺, 70), 64 (C₅H₄⁺, 25). Correct elemental analysis.

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

Crystal data: triclinic, space group $P\overline{I}$, a = 9.464(6), b = 9.754(4), c = 13.596 Å, $\alpha = 101.94(2)$, $\beta = 102.32(4)$, $\gamma = 103.37(4)^{\circ}$, V = 1149 Å³, Z = 2, $D_c = 1.17$ g cm⁻³, $\mu = 3.8$ cm⁻¹. 4351 reflections, 4068 independent, $\theta_{\text{max}} = 26^{\circ}$, solution with direct methods (SHELXS97),⁶ refinement on F^2 (SHELXL97),⁸ 252 variables, *wR*2 (all data) = 0.1162, *R*1 [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.

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