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Synthesis and structural characterization of $[H(OEt_2)_2]^+[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ — a Brønsted acid with an imidazole-derived 'non-coordinating' anion

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Dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday

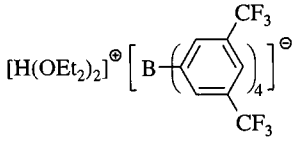
Abstract

Lithium imidazolide, generated by N–H deprotonation of imidazole with *n*-butyllithium, reacts with two molar equivalents of tris(pentafluorophenyl)borane with N–B bond formation to yield the product $Li^+[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ (**6a**, isolated in $>70\%$ yield). The analogous reaction sequence starting from 4,5-dimethylimidazole gives the corresponding salt **6b**. Its THF coordination product $[Li(THF)_4]^+[(C_3HMe_2N_2)\{B(C_6F_5)_3\}_2]^-$ (**6b**·THF) was characterized by X-ray diffraction. Deprotonation of benzimidazole followed by the addition of two $B(C_6F_5)_3$ equivalents gave the corresponding benzimidazolide-based anion, isolated as the lithium compound **6c**. The lithium salts **6** of the large 'non-nucleophilic' anion system $[(C_3HR_2N_2)\{B(C_6F_5)_3\}_2]^-$ were employed in the generation of Group 4 metallocene cations by salt metathesis. Treatment of **6a** with HCl in diethyl ether afforded the product $[H(OEt_2)_2]^+[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ (**9**), that was also characterized by X-ray crystal structure analysis. The Brønsted acid **9** was used to generate the Group 4 metallocene cation system $[Cp_2Zr(CH_3)(OEt_2)]^+$ (**11**) (with $[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ anion) starting from dimethylzirconocene. © 2002 Published by Elsevier Science B.V.

Keywords: Non-coordinating anion; Catalyst activation; Zirconocene complexes; Protonation; Metallocene cation formation

1. Introduction

The development of methods and reagents for the selective generation of alkyl Group 4 metallocene cations [1,2] and related systems is of great importance since such species can serve as very active homogeneous Ziegler–Natta catalysts under specific reaction conditions [3]. Among the various other methods, protonolytic removal of an alkyl group from, e.g. dimethylzirconocene provides an entry into stable $[Cp_2ZrR]^+$ systems [4], provided a suitable Brønsted acid that carries a low-nucleophilicity anion [5] with it is employed. Not only the trialkylammonium salts $[R_3NH]^+$ (or their dialkylanilinium analogs) with anions such as $[B(C_6H_5)_4]^-$, $[B(C_6F_5)_4]^-$ or $[B\{C_6H_3(CF_3)_2\}_4]^-$ (see Scheme 1) were successfully



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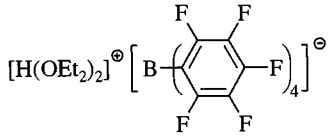

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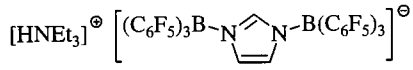

3 (LaPointe, Klosin)

Scheme 1.

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[1] X-ray crystal structure analyses.

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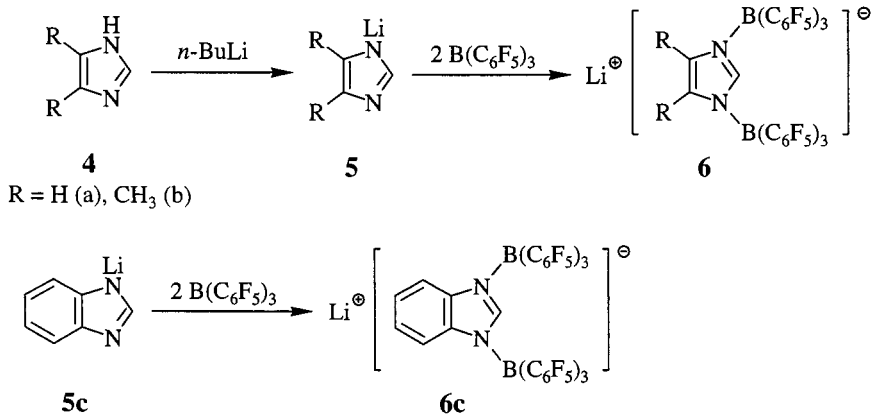


Scheme 2.

employed [2,4], but also the $[H(OEt_2)_2]^+$ salts with these anions [6]. The structural features of the $[H(OEt_2)_2]^+$ ion were characterized in the past in the case of salts with rather nucleophilic anions such as $[Zn_2Cl_6]^{2-}$ [7], but only recently was the X-ray crystal structure analysis of $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$ reported in the literature [8,9].

The large imidazole-based anion $[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ was introduced very recently into the homogeneous Ziegler–Natta catalyst activation chemistry. The corresponding triethylammonium salt, characterized by X-ray diffraction, was employed by LaPointe et al. [10] for activating a titanium-based 'constrained geometry' catalyst [11,12] used for the effective ethene–1-octene copolymerization. This has prompted us to report here the results of our related study, namely the preparation of the $[H(OEt_2)_2]^+$ salt of this imidazole–$B(C_6F_5)_3$-derived anion and its X-ray crystal structure analysis.

2. Results and discussion

2.1. Syntheses and reaction of the $[(C_3HR_2N_2)\{B(C_6F_5)_3\}_2]^-$ salts

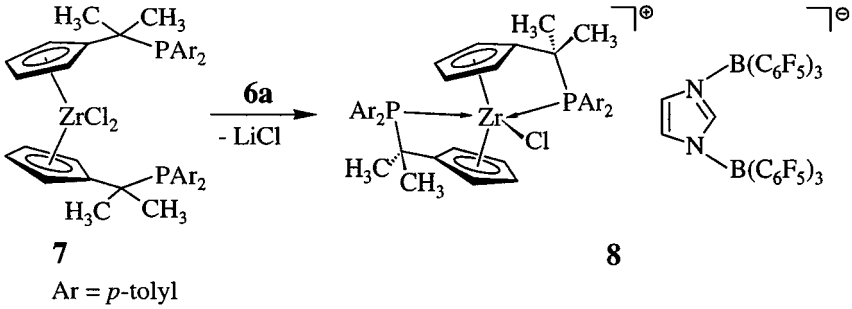
We took a synthetic approach that was slightly different from that reported by LaPointe et al. [10]. In our case, imidazole (**4a**) was N-deprotonated by the treatment with *n*-butyllithium in toluene. The resulting lithium imidazolide (**5a**) was then treated with two molar equivalents of $B(C_6F_5)_3$ [13] to yield the corresponding salt $Li^+[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ (**6a**). Compound **6a** shows a simple two line ^{1}H-NMR spectrum in benzene-d_6–THF-d_8 (10:1) solution [δ 7.95 (1H, 2-H), 6.84 (2H, 4-/5-H), with the corresponding ^{13}C-NMR signals at δ 141.4 (C-2) and 124.3 (C-4/-5)].

Analogous treatment of lithium 4,5-dimethylimidazolide (**5b**) with tris(pentafluorophenyl)borane afforded the corresponding $Li^+[(C_3HMe_2N_2)\{B(C_6F_5)_3\}_2]^-$ salt **6b** (93% isolated), and $B(C_6F_5)_3$ also added cleanly to both nitrogen atoms of the lithium benzimidazolide reagent **5c** to yield the corresponding salt **6c**, containing the benzannelated complex anion system (see Scheme 2).

The $B(C_6F_5)_3$-modified lithium imidazolide (**6a**) was employed as a chloride anion abstracting reagent [14] for the synthesis of an internally donor ligand-stabilized zirconocene cation. As a substrate we chose the zirconocene dichloride complex **7** described earlier bearing a 1-methyl-1-di(*p*-tolyl)phosphinoethyl substituent at each Cp-ligand [15]. Treatment of **7** with $Li^+[(C_3H_2N_2)\{B(C_6F_5)_3\}_2]^-$ (**6a**) in dichloromethane solution at room temperature resulted in a rapid precipitation of lithium chloride and formation of the $[(C_3H_2N_2)\{B(C_6F_5)_3\}_2]^-$ salt of the $[(\kappa P{:}\eta^5\text{-}Cp{-}CMe_2PAr_2)_2ZrCl]^+$ cation reported earlier [15]. The product **8** was isolated in ca. 80% yield (see Scheme 3).

We have used the anion $[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ for preparing a H^+-etherate salt. For that purpose, a suspension of the lithium salt **6a** was treated with one molar equivalent of HCl in ether at -30 °C. The resulting lithium chloride coproduct was removed from the reaction mixture by treatment with dichloromethane and the $[H(OEt_2)_2]^+[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ product (**9**, see Scheme 4) crystallized from CH_2Cl_2 at -30 °C (85% isolated). Product **9** was characterized by X-ray crystal structure analysis (see below). It shows typical ^{1}H-NMR singlets of the anion at δ 7.47 (1H, 2-H) and δ 6.80 (2H, 4-/5-H) and a broad H^+-resonance at δ 16.3 (in addition to the ether resonances).

The $[H(OEt_2)_2]^+$ reagent **9** was used as a Brønsted acid of a low-nucleophilicity anion for the generation of an alkyl-zirconocene cation. In dichloromethane-d_2 solution $Cp_2Zr(CH_3)_2$ (**10**) was treated with one molar equivalent of the reagent **9** at room temperature. Instantaneous methane evolution was observed by the formation of the cation $[Cp_2Zr(CH_3)(OEt_2)]^+$ (**11** with $[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ anion). The mono-etherate



Scheme 3.

complex of the Cp_2ZrMe^+ cation was identified spectroscopically (for details see Section 3). One equivalent of diethyl ether was set free in the course of this protonation reaction (identified by ^1H-/^{13}C-NMR spectroscopy).

2.2. X-ray crystal structure analyses

The new compounds **6b** and **9** were characterized by X-ray diffraction. The salt **6b** contains separated cation and anion moieties in the crystal. In the crystal of **6b** the lithium cation is tetrahedrally coordinated by four (disordered) THF molecules. The anion contains a central planar delocalized 4,5-dimethylimidazolide core.

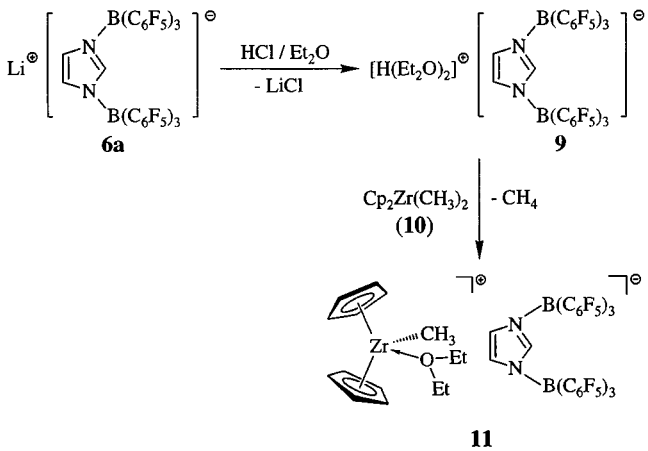
The N1–C2 (1.320(4) Å) and N3–C2 (1.331(4) Å) bonds (see Fig. 1) are both slightly shorter than the adjacent N1–C5 (1.393(4) Å) and N3–C4 (1.392(4) Å) bonds. The C4–C5 bond length in **6b** amounts to 1.350(4) Å. Both imidazolide nitrogen atoms are planar tricoordinate (for bond angles see Fig. 1). Each of the nitrogen centers contains a $B(C_6F_5)_3$ unit bonded to it (N1–B1: 1.589(4) Å; N3–B2: 1.582(4) Å). The boron centers B1 and B2 both show pseudotetrahedral coordination environments. The conformational arrangement of the three $-C_6F_5$ aryl groups and the planar hetaryl substituent at each boron atom is characterized by an approximate orientation of two C_6F_5 groups and the hetarene moiety at each boron center as a three-bladed propeller (of opposite chirality sense at B1 and B2) [16]. In each case, it is the $-C_6F_5$ substituent that occupies the 'pivot' position at each Ar_4B^- subgroup (i.e. the C11–C16 substituent at B1 and the C51–C56 group at B2, see Fig. 2). In each case, this specific $-C_6F_5$ ring is oriented coplanar with the adjacent B–N vector (coplanar orientation of the C11–C16, B1, N1 and C51–C51, B2, N3 centers, respectively).

Single crystals of the compound **9** were obtained from dichloromethane at -30 °C. The X-ray crystal structure analysis shows the presence of non-interacting $[H(OEt_2)_2]^+$ cations and $[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ anions.

The cation contains two diethyl ether molecules that are bridged by a proton (observed) located between the two ether molecules (of which one OEt_2 entity is disordered). Although the H^+ was found at a position between the two ether oxygen atoms, its large thermal parameters do not allow for a meaningful description of the hydrogen bond in compound **9** in detail [7,9].

The $[(C_3H_3N_2)\{B(C_6F_5)_3\}_2]^-$ anion of **9** also contains a planar imidazolide-derived core of atoms. The $C_3H_3N_2$ hetarene unit is delocalized with N1–C2 and N3–C2 bonds both amounting to 1.327(6) Å. The N1–C5 (1.389(6) Å) and N3–C4 (1.378(6) Å) bonds are again slightly longer (C4–C5: 1.340(7) Å). The conformational arrangement of the bulky $-B(C_6F_5)_3$ groups, that are bonded to the pair of nitrogen atoms, is slightly different in **9** than in **6c**. In the latter (see above) the two tris(pentafluoroaryl)borane groups are oriented relative to each other at the central $C_3HMe_2N_2-$ group in such a way that the resulting complex anion is almost C_s-symmetric (see Fig. 1). In **9** the conformational positions of the three aryl and the hetaryl group at each boron center is different, so that even in an idealized description the resulting overall rotameric structure of this anion in the crystal must be regarded of a chiral type.

We conclude that the salts $Li^+[(C_3HR_2N_2)\{B(C_6F_5)_3\}_2]^-$ (**6**) (with a range of imidazolide substituent variations) and $[H(OEt_2)_2]^+[(C_3H_3N_2)$-



Scheme 4.

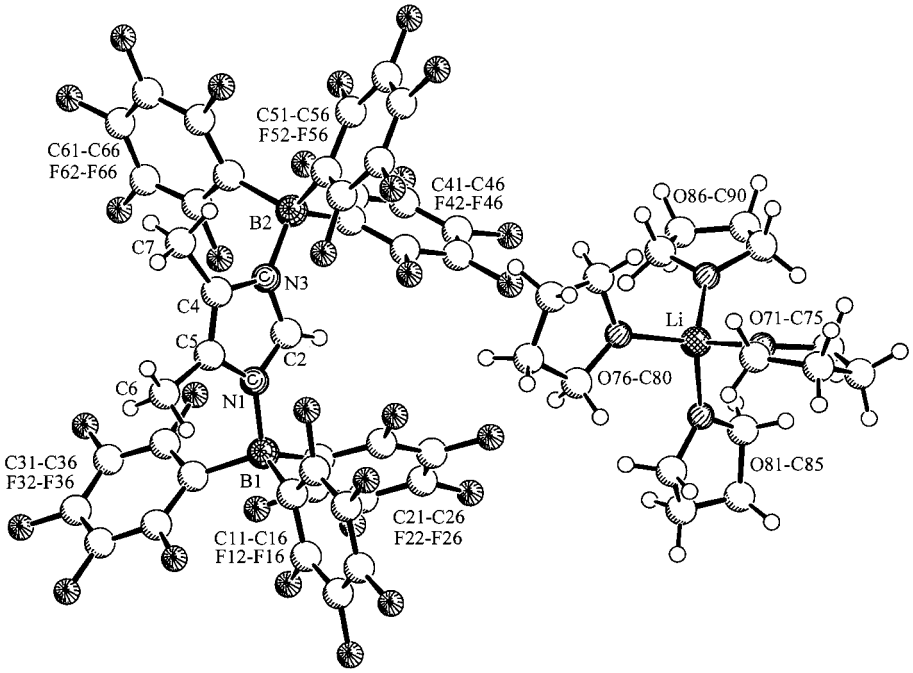


Fig. 1. Molecular structure of **6b**. Selected bond lengths (Å) and bond angles (°): N1–B1 1.589(4), N1–C2 1.320(4), N1–C5 1.393(4), C2–N3 1.331(4), N3–B2 1.582(4), N3–C4 1.392(4), C4–C5 1.350(4), C4–C7 1.492(4), C5–C6 1.491(4), B1–C11 1.653(5), B1–C21 1.650(4), B1–C31 1.644(5), B2–C41 1.656(5), B2–C51 1.645(5), B2–C61 1.657(5), Li–O71 1.918(8), Li–O76 1.912(9), Li–O81 1.870(9), Li–O86 1.917(9); B1–N1–C2 126.3(2), B1–N1–C5 127.3(2), C2–N1–C5 106.3(2), N1–C2–N3 112.2(2), B2–N3–C2 126.1(2), B2–N3–C4 127.9(2), C2–N3–C4 105.8(2), N3–C4–C5 108.0(3), N3–C4–C7 123.1(3), C5–C4–C7 128.9(3), N1–C5–C4 107.6(3), N1–C5–C6 123.3(3), C4–C5–C6 129.1(3), N1–B1–C11 111.8(3), N1–B1–C21 108.9(2), N1–B1–C31 105.1(2), C11–B1–C21 103.1(2), C11–B1–C31 114.7(3), C21–B1–C31 113.2(3), N3–B2–C41 109.0(2), N3–B2–C51 112.8(3), N3–B2–C61 104.3(2), C41–B2–C51 102.7(2), C41–B2–C61 113.0(3), C51–B2–C61 115.2(3), O71–Li–O76 105.9(4), O71–Li–O81 106.4(4), O71–Li–O86 113.8(4), O76–Li–O81 113.7(5), O76–Li–O86 113.0(4), O81–Li–O86 104.0(4).

$\{B(C_6F_5)_3\}_2]^-$ are easily synthesized starting from the respective lithium imidazolides and the bulky Lewis acid $B(C_6F_5)_3$. Both reagent types exhibit large, bulky anions that are probably of a low nucleophilicity. Thus, both reagent types have successfully been employed in the generation of Group 4 metallocene cation systems — the systems **6** by means of a salt metathesis, whereas the reagent **9** seems to be a useful Brønsted acid for the preparation of reactive alkyl Group 4 metallocene cations [17]. The potential of these and related compounds as activator reagents in homogeneous Ziegler–Natta catalysis is under investigation in our laboratory.

3. Experimental

Reactions with organometallic compounds were carried out in an inert atmosphere (Ar) using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under Ar prior to use. The following instruments were used for the physical characterization of the compounds: Bruker AC 200 P NMR spectrometer (^{1}H: 200 MHz; ^{13}C: 50 MHz; ^{11}B: 64 MHz) at 300 K and Varian Unity plus (^{1}H: 600 MHz; ^{13}C: 150 MHz; ^{19}F: 564 MHz; ^{31}P: 81 MHz) NMR spectrometer at 298 K (most NMR assignments were secured by 2D NMR experiments) [18]; a Nicolet 5 DXC FT-IR spectrometer; a Micromass Quattro LC-Z mass spectrometer was used for the HRMS determination; elemental analysis were carried out with a Foss–Heraeus CHN-rapid elemental analyzer or a Vario El III micro elemental analyzer; melting points were determined by differential scanning calorimetry (2010 DSC, Du Pont/STA Instruments). 4,5-Dimethyl-1*H*-imidazole (**4b**) [19], bis(η^5-cyclopentadienyl)dimethylzirconium (**10**) [20], and bis[η^5-{1-methyl-1-di(*p*-tolyl)phosphinoethyl}cyclopentadienyl]dichlorozirconium (**7**) [15] were prepared according to the literature procedures.

3.1. Preparation of the 1-lithium imidazolide derivatives *5a–c*, general procedure

A suspension of the respective 1-*H*-imidazole in 20 ml of toluene was cooled to 0 °C and reacted with one molar equivalent amount of *n*-butyllithium. After stirring for 2 days at room temperature (r.t.) the solvent was removed in vacuo. Pentane was added, the solid was collected by filtration and the product was dried in vacuo.

*3.1.1. Preparation of 1-lithium imidazolide (**5a**)*

Reaction of 1.56 g (22.9 mmol) of imidazole (**4a**) with 14.3 ml (22.9 mmol) of *n*-butyllithium in toluene carried out as described above yielded 1.62 g (95%) of the lithium salt **5a** as a white solid. ^{1}H-NMR (benzene-d_6–THF-d_8 10:1, 200 MHz): $\delta = 7.62$ (s, 1H, 2-H), 7.08 (s, 2H, 4-H and 5-H). ^{13}C-NMR (benzene-d_6–THF-d_8 10:1, 300 K, 50 MHz): $\delta = 142.7$ (CH, C-2), 124.3 (CH, C-4).

*3.1.2. Preparation of 1-lithium 4,5-dimethylimidazolide (**5b**)*

A sample of 1.00 g (10.4 mmol) of 4,5-dimethyl-1*H*-imidazole (**4b**) was reacted with 6.50 ml (10.4 mmol) of *n*-butyllithium in toluene as described above to yield 933 mg (88%) of the white product **5b**. ^{1}H-NMR (benzene-d_6–THF-d_8 10:1, 200 MHz): $\delta = 7.35$ (s, 1H, 2-H), 2.22 (s, 6H, 4-CH_3 and 5-CH_3). ^{13}C-NMR (benzene-d_6–THF-d_8 10:1, 300 K, 50 MHz): $\delta = 138.6$ (CH, C-2), 12.0 (CH_3, 4-CH_3 and 5-CH_3). The signals of the carbon atoms C-4 and C-5 were not detected.

*3.1.3. Preparation of 1-lithium benzimidazolide (**5c**)*

Deprotonation of 1.01 g (8.55 mmol) of 1*H*-benzimidazole (**4c**) with 5.30 ml (8.55 mmol) of *n*-butyllithium in toluene carried out according to the general procedure yielded 1.04 g (94%) of the lithium salt **5c** as a white solid. ^{1}H-NMR (benzene-d_6–THF-d_8 10:1, 300 K, 200 MHz): $\delta = 8.12$ (s, 1H, 2-H), 7.78, 7.12 (each m, each 2H, Ph–H). ^{13}C-NMR (benzene-d_6–THF-d_8 10:1, 50 MHz): $\delta = 153.7$ (CH, C-2), 146.4 (C, C-3a, C-7a), 118.3, 116.6 (each CH, each C–Ph).

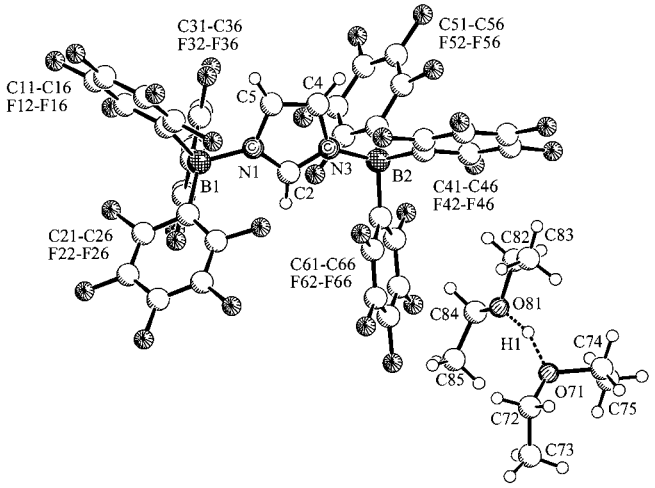


Fig. 2. Molecular structure of **9**. Selected bond lengths (Å) and bond angles (°) N1–B1 1.587(7), N1–C2 1.327(6), N1–C5 1.389(6), C2–N3 1.327(6), N3–B2 1.577(8), N3–C4 1.378(6), C4–C5 1.340(7), B1–C11 1.630(8), B1–C21 1.652(9), B1–C31 1.649(9), B2–C41 1.649(9), B2–C51 1.633(10), B2–C61 1.649(8), O71–H1 1.39, O81–H1 1.11; B1–N1–C2 125.0(4), B1–N1–C5 127.7(4), C2–N1–C5 105.8(4), N1–C2–N3 112.0(4), B2–N3–C2 127.9(4), B2–N3–C4 124.9(5), C2–N3–C4 106.0(4), N3–C4–C5 108.4(5), N1–C5–C4 107.8(5), N1–B1–C11 110.2(4), N1–B1–C21 111.9(4), N1–B1–C31 101.7(5), C11–B1–C21 103.1(5), C11–B1–C31 115.6(5), C21–B1–C31 114.5(5), N3–B2–C41 112.6(5), N3–B2–C51 102.3(4), N3–B2–C61 109.6(5), C41–B2–C51 113.8(5), C41–B2–C61 104.1(4), C51–B2–C61 114.8(5), O71–H1–O81 157.3.

*3.2. Preparation of the lithium imidazolide–bis[tris(pentafluorophenyl)borane] adduct (**6a**)*

To a suspension of the lithium imidazolide (**5a**) (74.0 mg, 1.00 mmol) in 10 ml of toluene 1.02 g tris(pentafluorophenyl)borane (2.00 mmol) was added at 0 °C. The reaction mixture was allowed to warm up to r.t. and then stirred for another 12 h. The addition of 10 ml of pentane precipitated the product **6a**. Filtration yielded a white solid (811 mg, 74%). M.p. (dec.) 256 °C. Anal. Calc. for $C_{39}H_3N_2B_2F_{30}Li$ (MW 1098): C, 42.66; H, 0.28; N, 2.55. Found: C, 42.53; H, 0.88; N, 1.27%. IR (KBr, cm^{-1}): *v* 3464, 1650, 1522, 1474, 1467, 1379, 1286, 1104, 979, 944, 793, 764 and 750. ^{1}H-NMR (benzene-d_6–THF-d_8 10:1, 600 MHz): $\delta = 7.95$ (s, 1H, 2-H), 6.84 (s, 2H, 4-H and 5-H). ^{13}C-NMR (benzene-d_6–THF-d_8 10:1, 150 MHz): $\delta = 148.6$ (dm, $^{1}J = 242$ Hz, *o*-Ph), 141.4 (CH, C-2), 140.0 (dm, $^{1}J = 249$ Hz, *p*-Ph), 137.5 (dm, $^{1}J = 248$ Hz, *m*-Ph), 124.3 (CH, C-4 and C-5), 121.3 (C, *ipso*-C). ^{19}F-NMR (benzene-d_6–THF-d_8 10:1, 564 MHz): $\delta = -132.4$ (m, 12F, *o*-Ph), -159.5 (m, 6F, *p*-Ph), -165.3 (m, 12F, *m*-Ph). ^{11}B-NMR (benzene-d_6–THF-d_8 10:1, 64 MHz): $\delta = -8.5$ ($v_{1/2} = 390$ Hz).

*3.3. Preparation of the lithium 4,5-dimethylimidazolide–bis[tris(pentafluorophenyl)borane] adduct (**6b**)*

Analogously as described above, lithium 4,5-dimethylimidazolide (**5b**) (117.0 mg, 1.00 mmol) in 20 ml of toluene was reacted with 1.02 g of tris(pentafluorophenyl)borane (2.00 mmol) to yield 965 mg (93%) of a white solid. M.p. 105 °C. Anal. Calc. for $C_{41}H_7N_2B_2F_{30}Li$ (MW 1126): C, 43.73; H, 0.63; N, 2.49. Found: C, 43.77; H, 0.70; N, 1.47%. IR (KBr, cm^{-1}): *v* 2984, 1646, 1518, 1472, 1462, 1375, 1284, 1089, 1047, 982, 800, 765 and 752. ^{1}H-NMR (benzene-d_6–THF-d_8 10:1, 600 MHz): $\delta = 7.92$ (s, 1H, 2-H), 1.82 (s, 6H, 4-CH_3 and 5-CH_3). ^{13}C-NMR (benzene-d_6–THF-d_8 10:1, 150 MHz): $\delta = 148.7$ (dm, $^{1}J = 247$ Hz, *o*-Ph), 140.7 (CH, C-2), 139.9 (dm, $^{1}J = 249$ Hz, *p*-Ph), 137.2 (dm, $^{1}J = 248$ Hz, *m*-Ph), 130.1 (CH, C-4 and C-5), 121.4 (C, *ipso*-C), 12.1 (CH_3, 4-CH_3 and 5-CH_3). ^{19}F-NMR (benzene-d_6–THF-d_8 10:1, 564 MHz): $\delta = -125.3$, -130.1, -131.5, -132.0, -134.6, -136.5 (each m, each 2F, *o*-Ph), -158.8, -159.8, -160.1 (each m, each 2F, *p*-Ph), -163.4, -164.9, -165.1 (each m, each 2F, *m*-Ph), -166.0 (br, 6F, *m*-Ph). ^{11}B-NMR (benzene-d_6–THF-d_8 10:1, 64 MHz): $\delta = -9.0$ ($v_{1/2} = 230$ Hz).

*3.3.1. X-ray crystal structure analysis of **6b***

Formula $C_{41}H_7N_2B_2F_{30}\cdot Li(C_4H_8O)_4$, $M = 1414.46$, colorless crystal $0.25 \times 0.20 \times 0.05$ mm, $a = 13.254(3)$, $b = 13.573(3)$, $c = 17.512(1)$ Å, $\alpha = 92.57(2)$, $\beta = 104.50(1)$, $\gamma = 98.60(2)°$, $V = 3004.5(11)$ Å^3, $\rho_{calc} = 1.563$ g cm^{-3}, $\mu = 14.47$ cm^{-1}, empirical absorption correction via ψ scan data ($0.714 \le T \le 0.931$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 12 704 reflections collected ($\pm h$, $\pm k$, $+l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 12 286 independent ($R_{int} = 0.046$) and 6674 observed reflections [$I \ge 2\sigma(I)$], 867 refined parameters, $R = 0.064$, $wR^2 = 0.189$, maximum residual electron density 0.67 (-0.47) e Å^{-3}, the THF molecules are heavily disordered, refinement with split positions is not working, the 'best' was taken as a model for the others (SAME restraint), hydrogens calculated and refined as riding atoms.

*3.4. Preparation of the lithium benzimidazolide–bis[tris(pentafluorophenyl)borane] adduct (**6c**)*

To a suspension of the lithium benzimidazolide (**5c**) (62.0 mg, 500 μmol) in 20 ml of CH_2Cl_2 was added at 0 °C 512 mg of tris(pentafluorophenyl)borane (1.00 mmol). The reaction mixture was allowed to warm up to r.t. and stirred for another 24 h. The precipitate was separated by filtration to yield a white solid 450 mg (78%). M.p. 145 °C. HRMS: calculated for $[C_{43}H_5N_2B_2F_{30}]^-$ 1141.0160. Found 1141.0096. IR (KBr, cm^{-1}): *v* 3475, 2987, 2888, 1646, 1518, 1469, 1378, 1284, 1261, 1095, 983, 888, 797 and 753. ^{1}H-NMR (benzene-d_6–THF-d_8 10:1, 600 MHz): $\delta = 8.49$ (s, 1H, 2-H), 7.61 (m, 2H, 4-H and 7-H), 6.90 (m, 2H, 5-H and 6-H). ^{13}C-NMR (benzene-d_6–THF-d_8 10:1, 150 MHz): $\delta = 148.7$ (dm, $^1J = 246$ Hz, *o*-Ph), 146.6 (CH, C-2), 140.0 (dm, $^1J = 251$ Hz, *p*-Ph), 137.7 (C, C-3a and C-7a), 137.3 (dm, $^1J = 253$ Hz, *m*-Ph), 124.0 (CH, C-5 and C-6), 120.5 (C, *ipso*-C), 115.3 (CH, C-4 and C-7). ^{19}F-NMR (benzene-d_6–THF-d_8 10:1, 564 MHz): $\delta = -127.4$, -130.2, -131.5, -132.6 (each m, each 2F, *o*-Ph), -134.6 (4F, *o*-Ph), -158.0 (m, 2F, *p*-Ph), -159.8 (br, 4F, *p*-Ph), -163.0, -164.8 (each m, each 2F, *m*-Ph), -165.6 (br, 8F, *m*-Ph). ^{11}B-NMR (benzene-d_6–THF-d_8 10:1, 64 MHz): $\delta = -8.1$ ($\nu_{1/2} = 320$ Hz).

*3.5. Treatment of compound **7** with the lithium imidazolide–bis[tris(pentafluorophenyl)borane] adduct (**6a**), formation of the metallocene cation complex **8***

To a mixture of 200 mg (250 μmol) of **7** with 272 mg (250 μmol) of the lithium compound **6a** 15 ml of CH_2Cl_2 was added. The resulting reaction mixture was allowed to stir for 1 h and then filtered to remove LiCl. The solvent was removed in vacuo, pentane was added and the yellow solid was isolated by filtration to yield 363 mg (81%) of **8**. M.p. 65 °C. IR (KBr, cm^{-1}): *v* 2964, 2927, 1645, 1600, 1518, 1469, 1283, 1263, 1156, 1096, 1018, 864, 805, 794 and 763. ^{1}H-NMR (CH_2Cl_2-d_2, 600 MHz): $\delta = 8.70$ (m, 8H, *o*-Ph), 7.47 (s, 1H, 2-H), 7.33 (m, 8H, *m*-Ph), 6.80 (s, 2H, 4-H and 5-H), 6.44 (m, 4H, Cp–H), 6.23, 6.13 (each m, each 2H, Cp–H), 2.41, 2.40 (each s, each 3H, tol-CH_3), 1.76 (t, $J_{PH} = 5.8$ Hz, 3H, CH_3), 1.55 (t, $J_{PH} = 5.2$ Hz, 3H, CH_3). ^{13}C-NMR (CH_2Cl_2-d_2, 150 MHz): $\delta = 148.3$ (dm, $^1J = 241$ Hz, *o*-Ph), 142.5 (C, *ipso*-CH_3–C), 142.2 (C, *ipso*-[P]–C), 141.3 (CH, C-2), 139.8 (dm, $^1J = 248$ Hz, *p*-Ph), 139.3 (C, *ipso*-Cp–C), 137.3 (dm, $^1J = 245$ Hz, *m*-Ph), 136.6 (CH, *o*-Ph–C), 131.7, 130.7 (each CH, *m*-Ph–C), 124.0 (CH, C-4 and C-5), 120.7 (C, *ipso*-C), 113.7, 107.1, 100.2 (each CH, each Cp–C), 35.5 (C, –$C(CH_3)_2$), 30.0, 26.8 (each CH_3, each –$C(CH_3)_2$), 21.9, 21.7 (each CH_3, tol-CH_3). ^{31}P-NMR (CH_2Cl_2-d_2, 81 MHz): $\delta = -35.5$. ^{19}F-NMR (CH_2Cl_2-d_2, 564 MHz): $\delta = -133.0$ (m, 12F, *o*-Ph), -160.1 (m, 6F, *m*-Ph), -165.6 (m, 12F, *m*-Ph). ^{11}B-NMR (CH_2Cl_2-d_2, 64 MHz): $\delta = -8.9$ ($\nu_{1/2} = 140$ Hz).

*3.6. Treatment of the lithium imidazolide–bis[tris(pentafluorophenyl)borane] adduct (**6a**) with hydrogen chloride, formation of complex **9***

To a suspension of the lithium salt **6a** (1.10 g, 1.00 mmol) in 20 ml of Et_2O was added at -30 °C 1.20 ml of a 1 M HCl solution in ether (1.20 mmol). The reaction mixture was allowed to warm up to r.t. and the solvent was removed in vacuo. Dichloromethane (20 ml) was added and the LiCl precipitate was removed by filtration. The solution was concentrated and the product was crystallized at -30 °C. The white crystals obtained (1.05 g (85%)) were suitable for an X-ray crystal structure analysis of **9**, m.p. 155 °C. Anal. Calc. for $C_{47}H_{24}N_2B_2F_{30}O_2$ (MW 1240): C, 45.51; H, 1.95; N, 2.26. Found: C, 45.16; H, 2.65; N, 1.35%. IR (KBr, cm^{-1}): *v* 3175, 3003, 1647, 1517, 1470, 1387, 1283, 1096, 978, 876, 752, 698 and 679. ^{1}H-NMR (CH_2Cl_2-d_2, 600 MHz): $\delta = 16.3$ (br, 1H, H^+), 7.47 (s, 1H, 2-H), 6.80 (s, 2H, 4-H and 5-H), 4.08 (q, $^3J_{HH} = 7.0$ Hz, 8H, O–CH_2), 1.44 (t, $^3J_{HH} = 7.0$ Hz, 12H, CH_3). ^{13}C-NMR (CH_2Cl_2-d_2, 150 MHz): $\delta = 148.3$ (dm, $^1J = 241$ Hz, *o*-Ph), 141.3 (C, C-2), 139.8 (dm, $^1J = 247$ Hz, *p*-Ph), 137.3 (dm, $^1J = 248$ Hz, *m*-Ph), 124.0 (CH, C-4 and

*3.3.1. X-ray crystal structure analysis of **6b***

Formula $C_{41}H_7N_2B_2F_{30}\cdot Li(C_4H_8O)_4$, $M = 1414.46$, colorless crystal $0.25 \times 0.20 \times 0.05$ mm, $a = 13.254(3)$, $b = 13.573(3)$, $c = 17.512(1)$ Å, $\alpha = 92.57(2)$, $\beta = 104.50(1)$, $\gamma = 98.60(2)°$, $V = 3004.5(11)$ Å^3, $\rho_{calc} = 1.563$ g cm^{-3}, $\mu = 14.47$ cm^{-1}, empirical absorption correction via ψ scan data ($0.714 \le T \le 0.931$), $Z = 2$, ether molecules from difference Fourier calculations, refined isotropically, other hydrogens calculated and refined as riding atoms.

Data sets were collected with Enraf–Nonius CAD4 and Nonius Kappa CCD diffractometer, the later one equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MOLEN [21] and DENZO-SMN [22], absorption correction for CCD data SORTAV [23,24], structure solution SHELXS-97 [25], structure refinement SHELXL-97 [26], graphics SCHAKAL [27].

3.7. Treatment of bis(η^5-cyclopentadienyl)dimethylzirconium (**10**) with compound **9**, formation of metallocene cation complex **11**

To a solid mixture of 10.0 mg (39.7 μmol) of the zirconocene complex **10** with 49.2 mg (39.7 μmol) of compound **9** 1.5 ml of CH_2Cl_2-d_2 was added. Methane evolution occurred immediately and complex **11** was generated for direct NMR observation. ^{1}H-NMR (CH_2Cl_2-d_2, 600 MHz): $\delta = 7.48$ (s, 1H, 2-H), 6.80 (s, 2H, 4-H and 5-H), 6.49 (s, 10H, Cp–H), 3.46 (q, $^3J = 7.0$ Hz, 2H, O–CH_2), 1.17 (t, $^3J_{HH} = 7.0$ Hz, 6H, CH_3), 0.92 (s, 3H, Zr–CH_3). ^{13}C-NMR (CH_2Cl_2-d_2, 150.8 MHz): $\delta = 148.3$ (dm, $^1J = 242$ Hz, *o*-Ph), 141.3 (C, C-2), 139.8 (dm, $^1J = 248$ Hz, *p*-Ph), 137.3 (dm, $^1J = 249$ Hz, *m*-Ph), 124.0 (CH, C-4 and C-5), 120.7 (C, *ipso*-C), 115.3 (CH, Cp–C), 66.1 (CH_2, O–CH_2), 44.7 (CH_3, Zr–CH_3), 15.3 (CH_3). ^{19}F-NMR (CH_2Cl_2-d_2, 564 MHz): $\delta = -133.0$ (m, 12F, *o*-Ph), -160.0 (m, 6F, *m*-Ph), -165.6 (m, 12F, *m*-Ph). ^{11}B-NMR (CH_2Cl_2-d_2, 64 MHz): $\delta = -8.9$ ($\nu_{1/2} = 250$ Hz).

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 166601–166602, for **6b** and **9** respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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