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Synthesis and structure of $[Zr\{\eta^5:\eta^1\text{-}C_9H_6B(N^iPr_2)NPh\}_2]$: a new complex with a boron-bridged amido-indenyl ligand

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Dedicated in honor of Professor Pierre Braunstein

Abstract

A boron-bridged amido-cyclopentadienyl ligand was recently shown to form constrained-geometry titanium-complexes that are capable of olefin polymerisation. Here, the synthesis of the corresponding amido-indenyl ligand η^1-$C_9H_7B(N^iPr_2)N(H)Ph$ (C_9H_7 = indenyl) (**2a**/**2v**) and its allyl–vinyl isomerisation are discussed. Deprotonated **2a** reacts with $ZrCl_4$ to give the strongly distorted zirconocene-type complex $[Zr\{\eta^5:\eta^1\text{-}C_9H_6B(N^iPr_2)NPh\}_2]$ (**3**) in a 2:1 reaction. All compounds have been characterised by multinuclear NMR methods and structures of both the ligand **2a** and the complex **3** have been confirmed by X-ray diffraction.

Keywords: Boron; Boranes; Amido-cyclopentadienyl ligand; Constitutional isomers; Zirconocene

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1. Introduction

Since 1990 [1] amido-cyclopentadienyl ligands (**I**) and corresponding 'constrained geometry' complexes (CGC) (**IIa**) have attracted considerable interest, because the latter exhibit some distinct advantages as catalysts for olefin polymerisation in comparison to metallocene-based Ziegler–Natta type catalysts [2]. CGC show a better copolymerisation performance with regard to higher olefins and an increased stability towards MAO even at elevated temperatures [1g]. A great number of ligands of this type have been synthesised over the past years by variation of either the cyclopentadienyl or amido fragment, or the bridging moiety, with silicon and carbon to be the most common elements in the bridge.

Recently, we started to investigate the chemistry of both strained [3] and unstrained [4] [1]b borametallocenophanes. This class of compounds exhibits an interesting chemistry due to the special characteristics of the incorporated boron atom. For example, the Lewis acidic three coordinate boron centre in the bridge of Group IV metallocenophanes enhances their catalytic activities [5] with respect to Ziegler–Natta type olefin polymerisation [4a,4b,4c,6]. In due course we extended our synthetic strategy to the synthesis of boron bridged amido-cyclopentadienyl ligands and the first boron-bridged CGC of titanium [7] in order to obtain catalysts that combine the advantageous properties of both the CGC and [1] borametallocenophanes (vide supra).

Synthesis of Group IV CGC is generally straightforward, applying the protonated ligand and a Group IV

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[1] X-ray crystallography.

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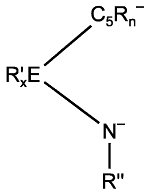
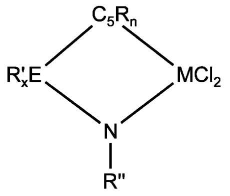
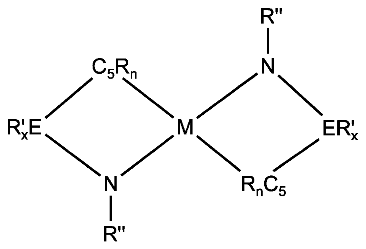


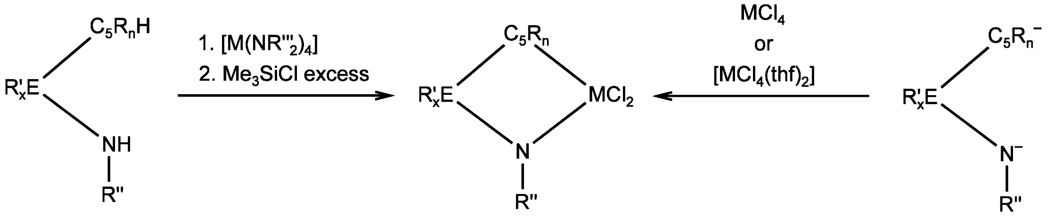
I



IIa



IIb

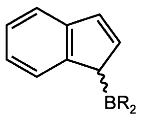


Scheme 1.

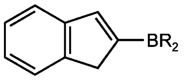
precursor such as $[M(NR_2)_4]$ (M = Ti, Zr, Hf, R = Me, Et) [8] or the deprotonated ligand and a precursor such as $[MCl_4(thf)_x]$ (M = Ti, $x = 2$ [1c]; M = Zr, Hf, $x = 0, 2$ [9]), respectively (Scheme 1). However, formation of metallocene-like complexes **IIb** with two ligands per transition metal can often be observed under these conditions, especially in the case of the larger metals zirconium and hafnium, and when the transition metal halides are used as precursors [9b,10]. Transition metal amides give the metallocene derivatives only when an excess of the ligand (more than a 1:1 ratio with respect to the transition metal) is employed [8c,8d], but they are only applicable as precursors when the ligands show a sufficiently high acidity, e.g. for less substituted cyclopentadienyl systems. Though formally being 20-electron complexes [9b], the metallocenes incorporating two linked amido-cyclopentadienyl ligands can catalyse the polymerisation of ethylene and propylene when activated with MAO [8c,8d].

In the present paper we report on the synthesis and structural details of a new boron bridged amino-indenyl ligand precursor and a corresponding zirconocene complex incorporating two of these ligands.

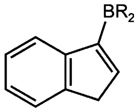
Starting from lithium indenide and boron halides, the boron can in principle end up being attached to either 1-(allyl), 2- (vinyl) or 3-position (vinyl) of the indenyl system (**IIIa**–**c**). In most cases, only 1-indenyl and 3-indenyl products can be observed [11], with the former being the kinetically favoured and the latter being the thermodynamically favoured product [4c,4d,11,12]. Isomerisation of the kinetically favoured product by prototropic rearrangement (1,3-shift) can generally be achieved at elevated temperature or in the presence of bases. In this paper, we also report on our investigations on the isomerisation of the ligand precursor and a related intermediate.



IIIa



IIIb



IIIc

2. Experimental

2.1. Syntheses

All manipulations were carried out under a dry nitrogen atmosphere with common Schlenk techniques. Solvents and reagents were dried by standard procedures, distilled, and stored under nitrogen over molecular sieves. $^{i}Pr_2NBCl_2$ [13] and lithium indenide ($Li[C_9H_7]$) [14] were obtained according to literature procedures, whereas lithium anilide ($Li[NHC_6H_5]$) was obtained by stoichiometric addition of $^{n}BuLi$ to a solution of aniline in toluene. NMR: Varian Unity 500 at 499.843 MHz (^{1}H, external standard TMS), 150.364 MHz (^{11}B, $BF_3 \cdot OEt_2$ in C_6D_6 as external standard), 125.639 MHz ($^{13}C\{^{1}H\}$, APT, internal standard TMS);

all NMR spectra were recorded in CD_2Cl_2 as solvent unless otherwise stated. Mass spectra were recorded on a Finnigan MAT 95 (70 eV) and elemental analyses (C, H, N) were obtained from a Carlo-Erba elemental analyser, model 1106.

2.1.1. η^1-$C_9H_7B(N^iPr_2)Cl$ (**1a**)

Li[C_9H_7] (2.11 g, 17.3 mmol) was suspended in 20 ml hexane and a solution of $^iPr_2NBCl_2$ (3.15 g, 17.3 mmol) in 15 ml hexane was added dropwise at 0 °C. The white suspension was allowed to come to ambient temperature and stirred for 16 h. The precipitated LiCl was filtered off and washed with 10 ml hexane. The filtrate was concentrated and stored at −30 °C to yield **1a** as colourless crystals (3.66 g, 98%).

^{1}H NMR (C_6D_6): $\delta = 1.25$, 1.27 (br 2d, 6H, Me); 3.14 (m, 2H, CH^iPr); 3.80 (m, 1H, B–CH_{ind}); 6.40–7.60 (m, 6H, CH_{ind}). ^{13}C NMR (−60 °C): $\delta = 22.38$, 23.23 (br, Me); 40.43 (CH^iPr); 48.38 (br, B–CH_{ind}); 121.48, 122.33, 123.92, 126.11, 131.91, 136.74 (CH_{ind}); 145.68, 147.35 (C_{ind}). ^{11}B NMR: $\delta = 37.6$. MS; *m/z* (%): 261(70) [M^+], 246(77) [$M^+ - Me$], 218(19) [$M^+ - C_3H_7$], 146(64) [$M^+ - C_9H_7$], 115(61) [C_9H_7], 43(100) [C_3H_7]. $C_{15}H_{21}BClN$ (216.60) Calc. C, 68.87; H, 8.09; N, 5.35. Found: C, 68.36; H, 8.12; N, 5.31%.

2.1.2. η^1-$C_9H_7B(N^iPr_2)Cl$ (**1v**)

Compound **1a** (3.92 g, 18.1 mmol) was dissolved in 50 ml hexane, a catalytic amount of triethylamine (0.2 ml, 1.4 mmol) was added and the solution was stirred for 16 h at ambient temperature. The solution was concentrated and stored at −30 °C to yield **1v** as a colourless crystalline solid (3.84 g, 98%).

^{1}H NMR (C_6D_6): $\delta = 0.83$, 1.40 (2d, 6H, Me); 3.11 (m, 2H, CH_{2ind}); 3.44, 3.79 (2m, 1H, $CH_{^iPr}$); 6.38 (m, 1H, 2-CH_{ind}); 7.00–7.60 (m, 4H, CH_{ind}). ^{13}C NMR: $\delta =$ 22.26, 23.22 (Me); 40.42 (CH_{2ind}); 46.88, 51.36 (CH^iPr); 122.31, 123.91, 124.88, 126.59, 137.20 (CH_{ind}); 144.21, 147.54 (C_{ind}), 149.43 (br, B–C_{ind}). ^{11}B NMR: $\delta = 34.7$. MS; *m/z* (%): 261 (100) [M^+], 246(88) [$M^+ - Me$], 218(41) [$M^+ - C_3H_7$], 146(34) [$M^+ - C_9H_7$], 115(32) [C_9H_7], 44(66) [C_3H_7]. $C_{15}H_{21}BClN$ (216.60) Calc. C, 68.87; H, 8.09; N, 5.35. Found: C, 68.33; H, 8.14; N, 5.34%.

2.1.3. η^1-$C_9H_7B(N^iPr_2)N(H)Ph$ (**2a**)

As described for **1a**, Li[C_9H_7] (3.42 g, 28.0 mmol) was reacted with $^iPr_2NBCl_2$ (5.10 g, 28.0 mmol). After removing LiCl by filtration, the filtrate was added dropwise at 0 °C to a suspension of Li[NHC_6H_5] (2.77 g, 28.0 mmol) in 50 ml toluene. The white suspension was allowed to come to ambient temperature and stirred for 16 h. The precipitated LiCl was filtered off, washed with 20 ml hexane and the solvent of the filtrate was removed in vacuo to give a slightly yellow amorphous solid. Recrystallisation from hexane at −30 °C yielded **2a** as colourless cubic crystals (8.54 g, 96%).

^{1}H NMR (−80 °C): $\delta = 0.14$ (d, 3H, $^3J = 6.71$, Me); 0.66 (d, 3H, $^3J = 6.71$, Me); 1.25, 1.27 (2d, 3H, $^3J = 7.02$, Me); 1.57 (m, 1H, CH^iPr); 3.04 (m, 1H, CH^iPr); 3.72 (m, 1H, B–CH_{ind}); 5.25 (s, 1H, NH); 6.70–7.50 (m, 11H, CH_{ind}, C_6H_5). ^{13}C NMR (−60 °C): $\delta = 19.45$, 23.32 (Me); 42.52 (br, B–CH_{ind}); 42.78, 46.62 (CH^iPr); 117.45, 118.14, 119.11, 120.62, 121.33, 123.51, 124.42, 128.09, 128.64, 128.93, 139.70 (CH_{ind}, C_6H_5); 144.34, 148.60 (C_{ind}). ^{11}B NMR: $\delta = 30.9$. MS; *m/z* (%): 318(30) [M^+], 303(40) [$M^+ - Me$], 203(80) [$M^+ - C_9H_7$], 161(100) [$M^+ - C_9H_7 - C_3H_7$], 115(25) [C_9H_7]. $C_{21}H_{27}BN_2$ (318.27) Calc. C, 79.25; H, 8.55; N, 8.80. Found: C, 78.66; H, 8.59; N, 8.78%.

2.1.4. η^1-$C_9H_7B(N^iPr_2)N(H)Ph$ (**2v**)

Li[NHC_6H_5] (1.30 g, 13.1 mmol) was suspended in 40 ml toluene and a solution of **1v** (2.84 g, 13.1 mmol) in 25 ml toluene was added dropwise at 0 °C. The reaction mixture was allowed to come to ambient temperature and stirred for 16 h. Precipitated LiCl was removed from the yellow–green suspension by filtration, washed with 10 ml hexane and the solvent of the filtrate was remove in vacuo. Recrystallisation of the crude product from hexane at −30 °C yielded **2v** as a colourless crystalline solid (3.70 g, 89%).

^{1}H NMR (−20 °C): $\delta = 1.04$ (d, 3H, $^3J = 6.72$, Me); 1.06 (d, 3H, $^3J = 6.72$, Me); 1.53 (d, 3H, $^3J = 6.71$, Me); 1.54 (d, 3H, $^3J = 7.02$, Me); 3.45 (m, 2H, CH_{2ind}); 3.53, 3.61 (2m, 1H, $CH_{^iPr}$); 5.33 (s, 1H, NH); 6.40–7.60 (m, 10H, CH_{ind}, C_6H_5). ^{13}C NMR (−60 °C): $\delta = 21.65$, 22.19, 23.98, 24.23 (Me); 40.45 (CH_{2ind}); 43.01, 49.73 ($CH_{^iPr}$); 119.33, 119.50, 121.66, 123.55, 124.07, 125.27, 126.00, 128.21, 129.01, 137.60 (CH_{ind}, C_6H_5); 144.34, 145.44 (C_{ind}); 148.55 (B–C_{ind}). ^{11}B NMR: $\delta = 28.2$. MS; *m/z* (%): 318(57) [M^+], 303(100) [$M^+ - Me$], 216(25) [$M^+ - {}^iPr_2NBH$], 115(19) [C_9H_7]. $C_{21}H_{27}BN_2$ (318.27) Calc. C, 79.25; H, 8.55; N, 8.80. Found: C, 78.55; H, 8.58; N, 8.78%.

2.1.5. [$Zr\{\eta^5{:}\eta^1$-$C_9H_6B(N^iPr_2)NPh\}_2$] (**3**)

Compound **2a** (1.27 g, 4.00 mmol) was dissolved in 40 ml toluene and 10 ml diethylether. LiBu (1.6 M) solution in hexane (5.00 ml, 8.00 mmol) was added dropwise at 0 °C. The resulting white suspension was allowed to come to ambient temperature and subsequently stirred for 6 h. The mixture was then cooled to −40 °C and $ZrCl_4$ (0.93 g, 4.00 mmol) was added. The red–brown suspension was warmed to ambient temperature and stirred for 16 h. Precipitated LiCl was filtered off and washed with 10 ml toluene. The filtrate was concentrated and stored for 3 days at ambient temperature to yield **3** as yellow crystals (1.37 g, 95%).

^{1}H NMR: $\delta = 0.85$, 1.01, 1.16, 1.25 (4d, 6H, Me); 3.21 (m, 2H, $CH_{^iPr}$); 3.55 (m, 2H, $CH_{^iPr}$); 5.30 (m, 2H,

CH_{ind}); 6.80–7.70 (m, 20H, CH_{ind}, C_6H_5). ^{13}C NMR: $\delta = 21.47$, 22.06, 26.32, 27.69 (Me); 44.40, 46.52 (CH_{iPr}); 100.23, 121.54, 123.55, 125.33, 125.77, 126.13, 127.34, 128.68, 129.91 (CH_{ind}, C_6H_5); 159.37 (C_i). ^{11}B NMR: $\delta = 27.5$. MS; m/z (%): 723(100) [M^+], 707(40) [$M^+ -$ Me], 115(50) [C_9H_7]. $C_{42}H_{50}B_2N_4Zr$ (723.73) Calc. C, 69.70; H, 6.96; N, 7.74. Found: C, 68.93; H, 7.24; N, 7.13%.

2.2. X-ray structure determination

2.2.1. Crystal structure of compound **2a** ($C_{23}H_{20}BN_2$)

The intensity data were collected on a Enraf–Nonius CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator) at −50 °C with $\omega - 2\theta$ scans [15]. The data were corrected by LP factors, and no absorption correction was done. The structure was solved by the direct method [16] and refined by full-matrix least-square method [17]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms are located from the difference Fourier map and refined isotropically. Atom scattering factors were taken from International Tables for X-Ray Crystallography (1983) [18].

Compound **2a**, $C_{23}H_{20}BN_2$, white plate of dimensions 0.44 × 0.36 × 0.16 mm, crystallises in the triclinic space group $P1$ (No. 2); $a = 8.222(3)$, $b = 10.106(8)$, $c = 13.018(4)$ Å, $\alpha = 111.61(4)°$, $\beta = 95.73(3)°$, $\gamma = 103.99(4)°$, $V = 954.2(9)$ Å^3, $Z = 2$, $\mu = 0.063$ mm^{-1}; 3591 reflections collected in the range 6.0–50.0° in 2θ, 3338 reflections independent, 1310 reflections observed ($I > 2\sigma(I)$); 324 parameters, R_1/wR_2-values 0.088/0.217, R_1/wR_2-values at $I > 2\sigma(I)$ 0.1848/0.2193, GOF 0.868; max/min residual electron density 0.246/−0.284 e Å^{-3}.

2.2.2. Crystal structure of compound **3** ($C_{42}H_{50}B_2N_4Zr$)

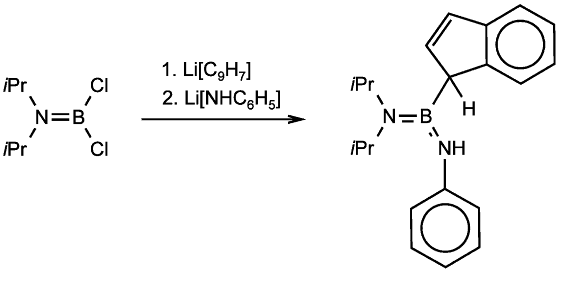
The intensity data were collected on an Stoe IDPS image plate diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator) at −103 °C. The data was corrected by LP factors and no absorption correction was done. The structure was solved by the direct method and refined by full-matrix least-square method [17,19,20]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms are located from the difference Fourier map and refined isotropically. Atom scattering factors were taken from International Tables for X-Ray Crystallography (1983) [18].

Compound **3**, $C_{42}H_{50}B_2N_4Zr$, yellow cube of dimensions 0.1 × 0.1 × 0.1 mm, crystallises in the monoclinic space group $C2/c$ (No. 15); $a = 19.797(3)$, $b = 15.400(7)$, $c = 12.917(2)$ Å, $\beta = 91.22(3)°$, $V = 3937.3(9)$ Å^3, $Z = 4$, $\mu = 0.260$ mm^{-1}; 18 604 reflections collected in the range 3.8–56.3° in 2θ, 4456 reflections independent, 3270 reflections observed ($I > 2\sigma(I)$); 322 parameters, R_1/wR_2-values 0.062/0.088, R_1/wR_2-values at $I > 2\sigma(I)$ 0.039/0.081, GOF 0.969; max/min residual electron density 0.34/−0.47 e Å^{-3}.

3. Results and discussion

3.1. Ligand synthesis

Synthesis of the diaminoindenyl borane **2a** is straightforward by subsequent reaction of $^iPr_2NBCl_2$ with 1 equiv. each of lithium indenide and lithium anilide in a hexane slurry at ambient temperature (Eq. (1)).



2a

(1)

No workup is required for the intermediate amino(indenyl)borane (**1a**), although this compound can be easily isolated and purified by recrystallisation. Both compounds **1a** and **2a** can be obtained via this route in almost quantitative yield and multinuclear NMR spectra proved them to be free of impurities. ^1H NMR spectra for both compounds reveal that the allylic boron indenyl derivatives were formed exclusively by this reaction sequence [4d], since only the allylic protons could be detected at 3.80 and 3.72 ppm, respectively. ^{13}C NMR spectra provide further proof since the boron substituted carbon atoms show signals at 48.38 and 42.52 ppm, respectively, that are generally attributed to allyl boranes, and no signals in the expected region for vinyl boranes at 145–150 ppm could be observed [12e].

At ambient temperature, the nitrogen bonded isopropyl groups of **2a** show coalescence in both ^1H and ^{13}C NMR spectra, whereas the isopropyl groups in **1a** are resolved at this temperature. This observation is due to a localisation of the B–N bond in the latter case, whereas in the former boron is bonded to two nitrogen atoms which lowers the double-bond character of both B–N bonds and allows for easier rotation of the N^iPr_2 moiety. At low temperature (−80 °C), the ^1H NMR spectrum of **2a** shows a resolution of the signals for the isopropyl groups, with four doublets at 0.14, 0.66, 1.25 and 1.27 ppm in an integral ratio of 3H:3H:3H:3H for the methyl groups and two multiplets at 1.57 and 3.04 for the CH-protons. Correlation of the dublets with the corresponding multiplets was achieved by a low temperature 2D-COSY NMR experiment. The first two doublets and the first multiplet are attributed to the isopropyl group,

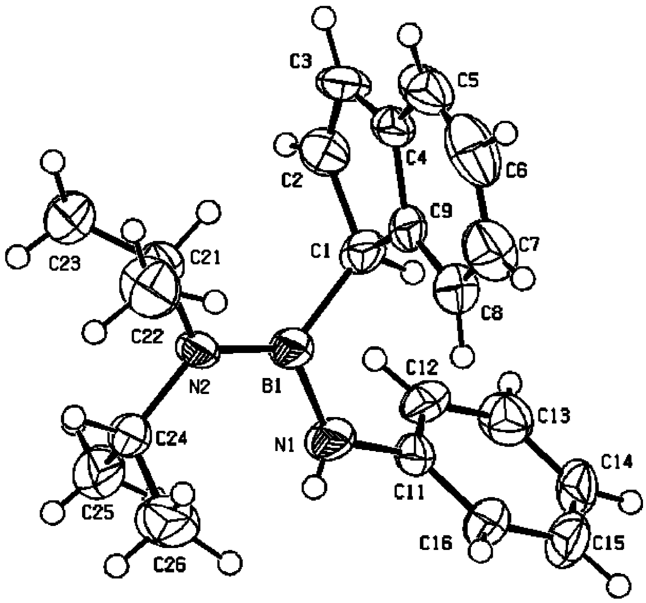
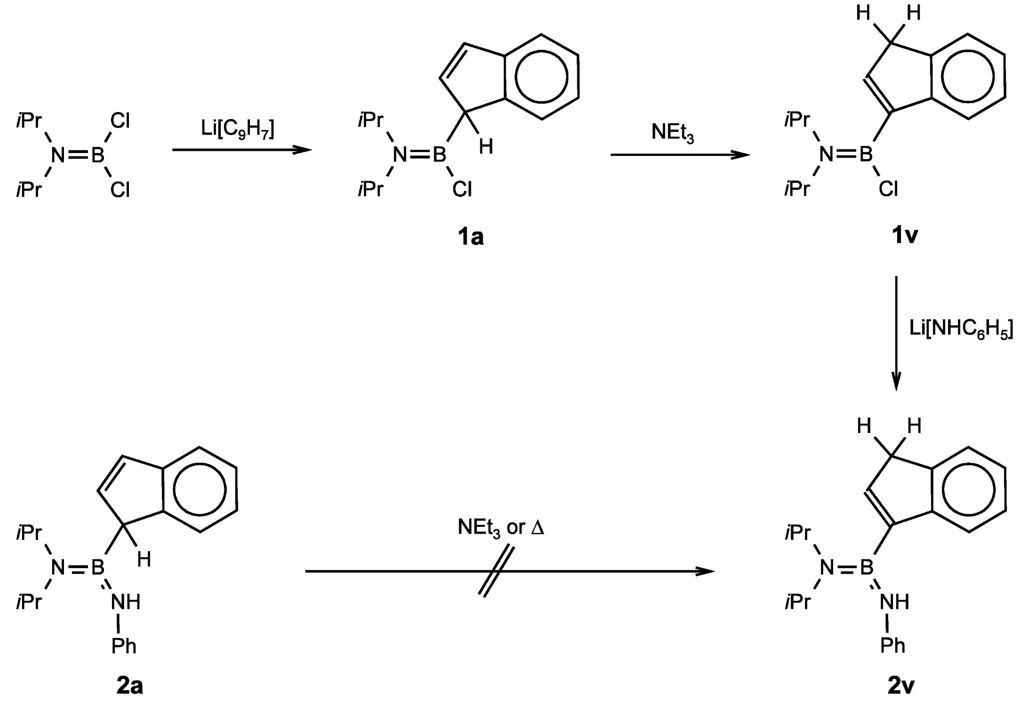


Fig. 1. Molecular structure of **2a**. Selected distances (Å) and angles (°): B–N1 1.430(6), B–N2 1.413(6), B–C1 1.610(7), N1–C11 1.425(6), N1–B–N2 118.9(4), N1–B–C1 117.1(4), C21–N2–C24 113.9(4), C24–N2–B–N1 −8.7, C21–N2–B–N1 168.9.

which is *cis* to the indenyl group. Their significant high field shift indicates a transfer of ring current from the π-system of the indenyl group towards the neighbouring isopropyl group. In the crystal (vide infra), the affected isopropyl group points deep into the anisotropic cone of the π-system and should be, therefore, fairly deshielded, provided the molecular structures in solution and solid state are similar as it was already observed in the case of the related $Me_2NB(C_{13}H_9)_2$ ($C_{13}H_9$ = fluorenyl) [4d]. The splitting of these methyl groups into two sets of signals appears to be due to a hindered rotation with respect to the C–N bond. Rotation of the ^{i}Pr-group would reduce the distance between distinct methyl protons and the indenyl plane to approximately 130 pm in comparison to about 230 pm in the solid state conformation, therefore, preventing free rotation [21]. The signals that correspond to the isopropyl group in *trans* position to the indenyl group are expectedly less deshielded, and show likewise resolution of both methyl groups into two sets of signals. This somehow unexpected observation may be due to a obstructed rotation of this isopropyl group with respect to the C–N bond, which may be caused by the hindered rotation of the neighbouring isopropyl group which is attached to the same nitrogen centre (vide supra).

A suitable single crystal of **2a** was obtained from a solution in hexane at −30 °C. The compound crystallises in the space group *P*1 and the molecule adopts C_1 symmetry (Fig. 1).

The boron and both nitrogen atoms are in a trigonal-planar environment. The B–N1 and B–N2 distances of 143.0(6) and 141.3(6) pm, respectively, indicate presence of some π-interaction in both cases. The B–C1 distance of 161.0(7) is similar to the corresponding distance in $^{i}Pr_2NB(\eta^1\text{-}C_5H_5)(\eta^1\text{-}C_9H_7)$ [4d], but in contrast to the crystal structure of the latter compound, the indenyl plane is not pointed away from the nitrogen bonded isopropyl group but towards it. This leads to a



Scheme 2.

comparably strong interaction of the isopropyl group with the π-system as was previously discussed in conjunction with the NMR spectroscopic data.

3.2. Indenyl borane isomerisation

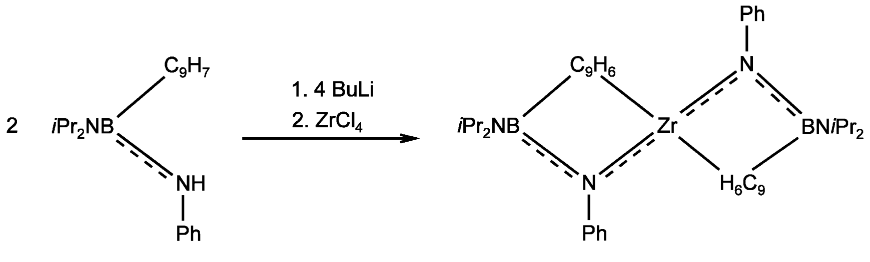
Isomerisation of indenyl boranes is well-known and occurs generally at elevated temperature or in the presence of bases [4d,12]. We, therefore, investigated the isomerisation of **1a** and **2a** that were obtained exclusively as the allylic isomers following our reaction sequence. Compound **1a** readily undergoes isomerisation by 1,3-prototropic rearrangement to the thermodynamically favoured product **1v** in the presence of catalytic amounts of NEt_3, whereas **2a** does not isomerise neither in the presence of NEt_3 nor in refluxing benzene. The thermodynamically favoured ligand precursor **2v**, therefore, can be obtained only by reaction of the intermediate **1v** with lithium anilide, but not directly from the allylic product **2a** (Scheme 2).

These observations may be explained by the effect various numbers of nitrogen atoms attached to the boron centre have on its Lewis acidity. A higher number of nitrogen atoms lowers the Lewis acidity of the boron atom, and hence, reduces the π-contribution of an attached vinylic system. At the same time, it is well-known that in pentamethylcyclopentadienyl boranes the activation energy for sigmatropic rearrangements is drastically higher for less Lewis acidic amino substituted derivatives in comparison to highly Lewis acidic alkyl or halide substituted compounds [22]. Therefore, the inability of **2a** to rearrange **2v** can be attributed to the low Lewis acidity of the boron centre caused by two amino groups, one of them even having a phenyl group attached which can donate further π-electron density [23]. These arguments explain as well, why previously synthesised $(^iPr_2N)BCl(C_9H_7)$ was exclusively obtained as the thermodynamically favoured isomer **1v** [24]. In this case the compound was synthesised via the dichloro(indenyl)borane as an intermediate, which underwent rapid rearrangement.

Compound **1v** and **2v** were analysed by multinuclear NMR techniques in solution. In comparison to the allylic isomers **1a** and **2a**, in the ^{13}C NMR spectra they show signals for the boron bonded vinylic carbon atoms at 149.43 and 148.55 ppm, respectively, and therefore, in the expected region. The ^{11}B NMR spectra of **1v** and **2v** show signals at 34.7 and 28.2 ppm, respectively, indicating a slightly deshielding effect on the boron atom by the attached vinylic system in comparison to their allylic counterparts **1a** and **2a** with signals at 37.6 and 30.9 ppm, respectively. In the ^1H NMR spectrum of **2v**, coalescence for the isopropyl groups is observed at ambient temperature, whereas at −20 °C the signals are resolved into four doublets for the methyl protons and two multiplets for the CH-protons. Assignment of the signals follows the same pattern as described for **2a** (vide supra).

3.3. Complex synthesis

Attempts to react the ligand precursor **2a** and $[Zr(NEt_2)_4]$ with amine elimination to yield a zirconium CGC failed probably due to insufficient acidity of the ligand precursor. Deprotonation of ligand precursor **2a** with BuLi and subsequent reaction with 1 equiv. $ZrCl_4$ in a 4:1 mixture of toluene and diethyl ether at −40 °C gave the zirconocene complex **3** in high yield (Eq. 2) [25]. After removing LiCl and excess $ZrCl_4$, recrystallisation from toluene at ambient temperature afforded yellow cubic crystals of **3** that were suitable for X-ray structure determination. Compound **3** is moderately soluble in common aliphatic and aromatic solvents, and fairly stable towards air, especially in its crystalline from. Although the general formation of both *rac* and *meso* forms can be expected in the case of **3**, the multinuclear NMR data strongly suggest the formation of only one diastereomer. As to be expected, NMR spectra of **3** are rather complex, but reveal single sets of signals for the



2a/2v **3**

(2)

C_{ipso} atoms of the phenyl groups and the CH-moieties of the *iso*propyl groups—the latter being doubled as to be expected for a hindered rotation with respect to the B=N double bond—and thus giving evidence for the presence of only one diastereomer. It should be noted, though that the methyl groups show a double set of signals in the ^{1}H and ^{13}C NMR spectra. This could be accounted for by a hindered rotation of the *iso*propyl groups due to sterical hindrance as previously discussed for the free ligand. The ^{11}B NMR signal at 27.5 ppm is in the expected region for aryl diamino boranes [26].

The compound crystallises in the space group *C*2/*c* and the molecule adopts C_2-symmetry in the crystal (Fig. 2). Both boron and nitrogen atoms are in a trigonal-planar environment. The boron–nitrogen distance for B–N2 of 140.8(1) pm indicates a boron–nitrogen double bond, whereas the boron–nitrogen distance for B–N1 of 144.6(7) pm is slightly elongated, probably due to steric constraints in the compound.

The zirconium–nitrogen distances of 215.7(0) pm are significantly longer than the zirconium–nitrogen distance in the related Zr CGC [{(η^5-C_5Me_4)$SiMe_2$(N^t-Bu)}$ZrCl_2$] (205.2(2) pm) [8e] and slightly longer than in the analogue zirconocene complex [{(η^5-C_5H_4)Si-Me_2(NPh)}$_2$Zr] (212.7(2) and 213.7(2) pm) [8c,8d]. This may be due to an electronic 'oversaturation' of the zirconium centre with formally 20 electrons [9b] in the case of **3** and the bridging boron atoms withdrawing π-electron density from the nitrogen centres. The deformation angle ind^c–Zr–ind$'^c$ of 138.1(8)°, the Zr–ind^c distance of 222.8(4) pm and the N1–Zr–N1′ angle of 98.2(9)° indicate strong distortion in comparison to the analogue complexes [(η^5-C_5H_5)$_2$$ZrCl_2$] [27], [$Me_2NB$($\eta^5$-$C_5H_4$)$_2$$ZrCl_2$] [4c] or even [{($\eta^5$-$C_5H_4$)Si-$Me_2$(NPh)}$_2$Zr] [8c,8d]. The intramolecular distance of zirconium and boron with 284.7(2) pm is about 30 pm shorter than the analogue distance in the complex [Me_2NB(η^5-C_5H_4)$_2$$ZrCl_2$] [4c], and only about 27 pm longer than the sum of the respective van der Waals radii. No data for classical Zr–B bonds are available for direct comparison. It should be noted though, that a corresponding close contact between iron and boron was observed in [1] boraferrocenophanes [^{i}Pr_2NB(η^5-C_5H_4)$_2$Fe], however, without indication of a bonding interaction between the two atoms [3c]. The interaction of zirconium and boron in **3** is subject of further investigations.

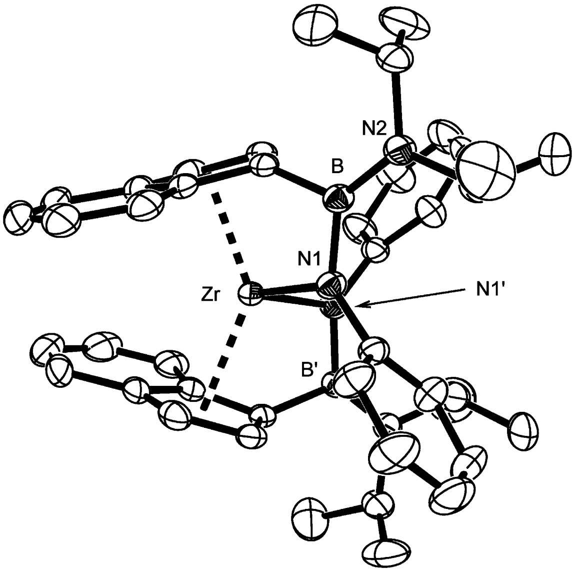


Fig. 2. Molecular structure of **3**. Selected distances (Å) and angles (°): Zr–N1 2.157(0), Zr–B 2.847(2), Zr–ind^c 2.228(4), B–N1 1.446(7), B–N2 1.408(1), B–C2 1.604(3), N1–C10 1.418(2), ind^c–Zr–ind$'^c$ 138.1(8), N1–Zr–N1′ 98.2(9), N1–B–C2 104.0(2).

4. Conclusions

With η^1-C_9H_7B(N^iPr_2)N(H)Ph (**2a/v**) we synthesised a new boron bridged amino-cyclopentadienyl precursor that is potentially suitable for the synthesis of new CGC with increased activity towards polymerisation of olefines. Isomerisation studies on the boron bonded indenyl moiety of the ligand precursor and a reaction intermediate showed a inhibited isomerisation in the presence of two attached amino groups on the boron atom, whereas in the case of only one amino group rapid isomerisation occurs. Finally, we established the synthesis of the zirconocene type complex [Zr{η^5:η^1-C_9H_6B(N^iPr_2)NPh}$_2$] (**3**) incorporating two of the described ligands in high yield. Work on the application of the ligand precursor to the synthesis of CGC, the nature of the Zr–B interaction in the described zirconocene and the activity of this complex are in progress.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 193253 (**2a**) and 193255 (**3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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