Synthesis and Structure of [1]Borametallocenophanes of Titanium, Zirconium, and Hafnium

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Various [1]borametallocenophane complexes of all the group IV metals were obtained in high yield by a very efficient multistep, one-pot synthesis. By this method not only the biscyclopentadienyl and diindenyl complexes [{$R_2NB(\eta^5$-$C_5H_4)_2$}MCl_2] (M = Zr, R = Me, $SiMe_3$, **4a**, **b**; M = Hf, R = $SiMe_3$, **5**) and [{$(Me_3Si_2)NB(\eta^5$-$C_9H_6)_2$}MCl_2] (M = Ti, **6**; M = Zr, **7**) were obtained, but also complexes with two different η^5-coordinated ligands such as [{$i$$Pr_2NB(\eta^5$-$C_5H_4)(\eta^5$-$C_9H_6)$}$MCl_2$] (M = Zr, **8**; M = Hf, **9**). Some of compounds **4–9** were chosen to investigate their catalytic properties with respect to Ziegler-Natta-type polymerisation of olefins, and proved to be highly efficient for the preparation of polyethylene.

Introduction

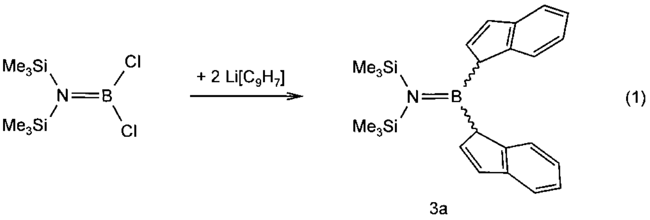
In the course of our investigations on both strained[1a,1b] and unstrained[2a,2b] [1]borametallocenophanes, we recently reported the first [1]boratitanocenophanes, which were obtained in high yields from a convenient one-pot synthesis. Metallocenophanes of group IV elements are of special interest due to their remarkable qualities as highly active Ziegler-Natta-type catalysts for olefin polymerisation.[3] Such catalytic processes could be accelerated by a bridging Lewis acidic centre such as boron.[4] Structurally authenticated boron-bridged metallocenophanes of group IV metals are restricted to a very few examples, including [{$(Me_2S)PhB(\eta^5$-$C_5H_4)_2$}$ZrCl_2$] (**1**) which has a four-coordinate boron atom in the bridge.[5] During the preparation of this paper, further zirconium complexes with three- and four-coordinate boron atoms [{$i$$Pr_2NB(\eta^5$-$C_5H_4)_2$}$ZrCl_2$] (**2a**), [{$i$$Pr_2NB(\eta^5$-$C_9H_6)_2$}$ZrCl_2$] (**2b**), [{(L)$PhB(\eta^5$-$C_9H_6)_2$}$ZrCl_2$] (L = PMe_3, thf, OEt_2; **2c**), obtained by an analogous method to that described for the synthesis of [{$(Me_3Si)_2NB(\eta^5$-$C_5H_4)_2$}$TiCl_2$],[2a,2b] were reported by Ashe and Reetz.[6a,6b]

In the present paper we report on the synthesis, structure and catalytic properties of several [1]borametallocenophanes of Ti, Zr, and Hf, which were obtained by convenient reactions in high yields.

Results and Discussion

Synthesis and Structure of $(Me_3Si)_2NB(C_9H_7)_2$ (3a, b)

As already reported for $(Me_3Si)_2NB(C_5H_5)_2$[2a] the corresponding diindenylborane $(Me_3Si)_2NB(C_9H_7)_2$ (**3a**) is obtained in almost quantitative yields as a colourless solid from the reaction of $(Me_3Si)_2NBCl_2$ with $Li[C_9H_7]$ according to Equation 1.



The 1-indenyl isomer **3a**, in which boron is bound to a saturated carbon atom and thus adopts an allylic position, represents the kinetically controlled product of this reaction. A quantitative rearrangement yielding the thermodynamically more stable vinylic isomer **3b** is achieved by either heating **3a** for 2 h to 60 °C in benzene or by treating **3a** with catalytic amounts of NEt_3 in benzene at room temperature (Equation 2). The spectroscopic data of **3a, b**, such as the distinct low-field shift in the ^{11}B NMR spectrum for the allylic isomer with respect to the vinylic isomer [δ = 57.6 (**3a**) and 50.6 (**3b**)], resemble those of corresponding diindenyl(organyl)boranes,[6b] diorganyl(indenyl)boranes[7a,b] and 1,2-diindenyldiboranes(4),[8] which were reported very recently to undergo the same type of rearrangement. Compound **3a**, with two stereocentres, is expected to form a mixture of a C_2-symmetrical *rac* and a C_S-symmetrical *meso* isomer. The presence of both isomers is evident from the double set of signals in the ^{13}C NMR spectra.

Single crystals of **3b** suitable for an X-ray structure analysis were obtained from hexane at −30 °C. The compound crystallises in the monoclinic space group *C*2/*c* and the molecule adopts almost C_2 symmetry in the solid state (Figure 1). Both the boron and nitrogen atoms are in a trigonal-planar environment, and due to the steric demand of the bulky Me_3Si groups, the Si1−N−Si2 plane is twisted with respect to the C11−B−C21 plane. The corresponding torsion angles are −51.28° (Si1−N−B−C21) and −50.73° (Si2−N−B−C11). Hence, together with an extended B−N

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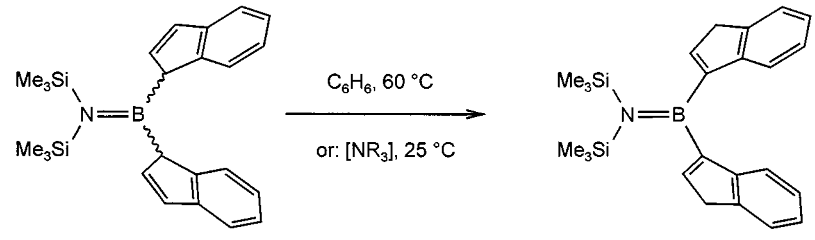


(2)

3a **3b**

bond length of 144.3(5) pm a less effective backbonding from nitrogen to boron can be assumed. Both B−C and C−C bond lengths are in the expected range and resemble the data known for the corresponding 1,2-diindenyldiborane(4) derivative.[8]

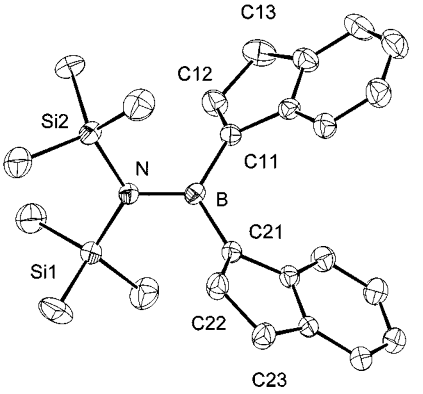


Figure 1. Structure of **3b** in the crystal (ellipsoids at 30% probability); selected distances (pm) and angles (°): B−N 144.3(5), B−C11 157.5(5), C11−C12 133.8(6), C12−C13 150.3(5); Si1−N−B 118.3(3); N−B−C11 120.1(4), C11−B−C21 118.9(3)

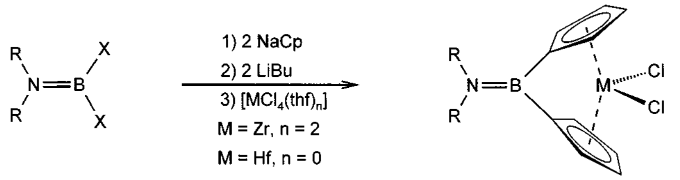
Synthesis and Structure of the [1]Borametallocenophanes

In analogy to the synthesis of [{(SiMe$_3$)$_2$NB(η^5-C$_5$H$_4$)$_2$}TiCl$_2$][2a,2b] the [1]borametallocenophanes [{R$_2$NB-(η^5-C$_5$H$_4$)$_2$}MCl$_2$] (M = Zr, R = Me, SiMe$_3$, **4a**, **b**; M = Hf, R = SiMe$_3$, **5**) were obtained in three-step, one-pot syntheses according to Equation 3.[2b] In the case of **4a** the dibromoborane Me$_2$NBBr$_2$ served as starting material, whereas **4b** and **5** were obtained from the dichloro derivative (Me$_3$Si)$_2$NBCl$_2$. Although being sterically rather demanding, the latter aminodihaloborane is known to undergo substitutions of both chloride ligands more easily than the much smaller Me$_2$NBCl$_2$.[9a,9b] This is due to the electron-withdrawing effect of the silyl ligands, which enhances the electrophilicity of the boron centre. All products were isolated as yellow crystalline solids in high yields (**4a,** 91%; **4b,** 96%; **5,** 85%). These zirconium and hafnium complexes are readily soluble in CH$_2$Cl$_2$ and proved to be more stable towards decomposition in solution than the corresponding titanium derivative [{(SiMe$_3$)$_2$NB(η^5-C$_5$H$_4$)$_2$}-TiCl$_2$].[2a]

The structure of **4a**, **b** and **5** in solution was derived from multinuclear NMR spectra, showing the expected two pseudo triplets in the ^{1}H NMR spectra for the AA′BB′ spin system of the cyclopentadienyl protons at δ = 5.28, 6.62 (**4a**), 5.16, 6.61 (**4b**), and 5.54, 6.68 (**5**). The resonances in the ^{11}B NMR spectrum of **4b** and **5** at about δ = 47 resemble the signal of the uncoordinated ligand[2a] and show the expected low-field shift with respect to the signal of the dimethylamino derivative **4a** at δ = 38.7.

Suitable single crystals of **4a** were obtained by recrystallisation from a 70:30 mixture of CH$_2$Cl$_2$ and Et$_2$O at −30°C. The compound crystallises in the space group $P2_1/n$, and the molecule exhibits a slight deviation from the C_{2v} symmetry, which was assumed from its structure in solution (Figure 2). The B−N distance was found to be 138.4(4) pm, thus indicating a B−N double bond. As expected the two cyclopentadienyl ligands adopt an eclipsed orientation, and the geometry of **4a** is very similar to that of [{(SiMe$_3$)$_2$NB(η^5-C$_5$H$_4$)$_2$}TiCl$_2$],[2a] and to the corresponding zirconium complex [{*i*Pr$_2$NB(η^5-C$_5$H$_4$)$_2$}ZrCl$_2$] (**2a**), the structure of which was described very recently.[6a]

The boron-bridged diindenyl complexes [{(Me$_3$Si$_2$)-NB(η^5-C$_9$H$_6$)$_2$}MCl$_2$] (M = Ti, **6**; M = Zr, **7**) were obtained according to the procedures described in Equations 4a and 4b. (Me$_3$Si$_2$)NBCl$_2$ was treated with two equivalents of Li[C$_9$H$_7$] in hexane, LiCl was removed by filtration, and after addition of Et$_2$O, the filtrate was treated with two equivalents of BuLi. The obtained slurry was subsequently reacted with [TiCl$_3$(thf)$_3$] or [ZrCl$_4$(thf)$_2$] at low tempera-



(3)

4a, b; M = Zr, R = Me, X = Br; R = Me$_3$Si, X = Cl
5; M = Hf, R = Me$_3$Si, X = Cl

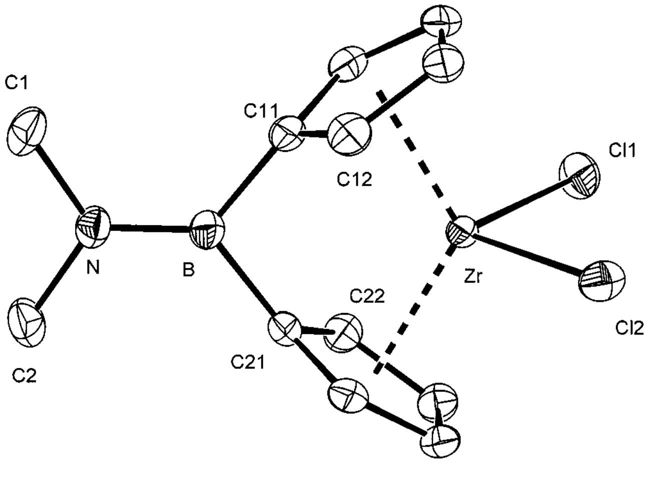


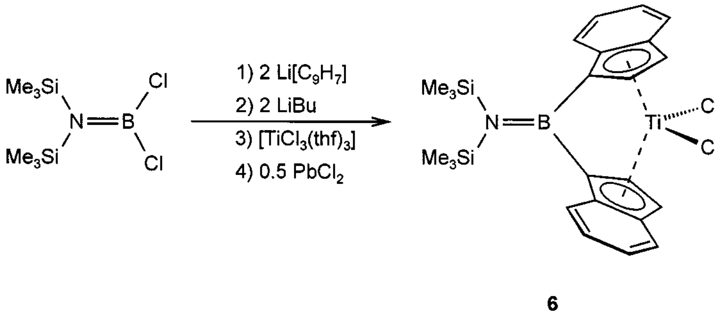
Figure 2. Structure of **4a** in the crystal (ellipsoids at 30% probability); selected distances (pm) and angles (°): Zr−Cl1 242.92(8), Zr−Cl2 245.79(9), B−N 138.4(4); Cl1−Zr−Cl2 100.87(3), C11−B−C21 105.9(3), C11−B−N 127.5(3), C21−B−N 126.5(3)

tures. In the case of the titanium complex **6** the intermediate Ti^{III} species was oxidised with $PbCl_2$.[10] The two complexes were isolated as dark red or orange crystalline materials, respectively, in yields of 71% (**6**) and 82% (**7**) and their constitutions in solution deduced from multinuclear NMR spectra. Although the general formation of a mixture of both *rac* (C_2 symmetry) and *meso* (C_s symmetry) isomers was reported for related element-bridged diindenyl complexes,[6a,6b,11] single sets of signals in the ^{13}C NMR spectra of **6** and **7** reveal the presence of only one isomer in our case. After reaction of **7** with two equivalents of LiMe, the corresponding complex $[\{(Me_3Si_2)NB(\eta^5\text{-}C_9H_6)_2\}ZrMe_2]$ was obtained,[12] and a single resonance for both metal-coordinated methyl groups in the NMR spectra indicates the presence of the *rac* isomer. This is further demonstrated by the formation of predominantly isotactic polypropylene (M.p. 116°C, triad ratio mm/mr/rr = 86:7:7 determined by ^{13}C NMR spectroscopy[13]) from **7** as a catalyst for the polymerisation of propene.

The preparation of [1]borametallocenophanes by the present method can be extended to the corresponding boron-bridged complexes with two different η^5-coordinated ligands, which have not previously been reported. This is demonstrated by the synthesis of $[\{iPr_2NB(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_9H_6)\}MCl_2]$ (M = Zr, **8**; M = Hf, **9**) according to Equation 5. Stepwise treatment of iPr_2NBCl_2 with $Na[C_5H_5]$ and $Li[C_9H_7]$, subsequent reaction with two equivalents of BuLi, and addition of $[MCl_4(thf)_n]$ (M = Zr, n = 2; M = Hf, n = 0) afforded the mixed [1]borametallocenophanes **8**, **9** in 82% and 74% yield, respectively, as orange, crystalline solids. The spectroscopic data of both compounds, such as the ^{11}B NMR signals at about $\delta = 40$, together with the expected patterns for η^5-cyclopentadienyl and η^5-indenyl ligands in the ^1H and ^{13}C NMR spectra prove their constitution in solution. A restricted rotation with respect to the boron−nitrogen double bond is indicated by double sets of signals for the isopropyl groups in both the ^1H and ^{13}C NMR spectra.

Conclusion

The synthetic method described in this paper and previously reported for $[\{(Me_3Si)_2NB(\eta^5\text{-}C_5H_4)_2\}TiCl_2]$ provides a convenient and general route to group IV [1]borametallocenophanes showing either η^5-cyclopentadienyl or η^5-indenyl ligands such as $[\{R_2NB(\eta^5\text{-}C_5H_4)_2\}MCl_2]$ (M = Zr, R = Me, $SiMe_3$, **4a**, **b**; M = Hf, R = $SiMe_3$, **5**) and $[\{(Me_3Si_2)NB(\eta^5\text{-}C_9H_6)_2\}MCl_2]$ (M = Ti, **6**; M = Zr, **7**). The novel complexes $[\{iPr_2NB(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_9H_6)\}MCl_2]$



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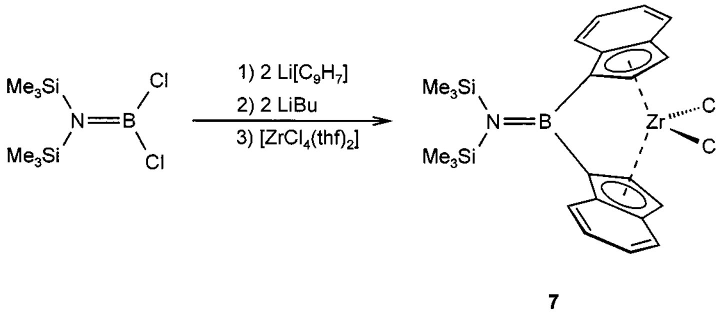
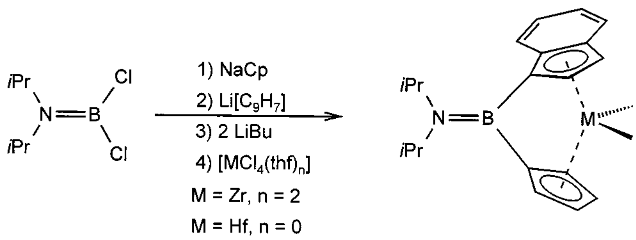
(4a)



7

(4b)



(5)

8; M = Zr
9; M = Hf

(M = Zr, **8**; M = Hf, **9**) showing two different η^5-coordinated ligands are obtained in a similar manner. Further studies will focus on the catalytic properties of these [1]Borametallocenophanes. Preliminary investigations have already shown them to be highly efficient catalysts for the Ziegler-Natta-type polymerisation of olefins, showing, for example, activities of 5258 kg PE·mol[catalyst]$^{-1}$h^{-1} (**6**) and 8905 kg PE·mol[catalyst]$^{-1}$h^{-1} (**4a**)

Experimental Section

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. $(Me_3Si)_2NBCl_2$,[14] $i$$Pr_2NBCl_2$,[15] $Na[C_5H_5]$,[16] $[ZrCl_4(thf)_2]$,[17] $[TiCl_3(thf)_3]$[17] and Me_2NBBr_2[18] were obtained according to literature procedures. NMR: Varian Unity 500 at 499.843 MHz (^{1}H, internal standard TMS), 150.364 MHz (^{11}B, BF3·OEt2 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 analyzer, model 1106.

$(Me_3Si)_2NB(1\text{-}C_9H_7)_2$ (3a): $Li[C_9H_7]$ (7.38 g, 60.41 mmol) was suspended in 100 mL hexane, and a solution of $(Me_3Si)_2NBCl_2$ (7.31 g, 30.20 mmol) in 20 mL hexane was added at 0°C. The yellow suspension was allowed to warm to ambient temperature and stirred for 2 h. All volatiles were removed in high vacuum, and the remaining solid was extracted with 50 mL of hexane. After filtration **3a** was obtained as a white crystalline solid by cooling to −30°C (11.64 g, 96%). − ^{1}H NMR (C_6D_6): δ = 0.24 (s, 18 H, $SiMe_3$), 3.61 (m, 2 H, B−CH_{ind}), 6.06−7.43 (m, 12 H, CH_{ind}) − ^{11}B NMR: δ = 57.6 (s). − ^{13}C NMR: δ = 3.75 (isomer 1), 4.83 (isomer 2) ($SiMe_3$), 54.8 (br, B−C_{ind}), 120.8 (1), 121.0 (2), 123.6 (1), 123.9 (2), 124.8 (1), 125.4 (2), 125.9 (1), 126.4 (2), 131.3 (1), 131.9 (2), 135.0 (1), 136.3 (2) (CH_{ind}), 144.1 (1), 144.3 (2), 146.3 (1), 146.7 (2) (C_{ind}). − MS; *m/z* (%): 401 (90) [M$^+$], 386 (25) [M$^+$ − Me], 286 (40) [M$^+$ − ind]. − $C_{24}H_{32}BNSi_2$ (401.51): calcd. C 71.80, H 8.03, N 3.49; found C 71.69, H 8.21, N 3.25.

$(Me_3Si)_2NB(3\text{-}C_9H_7)_2$ (3b): Compound **3b** was quantitatively obtained by a) refluxing a solution of **3a** (2.00 g, 4.98 mmol) in 50 mL benzene for 3 h, or by b) treatment of **3a** (1.50 g, 3.74 mmol) with a catalytic amount of NEt_3 (0.1 mL) in 40 mL benzene for 2 h at ambient temperature. Suitable single crystals of **3b** were obtained by recrystallisation from hexane at −30°C. − ^{1}H NMR (C_6D_6): δ = 0.23 (s, 18 H, $SiMe_3$), 3.22 (m, 4 H, CH_{2ind}), 6.70−7.29 (m, 10 H, CH_{ind}) − ^{11}B NMR: δ = 50.6 (s). − ^{13}C NMR: δ = 4.66 ($SiMe_3$), 40.18 (CH_{2ind}), 122.97, 123.78, 124.74, 126.42, 128.29, 142.70, 144.29 (C_{ind}).

[{$Me_2NB(\eta^5\text{-}C_5H_4)_2$}$ZrCl_2$] (4a): $Na[C_5H_5]$ (1.69 g, 19.20 mmol) was suspended in 40 mL hexane and a solution of Me_2NBBr_2 (2.05 g, 9.55 mmol) in 10 mL hexane was added dropwise at 0°C. After warming to ambient temperature, the yellow suspension was stirred for 2 h. NaBr was removed by filtration, and the residue was washed with 15 mL of diethyl ether. The filtrate was cooled to 0°C and 13.00 mL (20.80 mmol) of 1.6 M BuLi in hexane was slowly added . A white precipitate was formed immediately, the suspension was allowed to come to ambient temperature and stirred for 16 h. The yellow suspension was cooled to −70°C and $[ZrCl_4(thf)_2]$ (3.62 g, 9.60 mmol) and 15 mL of diethyl ether was added. After warming to ambient temperature and stirring for an additional 2 h, the yellow suspension was filtered. The filtrate was stored overnight at −30°C to yield **4a** as a yellow, crystalline solid (3.02 g, 91%). − ^{1}H NMR ([D$_8$]toluene): δ = 2.49 (s, 6 H, NMe_2), 5.28 (m, 4 H, C_5H_4), 6.62 (m, 4 H, C_5H_4). − ^{11}B NMR: δ = 38.7 (s). − ^{13}C NMR: δ = 39.43 (NMe_2), 111.58, 125.69 (C_5H_4), 137.52 (C_{ipso}). − MS; *m/z* (%): 345 (60) [M$^+$], 330 (5) [M$^+$ − Me], 301 (20) [M$^+$ − NMe_2]. − $C_{12}H_{14}BCl_2NZr$ (345.19): calcd. C 41.75, H 4.09, N 4.06; found C 41.45, H 3.80, N 3.87.

[{$(Me_3Si)_2NB(\eta^5\text{-}C_5H_4)_2$}$ZrCl_2$] (4b): As described for **4a** $Na[C_5H_5]$ (1.94 g, 22.00 mmol) was treated with $(Me_3Si)_2NBCl_2$ (2.66 g, 11.00 mmol) and subsequently with 1.6 M BuLi (13.75 mL, 22.00 mmol) and $[ZrCl_4(thf)_2]$ (4.15 g, 11.00 mmol). Compound **4b** was obtained as a yellow crystalline material (4.87 g, 96%). − ^{1}H NMR (C_6D_6): δ = 0.11 (s, 18 H, $SiMe_3$), 5.16 (m, 4 H, C_5H_4), 6.61 (m, 4 H, C_5H_4). − ^{11}B NMR: δ = 47.4 (s). − ^{13}C NMR: δ = 5.05 ($SiMe_3$), 109.63, 124.95 (C_5H_4). − MS; *m/z* (%): 461 (100) [M$^+$], 446 (50) [M$^+$ − Me], 315 (45) [M$^+$ − 2($SiMe_3$)$_2$]. − $C_{16}H_{26}BCl_2NSi_2Zr$ (461.50): calcd. C 41.64, H 5.68, N 3.04; found C 41.50, H 5.80, N 3.09.

[{$(Me_3Si)_2NB(\eta^5\text{-}C_5H_4)_2$}$HfCl_2$] (5): As described for **4a** $Na[C_5H_5]$ (1.96 g, 22.23 mmol) was treated with $(Me_3Si)_2NBCl_2$ (2.69 g, 11.10 mmol) and subsequently with 1.6 M BuLi (13.94 mL, 22.30 mmol) and $HfCl_4$ (3.56 g, 11.10 mmol). Compound **5** was obtained as a yellow crystalline material (5.18 g, 85%). − ^{1}H NMR (CD_2Cl_2): δ = 0.30 (s, 18 H, $SiMe_3$), 5.54 (m, 4 H, C_5H_4), 6.68 (m, 4 H, C_5H_4). − ^{11}B NMR: δ = 46.7 (s). − ^{13}C NMR: δ = 4.91 ($SiMe_3$), 108.38, 123.96 (C_5H_4), 140.09 (C_{ipso}). − MS; *m/z* (%): 549 (35) [M$^+$], 534 (50) [M$^+$ − Me], 441 (20) [M$^+$ − $SiMe_3$ − Cl]. − $C_{16}H_{26}BCl_2HfNSi_2$ (548.77): calcd. C 35.02, H 4.78, N 2.55; found C 34.78, H 4.81, N 2.45.

[{$(Me_3Si)_2NB(\eta^5\text{-}C_9H_6)_2$}$TiCl_2$] (6): $Li[C_9H_7]$ (3.48 g, 28.50 mmol) was suspended in 40 mL hexane and a solution of $(Me_3Si)_2NBCl_2$ (3.44 g, 14.20 mmol) in 20 mL hexane was added dropwise at 0°C. After warming to ambient temperature, the yellow suspension was stirred for 2 h. LiCl was removed by filtration and the residue washed with 15 mL of diethyl ether. The filtrate was cooled to 0°C and 17.81 mL (28.50 mmol) 1.6 M BuLi in hexane was slowly added. A white precipitate was formed immediately, the suspension was allowed to come to ambient temperature and stirred for 16 h. The orange suspension was cooled to −100°C and $[TiCl_3(thf)_3]$ (5.26 g, 14.20 mmol) was added. Whilst warming to ambient temperature the colour changed to dark violet. The suspension was stirred for 2 h and then treated with $PbCl_2$ (1.97 g, 7.10 mmol). After stirring for 16 h, all volatiles were removed in high vacuum, the remaining solid was extracted with 40 mL of CH_2Cl_2, and filtered. The filtrate was stored overnight at −30°C to yield **6** as a dark violet, crystalline solid (5.23 g, 71%). − ^{1}H NMR (CD_2Cl_2): δ = 0.29 (s, 18 H, $SiMe_3$), 6.84−7.52 (m, 12 H, CH_{ind}). − ^{11}B NMR: δ = 48.6 (s). − ^{13}C NMR: δ = 4.81 ($SiMe_3$), 115.83, 123.52, 124.82, 126.40, 127.62, 129.51 (CH_{ind}). − MS; *m/z* (%): 518 (10) $[M^+]$, 503 (25) $[M^+ - Me]$, 468 (50) $[M^+ - Me - Cl]$. − $C_{24}H_{30}BCl_2NSi_2Ti$ (518.30): calcd. C 55.62, H 5.83, N 2.70; found C 55.31, H 5.76, N 2.58.

$[\{(Me_3Si)_2NB(\eta^5\text{-}C_9H_6)_2\}ZrCl_2]$ (7): As described for **4a** $Li[C_9H_7]$ (2.76 g, 22.60 mmol) was treated with $(Me_3Si)_2NBCl_2$ (2.74 g, 11.30 mmol) and subsequently with 1.6 M BuLi (14.13 mL, 22.60 mmol) and $[ZrCl_4(thf)_2]$ (4.26 g, 11.30 mmol). Compound **7** was obtained as an orange crystalline material (5.20 g, 82%). − ^{1}H NMR (CD_2Cl_2): δ = 0.37 (s, 18 H, $SiMe_3$), 6.71−7.53 (m, 12 H, CH_{ind}). − ^{11}B NMR: δ = 48.5 (s). − ^{13}C NMR: δ = 5.18 ($SiMe_3$), 112.81, 113.32, 123.90, 125.94, 126.80, 127.54 (CH_{ind}). − MS; *m/z* (%): 561 (35) $[M^+]$, 546 (5) $[M^+ - Me]$, 399 (40) $[M^+ - Zr - 2Cl]$, 285 (100) $[M^+ - Zr - C_9H_6 - 2Cl]$. $C_{24}H_{30}BCl_2NSi_2Zr$ (561.62): calcd. C 51.33, H 5.38, N 2.49; found C 51.02, H 5.45, N 2.28.

$[\{iPr_2NB(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_9H_6)\}ZrCl_2]$ (8): $Na[C_5H_5]$ (1.51 g, 17.20 mmol) was suspended in 40 mL hexane and a solution of iPr_2NBCl_2 (3.13 g, 17.20 mmol) in 5 mL hexane was added dropwise at 0°C. After warming to ambient temperature, the suspension was stirred for 2 h. NaCl was removed by filtration, the residue was washed with 5 mL hexane and the filtrate added dropwise to a suspension of $Li[C_9H_7]$ (2.10 g, 17.20 mmol) in 20 mL hexane at 0°C. After stirring for 4 h at ambient temperature the LiCl was removed by filtration, washed with 5 mL hexane, and 10 mL of diethyl ether was added to the filtrate. The filtrate was cooled to 0°C and 21.50 mL (34.40 mmol) 1.6 M BuLi in hexane was added slowly. A white precipitate was formed immediately, the suspension was allowed to come to ambient temperature and stirred for 16 h. The suspension was cooled to −70°C and $[ZrCl_4(thf)_2]$ (6.49 g, 17.20 mmol) was added. After warming to ambient temperature and stirring for an additional 4 h, the orange suspension was filtered, evaporated to dryness, and the remaining solid was extracted with 30 mL CH_2Cl_2. After filtration compound **8** was obtained as an orange crystalline solid at −30°C (6.37 g, 82%). − ^{1}H NMR (CD_2Cl_2): δ = 1.18 (d, 6 H, Me), 1.39 (d, 6 H, Me), 3.50 (m, 1 H, C*H*Me_2), 4.08 (m, 1 H, C*H*Me_2), 6.21 (m, 1 H, CH_{ind}), 6.53 (m, 1 H, CH_{ind}), 6.46, 6.71 (2m, 4 H, C_5H_4), 7.28 (m, 2 H, CH_{ind}), 7.60 (m, 2 H, CH_{ind}). − ^{11}B NMR: δ = 40.0 (s). − ^{13}C NMR: δ = 23.42, 26.16 (Me), 40.07, 44.34 (*C*HMe_2), 116.23, 122.09, 122.96, 125.10 (C_5H_4), 126.19, 126.74, 127.65, 127.90, 133.61, 134.28 (CH_{ind}). − MS; *m/z* (%): 451 (5) $[M^+]$, 436 (20) $[M^+ - Me]$, 115 (100) $[C_9H_6^+]$. − $C_{20}H_{24}BCl_2NZr$ (451.36): calcd. C 53.22, H 5.36, N 3.10; found C 52.97, H 5.44, N 2.91.

$[\{iPr_2NB(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_9H_6)\}HfCl_2]$ (9): As described for **8** $Na[C_5H_5]$ (0.30 g, 3.41 mmol) and $Li[C_9H_7]$ (0.42 g, 3.41 mmol) were treated with iPr_2NBCl_2 (0.62 g, 3.41 mmol) and subsequently 1.6 M BuLi with (4.26 mL, 6.82 mmol) in hexane and $HfCl_4$ (1.09 g, 3.41 mmol). Compound **9** was obtained as an orange, crystalline solid (1.36 g, 74%). − ^{1}H NMR (CD_2Cl_2): δ = 1.18 (d, 6 H, Me), 1.40 (d, 6 H, Me), 3.51 (m, 1 H, C*H*Me_2), 4.06 (m, 1 H, C*H*Me_2), 6.05, (m, 2 H, C_5H_4) 6.36 (m, 1 H, CH_{ind}), 6.48 (m, 2 H, C_5H_4), 6.55 (m, 1 H, CH_{ind}), 7.28 (m, 2 H, CH_{ind}), 7.61 (m, 2 H, CH_{ind}). − ^{11}B NMR: δ = 39.6 (s). − ^{13}C NMR: δ = 22.40, 25.56 (Me), 39.47, 46.34 (*C*HMe_2), 117.63, 121.19, 121.86, 124.00 (C_5H_4), 124.89, 125.64, 126.40, 126.60, 132.21, 134.18 (CH_{ind}). − MS; *m/z* (%): 539 (15) $[M^+]$, 524 (40) $[M^+ - Me]$, 504 (25) $[M^+ - Cl]$, 115 (100) $[C_9H_6^+]$. − $C_{20}H_{24}BCl_2HfN$ (538.63): calcd. C 44.60, H 4.49, N 2.60; found C 43.95, H 4.44, N 2.31.

X-ray Structure Determination of 3b: $C_{24}H_{32}BNSi_2$; formula mass 401.51 g·mol^{-1}, monoclinic spacegroup *C2/c* (No. 15); a = 33.283(6), b = 7.069(2), c = 23.734(5) Å, β = 120.08(3)°, V = 4832(5) Å^3, Z = 8, ρ_{calcd} = 1.10 g·cm^{-3}, μL_{in} = 1.38 mm^{-1}. ENRAF-Nonius CAD4 diffractometer; CuK_α-radiation (λ = 1.54184 Å); graphite monochromator. Data collection at 293 K on a colourless crystal of about 0.44 × 0.22 × 0.16 mm^3 using ω scans in the diffraction range $3 < 2\Theta < 65°$ yielded 8368 reflections. The data were corrected for Lorentz and polarization effects, and a numerical absorption correction by Gaussian integration[19] (min. trans. 0.669, max. trans. 0.817) was applied. After merging symmetry-equivalent data 4159 unique reflections remained for structure solution by direct methods[20] and subsequent Fourier difference syntheses. Least-squares refinement on structure factors[21] was performed with anisotropic displacement parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions $\{C-H = 0.98$ Å, $U_{iso}(H) = 1.3\ U_{eq}(C)\}$. Convergence was obtained for 253 variables, 2382 unique observations with $I > 1.0\ \sigma(I)$ and R = 0.064, R_w = 0.069, GOF = 1.145. A final difference Fourier map showed fluctuations of less than 0.65 eÅ^{-3}.

X-ray Structure Determination of 4a: $C_{12}H_{14}BCl_2NZr$; formula mass 345.19 g·mol^{-1}, monoclinic spacegroup *P*2$_1$/*n* (No. 14); a = 11.532(3), b = 10.099(4), c = 12.179(4) Å, β = 104.70(2)°, V = 1372(1) Å^3, Z = 4, ρ_{calcd} = 1.67 g·cm^{-3}, μL_{in} = 2.67 mm^{-1}. ENRAF-Nonius CAD4 diffractometer; AgK_α-radiation (λ = 0.56087 Å); graphite monochromator. Data collection at 293 K on a colourless rod of about 0.40 × 0.20 × 0.15 mm^3 using $\omega-2\Theta$ scans in the diffraction range $1 < \Theta < 24°$ resulted in 9114 reflections. The data were corrected for Lorentz and polarization effects. After merging symmetry-equivalent data 4368 unique reflections remained for structure solution by direct methods;[20] the structure model was completed by Fourier difference syntheses. Least-squares refinement on structure factors[21] was performed with anisotropic displacement parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions $\{C-H = 0.98$ Å, $U_{iso}(H) = 1.3\ U_{eq}(C)\}$. Convergence was obtained for 168 variables, 3408 observed data with $I > 1.0\ \sigma(I)$ and R = 0.041, R_w = 0.039, GOF = 0.964. A final difference Fourier map showed fluctuations of less than 0.96 eÅ^{-3}.

Crystallographic data (excluding structure factors) for the structures) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127944 (**3b**) and CCDC-127945 (**4a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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