Synthesis, Structures and Reactivity of *N*-Borane-Protected 1,1′-Bisimidazoles with Different Bridging Functions

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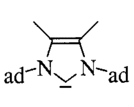
Dedicated to Prof. Dr. Otto J. Scherer

Keywords: Boranes / Carbenes / Carbene complexes / Nitrogen heterocycles / Macrocycles

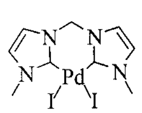
The bridging functions Me_2Si, $[(CH_2)_3(CMe_2)_2N]B$ and CH_2 have been used to connect two imidazoles in the 1,1′-position. The bisimidazolyl compounds were treated with BH_3 or BEt_3, and the resulting *N*,*N*′-bisborane-protected products **1**, **3b**, **4a**, and **5b** were characterized by X-ray structure analyses. Reaction of 1,1′-bis(4,5-dimethylimidazolyl)methane with BBr_3 yielded the macrocyclic dicationic tetraimidazolyl compound **6**. The behavior of the N-protected bisimidazoles **1** and **3**–**5** towards deprotonating agents was investigated and it was found that 1,1′-bis(3-borane-4,5-dimethylimidazolyl)methane (**5b**) is deprotonated to give a dianionic dicarbene compound. Its reaction with Cp_2MCl_2 allowed the formation of the corresponding titanocene and zirconocene complexes **8** and **9**, which were characterized by X-ray structure analyses. In **9** a 3c,2e B–H–Zr bond is present.

Introduction

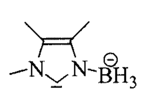
The coordination behavior of *N*-heterocyclic carbenes has been studied very intensely since the isolation of 1,3-bis(adamantyl)imidazolin-2-ylidene **A** by Arduengo et al. in 1991.[1] Many *N*,*N*-methylene- and -ethylene-bridged bis(imidazolin-2-ylidene)metal complexes have since been prepared.[2] Recently the catalytic activity in Heck and Suzuki coupling reactions of the diiodopalladium(II) complex of 1,1′-methylenebis(3-methylimidazolin-2-ylidene) **B** has been investigated.[3]



A



B



C (= L)

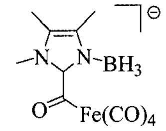
Addition of BH_3 to 1-alkylimidazoles leads to neutral *N*-borane adducts, which are deprotonated by butyllithium to give anionic 3-borane-1-alkylimidazol-2-ylidenes **C** (L). These anions were found to be excellent ligands to form transition metal complexes of manganese[4] (**D**), titanium[5] (**E**), iron[4−6] (**F**−**H**) and the distorted tetrahedral anionic complexes of vanadium[5,6] (**I**) and scandium[6] (**J**). In the latter case the formation of four 3c,2e B−H−Sc bonds was observed.

The dinuclear compound **K**[7] is the only structurally characterized imidazol-2-ylidene complex of titanium.

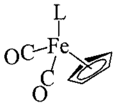
In the following we report on new N,N-bridging functions in 1-borane-protected bisimidazolyl compounds and their behavior towards treatment with butyllithium to give chelating dianionic dicarbene ligands.

L-Mn$(CO)_5$
D

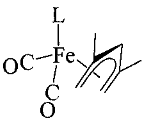
L-TiCp_2
E



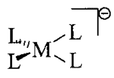
F



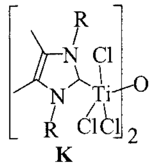
G



H



M | V Sc
| **I J**



K

Results and Discussion

Formation and Reactivity of Bisimidazolyl Compounds 1, 2a−b, 3a−b, 4a, and 5a−b

The addition of two equivalents of BH_3·thf to a solution of 1,1′-bis(imidazolyl)dimethylsilane[8] yields the colorless *N*,*N*-bis-borane adduct **1**, which crystallizes from a saturated THF solution (Scheme 1).

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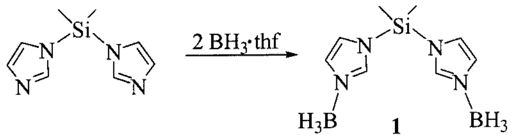


Scheme 1

The ^{11}B NMR spectrum shows a quadruplet at $\delta = -21.5$; three imidazole signals in the proton NMR spectrum and one singlet for the methyl groups prove the symmetry of the molecule. In the crystal, **1** has a twofold rotation axis (Figure 1). The N2−B1 distance [1.580(2) Å] is typical for borane adducts of nitrogen compounds. The coordination geometry at the silicon atom is distorted tetrahedral with N1−Si−N1A and C4−Si−C4A angles of 104.4(1)° and 117.7(1)°, respectively. Attempts to doubly deprotonate **1** in the 2,2′-positions with alkyllithium compounds (MeLi, *t*BuLi, *n*BuLi) to generate a dicarbene were unsuccessful due to decomposition.

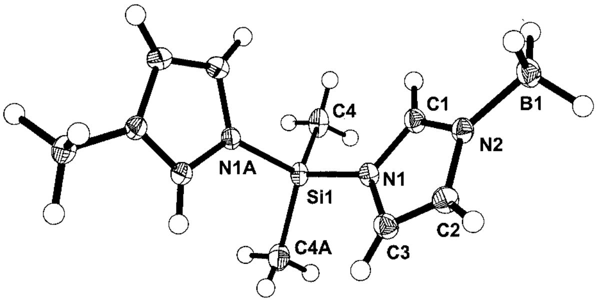
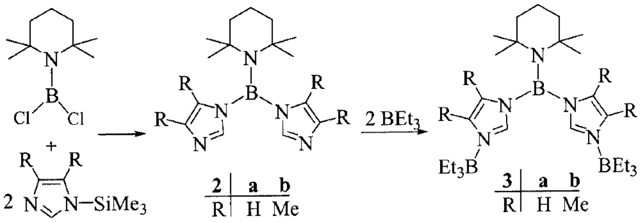


Figure 1. Structure of **1** in the crystal; selected bond lengths [Å] and angles [°]: Si−N1 1.776(1), N1−C3 1.392(1), C2−C3 1.350(2), C2−N2 1.381(1), N2−C1 1.315(1), C1−N1 1.356(1), N2−B1 1.580(2); N1−Si−N1A 104.4(1), C4−Si−C4A 117.7(1), Si−N1−C1 126.0(1), N1−C1−N2 111.2(1)

We have shown that attempts to synthesize imidazolylboranes by reaction of 1-trimethylsilylimidazoles with haloboranes lead to polymeric or (under certain conditions) oligomeric products.[9] This is caused by donor/acceptor interactions of the electron pair at the nitrogen in the 3-position with the empty p_z orbital at the boron atom. Formation of oligomeric adducts is avoided when the borane compound is substituted by a sterically demanding and electron-donating group such as 2,2′,6,6′-tetramethylpiperidide (TMP): reactions of (tmp)BCl_2 with two equivalents of 1-trimethylsilylimidazole or 4,5-dimethyl-1-trimethylsilylimidazole yielded the first monomeric bis(imidazolyl)boranes **2a** and **2b**, respectively (Scheme 2).



Scheme 2

The ^{11}B NMR chemical shifts [δ = 28.2 (**2a**), 28.5 (**2b**)] indicate a trigonal coordination at the boron atoms. Compound **2a** shows the expected set of signals in the proton NMR spectrum (three imidazolic protons, one singlet for methyl groups and a multiplet for methylene groups of TMP), whereas the methyl groups of the TMP substituent in **2b** appear as two singlets ($|\nu_a - \nu_b| = 14.8$ Hz), caused by restricted rotation at the N−B bond. Proton NMR spectra at different temperatures (Figure 2) provide a coalescence temperature of 26 °C. The resulting free activation enthalpy of rotation ($\Delta G^{\#}$) at the B−N bond is 64.6 kJ/mol, calculated by the Eyring equation.[10]

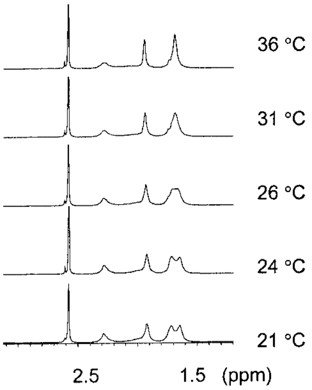


Figure 2. ^1H NMR spectra of **2b** at different temperatures

Attempts to alkylate **2a** in the 3,3′-positions (with CH_3I, 2-iodopropane, or Me_3OBF_4) led to decomposition products, and treatment with Me_3SiBr or BH_3·thf to quaternization of the boron atoms. The reaction of **2a** and **2b** with two equivalents of BEt_3 yields the 3,3′-bis(triethylborane) adducts **3a** and **3b** (Scheme 2), as indicated by an additional signal in the ^{11}B NMR spectra at $\delta \approx -1$. Restricted rotation at the B−N bond also exists in **3b**; there are two signals for the methyl groups.

The X-ray structure analysis of a single crystal of **3b** confirms the steric demand of the substituents coordinated at B1 (Figure 3). The angle of 55° between the C23−N5−C27 and N1−B1−N3 planes is a compromise between the mutual repulsion of the TMP and imidazolyl substituents and donation of the electron pair of N5 to the p_z orbital of B1. The planarity around N5 and the bond length of B1−N5 [1.405(2) Å] show that an effective overlap of the p_z orbitals is possible even at a torsion angle of 55°. Electron donation to the central boron atom from the imidazole rings is negligible because the B1−N1,3 distances (1.476 Å) are in a range typical of B−N single bonds. The N1−B1−N3 angle [115.1(1)°] is smaller than the two neighboring angles [N1−B1−N5: 121.9(2)°; N3−B1−N5: 123.0(1)°].

Treatment of **3a** and **3b** with *n*BuLi or *t*BuLi to yield bisimidazol-2-ylidenes always led to decomposition (quaternisation of the central boron atom is observed by ^{11}B NMR spectroscopy). Further reactions of **3a,b** with metal compounds such as $M(OAc)_2$ (M = Zn, Ni, Pd) and $Ti(NMe_2)_4$ to give metal carbene complexes were unsuccessful.

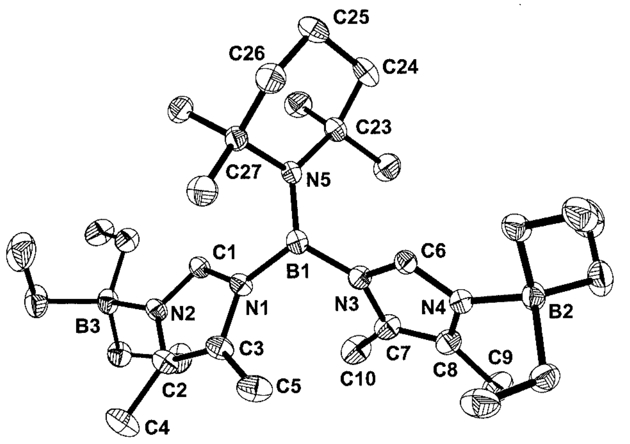
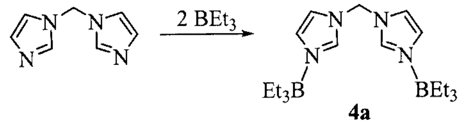


Figure 3. Structure of **3b** in the crystal; the hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: N1−C1 1.352(2), N1−C3 1.401(2), N1−B1 1.475(2), N2−C1 1.307(2), N2−C2 1.406(2), N2−B3 1.645(2), N3−B1 1.477(2), N5−B1 1.405(2), C2−C3 1.364(3), C2−C4 1.486(3); C1−N1−C3 106.2(1), C1−N1−B1 122.1(1), N5−B1−N1 121.9(2), N5−B1−N3 123.0(1), N1−B1−N3 115.1(1), N2−C1−N1 112.4(1)

Addition of two equivalents of BEt_3 to 1,1′-bis(imidazolyl)methane yields the crystalline bis(triethylborane) adduct **4a** (80%; Scheme 3).



4a

Scheme 3

The ^{11}B NMR signal of **4a** ($\delta = -1.6$) is in the same region as that of **3a,b**. In the ^1H NMR spectrum the signals of the ethyl groups appear at $\delta = 0.30$ (CH_2) and 0.58 (CH_3), the methylene signal is at $\delta = 6.09$ and the signals of imidazolic protons are at $\delta = 7.06$, 7.23 and 7.91. These shifts show that the imidazolic protons are not as strongly deshielded when forming a triethylborane adduct as when they are alkylated to form imidazolium cations.

The molecular structure of **4a** is shown in Figure 4. In the crystal, **4a** has a C_2 symmetry. The N1−C1−N1A angle [110.6(1)°] is smaller than the comparable angle of **3b** as a result of the tetrahedral bridging function. The coordination geometry at the boron atoms is distorted tetrahedral. While the average C−B1−C angle is 112.5°, the angles C−B1−N2 [av. 106.3(1)°] are smaller. The imidazole rings are nearly symmetric: the C2−N2 and N2−C3 distances barely deviate from those of C2−N1 and N1−C4.

Treatment of 1,1′-bis(imidazolyl)methane or 1,1′-bis(4,5-dimethylimidazolyl) methane with $BH_3{\cdot}thf$ gives the corresponding 3,3′-bisborane adducts **5a,b** as air- and moisture-sensitive solids in quantitative yields.

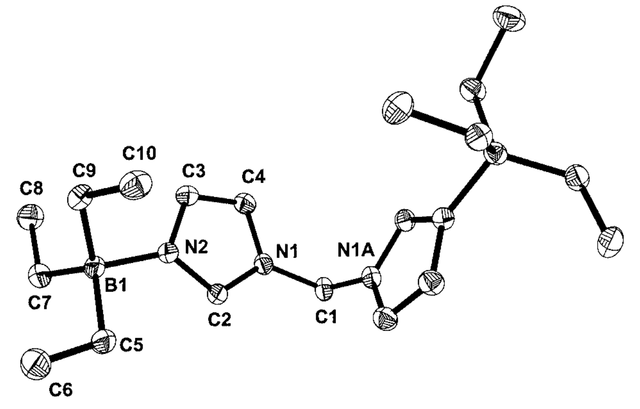
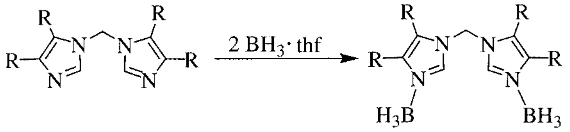


Figure 4. Structure of **4a** in the crystal; the hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: C1−N1 1.454(1), N1−C2 1.349(1), C2−N2 1.322(1), N2−C3 1.384(1), C3−C41.349(2), C4−N11.380(1), N2−B11.649(1); N1−C1−N1A 110.6(1), C1−N1−C2125.6(1), C2−N2−B1127.1(1), N2−B1−C5106.1(1)



5	**a**	**b**
R	H	Me

Scheme 4

In the mass spectra, the molecular peak of **5a** could not be found as it easily loses a BH_3 ligand under EI-MS conditions to give $m/z = 161$ $[M - H - BH_3]^+$. The ^1H NMR spectrum of **5a** shows four signals of equal intensity. The methylene signal ($\delta = 6.32$) and the imidazole protons at C4,5 ($\delta = 7.10$, 7.67) have almost the same chemical shifts as in **4a**. In contrast, however, the signal for the proton at C2 is shifted toward lower field ($\delta = 8.64$). A very broad signal at $\delta = 2$ indicates the presence of boron-bonded hydrogen atoms. No proton coupling was observed to the ^{11}B NMR signal at $\delta = -18.4$. Similar spectroscopic results were obtained for **5b**: an ^{11}B NMR signal at $\delta = -20.3$ indicates addition of BH_3, and the ^1H NMR spectrum confirms the formation of **5b**. Its structure was determined by an X-ray diffraction analysis (Figure 5).

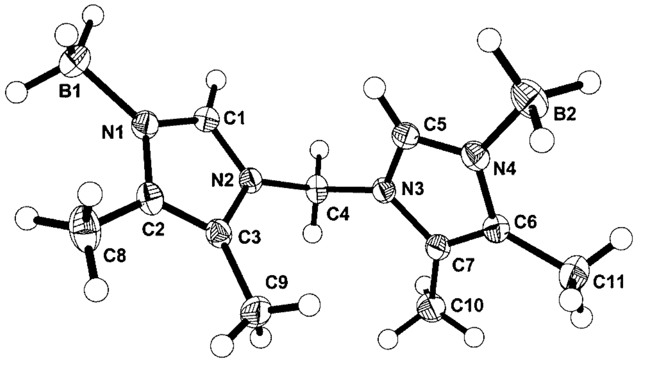
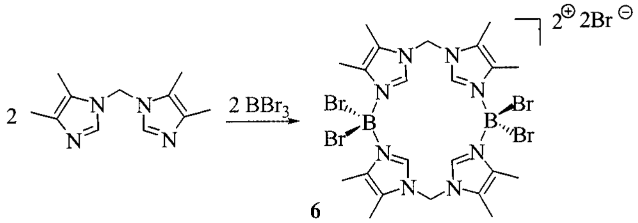


Figure 5. Structure of **5b** in the crystal; selected bond lengths [Å] and angles [°]: B1−N1 1.577(1), N1−C1 1.318(1), C1−N2 1.346(1), N2−C3 1.395(1), C2−C3 1.359(1), N1−C2 1.392(1), N2−C4 1.448(1), C2−C8 1.488(1); B1−N1−C1 125.9(1), N1−C1−N2 109.8(1), N2−C4−N3 110.9(1)

The bond lengths and angles in **5b** are similar to those of **4a**. The N1−C1−N3 angle is 110.9(1)°, and the tetrahedral coordination geometry at the boron atoms is not as strongly distorted as in **4a** [av. angle H−B−H: 111.4(1)°; N−B−H: 107.5(1)°]. The imidazole rings are not symmetric, the N2−C2 and N4−C5 bonds are 0.03(1) Å shorter than N1−C2 and N3−C5.

When 1,1′-bis(4,5-dimethylimidazolyl)methane is allowed to react with BBr_3 in a 1:1 ratio, a yellow solid is obtained that is soluble only in Me_2SO (Scheme 5). The ^{11}B NMR spectrum shows one signal at δ = −12.3, and the ^1H NMR spectrum indicates the formation of a highly symmetric product: two signals are observed for the methyl groups at δ = 2.21 and 2.23, a singlet for the methylene protons is at δ = 6.70 and a signal for the proton at the C2 position is detected at δ = 9.38. In comparison with the compounds **4** and **5** this signal is shifted significantly towards low-field, and is found in a region typical of imidazolium cations rather than borane adducts. This observation together with the very high polarity and symmetry of the product indicate the formation of the cyclic diboronium dibromide **6**.



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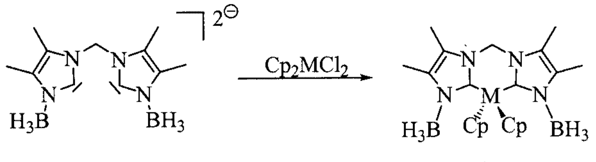
Scheme 5

The signals for the carbon atoms of the imidazole rings are observed at δ = 135.4, 126.4 and 126.1, the methylene bridging carbon atoms at δ = 55.7 and the methyl groups at δ = 9.1 and 8.0. The FAB mass spectrum exhibits peaks derived from the cation of **6** at *m*/*z* = 749 $[M - H]^+$ and *m*/*z* = 579 $[M - BBr_2]^+$.

Attempts to generate dianionic bis(imidazol-2-ylidene) species were unsuccessful starting either from borane adducts of bis(imidazolyl)silane **1** or from the bis(imidazolyl)boranes **3**. However, the reaction of **5b** with two equivalents of butyllithium at −78 °C causes the ^1H NMR signal of the C2 bonded hydrogen atoms to disappear when the reaction is carried out in $[D_8]$thf and the solution is kept cold. After warming to 20 °C only decomposition products of the dianionic dicarbene **7** were detected, and these could not be characterized. In order to stabilize **7** the titanium complex **8** and the zirconium complex **9** were synthesized by adding a freshly prepared solution of **7** to a solution of the corresponding metallocene dichloride at −78 °C (Scheme 6). Bis(imidazol-2-ylidene)titanium complexes have been prepared previously.[1b]



7

	8	**9**
M	Ti	Zr

Scheme 6

Compound **8** is an extremely air- and moisture-sensitive red solid. On exposure to air the color changes to green immediately. Remarkably, in the proton NMR spectrum two signals for the Cp rings are observed at δ = 6.45 and 6.53 and two signals for the methylene bridge at δ = 6.08 and 6.31. In the ^{13}C NMR spectrum two signals for Cp rings are found at δ = 109.9 and 111.8, the signal of the methylene carbon is located at δ = 42.1, and the imidazole carbons (C4,4′ and C5,5′) are observed at δ = 132.9 and 134.1. No signal was found for the metal-bonded carbon atoms. In the EI-MS the molecular peak $[M - H]^+$ is detected at *m*/*z* = 407 as well as a peak for $[M - BH_2]^+$ at *m*/*z* = 395. A different fragmentation pattern was found for the colorless **9**: $[M]^+$ was not observed but rather $[M - Cp - H]^+$ at *m*/*z* = 384. More differences are seen in the NMR spectra: **8** exhibits one ^{11}B NMR signal at δ = −22.3, whereas **9** shows two signals at δ = −17.8 and −20.9, respectively. In the proton NMR spectrum of **9**, only one signal is observed for the methylene bridge (δ = 5.47) and for the Cp rings (δ = 6.27). The zirconium-bonded carbon atoms show a signal at δ = 173.6.

The differences in the NMR spectra of **8** and **9** can be explained on results of their X-ray structure analyses. Compound **8** crystallizes with two independent, and almost identical, molecules in the unit cell (Figure 6). The methylene bridge of **8** is turned out of the coordination plane formed by the imidazole rings and the titanium, and, subsequently, the methylene protons become different, one be-

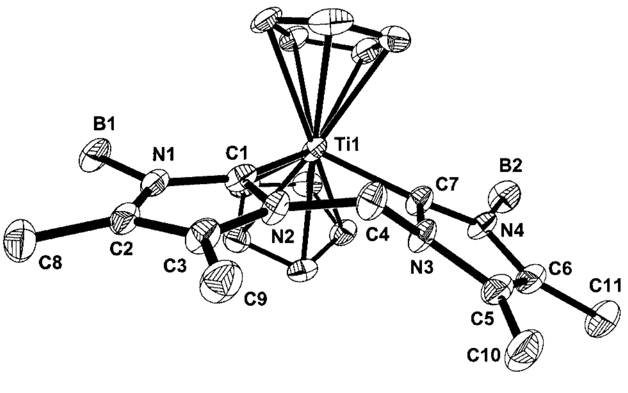


Figure 6. Structure of **8** in the crystal; the CH_2Cl_2 molecule and the carbon-bonded hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: C1−Ti 2.210(5), C7−Ti 2.215(5), N1−B1 1.574(6), N1−C1 1.347(6), C1−N2 1.369(6), N2−C3 1.400(6), C2−C3 1.345(7), N1−C2 1.391(6); N2−C4 1.442(6); C1−Ti−C7 88.3(2), Ti−C1−N2 122.7(3), C1−N2−C4 124.9(4), N2−C4−N3 113.0(4), B1−N1−C1 127.3(4)

coming axial and the other equatorial. The ligand is folded along the C1−Ti axis. A similar behavior of bisimidazolyl ligands has been described by Herrmann et al.[2c] and of a palladium(II) carbene complex of a bistriazole ligand by Diez-Barra et al.[11] Flipping up and down of the methylene bridge does not occur in solution at 20 °C, and this rigid six-membered ring is obviously also the reason for the two different signals of the Cp rings. The C2−Ti−C5 angle is 88.3(2)°, and the N1−C1−N3 angle is a little larger than in **5b** [113.0(4)° vs. 110.9(1)°]. The carbene-carbon to titanium distances are between 2.202(5) and 2.215(5) Å (values for both independent molecules).

The methylene bridge of **9** in the crystal is weakly turned out of the coordination plane and there is no folding observed along the C1−Zr axis (Figure 7). That is the reason why only one signal is found for the methylene protons and for the Cp rings in the ^{1}H NMR spectrum. The C2−Zr−C5 angle is smaller than in **8** (75.4°), and the N1−C1−N3 angle is similar (114.2°), although the carbene-carbon to zirconium distances are quite different: 2.38 (C2−Zr) and 2.30 Å (C5−Zr). This difference is caused by a 3c,2e interaction between B2−H2A−Zr which is non-fluxional in solution at 20 °C according to the two signals in ^{11}B NMR spectrum. Because of this bond compound **9** is an 18-electron complex, while **8** has only 16 valence electrons, which may be the reason for its lower stability.

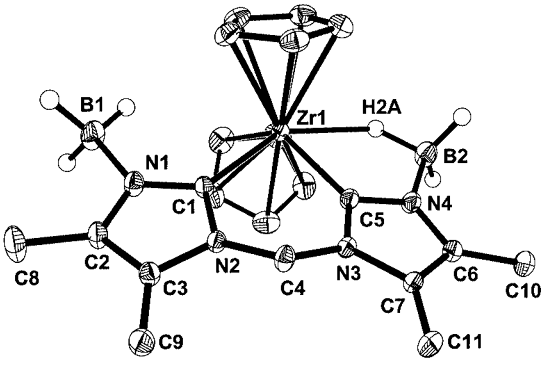


Figure 7. Structure of **9** in the crystal; the carbon-bonded hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: C1−Zr 2.383(1), C5−Zr 2.299(1), N1−B1 1.577(2), N1−C1 1.357(2), C1−N2 1.379(2), N2−C3 1.396(1), C2−C3 1.353(2), N1−C2 1.394(2), N2−C4 1.455(1), B2−H2A 1.23(2), H2A−Zr 2.16(2); C1−Zr−C5 75.4(1), Zr−C1−N2 128.7(1), C1−N2−C4 128.7(1), N2−C4−N3 114.2(1), B1−N1−C1 129.9(1), B2−N4−C5 117.5(1)

Conclusion

It is possible to synthesize monomeric bis(imidazolyl)boranes when a large, electron-donating substituent such as tetramethylpiperidide is used. Due to the steric requirements of TMP a restricted rotation at the B−N bond is observed for **2b** and **3b**. Treatment of *N,N′*-borane-protected bis(4,5-dimethylimidazolyl)methane (**5b**) with butyllithium yields a dianionic dicarbene which coordinates to titanocene and zirconocene complex fragments to form the neutral compounds **8** and **9**. Different coordination numbers at the titanium and the zirconium atom are observed in the X-ray structure analyses of the complexes **8** and **9**.

Experimental Section

General: All reactions were carried out under dry argon, using standard Schlenk techniques. Solvents were dried, distilled and saturated with nitrogen. Glassware was dried with a heat-gun under high vacuum. 1,1′-Bis(imidazolyl)dimethylsilane,[8] 2,2′,6,6′-tetramethylpiperidyldichloroborane,[12] 1,1′-bis(imidazolyl)methane,[13] 1,1′-bis(4,5-dimethylimidazolyl)methane,[13] and 4,5-dimethyl-1-trimethylsilylimidazole[14] were prepared according to literature procedures.

1,1′-Bis(3-borane-imidazolyl)dimethylsilane (1): A 1 M solution of BH_3·thf (20.5 mL) in THF was added dropwise at −78 °C to a solution of 1,1′-bis(imidazolyl)dimethylsilane (1.93 g, 10.0 mmol) in 60 mL of THF. After warming to 20 °C the solvent was removed and the residue washed with pentane, CH_2Cl_2 and recrystallized from a hot saturated solution in THF at −20 °C. The yield was increased by further concentration of the solution to give colorless cubes (1.77 g, 80%). ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.11 (s, 6 H, CH_3), 2.2 (br., 6 H, BH_3), 7.15 (s, 2 H, CH=C*H*−N), 7.27 (s, 2 H, C*H*=CH−N), 8.19 (s, 2 H, N=CH−N). ^{11}B NMR (64.2 MHz, [D$_8$]THF): δ = −21.5 (q, $^1J_{B\text{-}H}$ = 91 Hz). ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = −5.9 (CH_3), 119.9 (*C*H=CH−N), 127.9 (CH=*C*H−N), 139.2 (N=CH−N).

1,1′-Bis(imidazolyl)-1-(2,2′,6,6′-tetramethylpiperidyl)borane (2a): 1-Trimethylsilylimidazole (5.25 g, 37.5 mmol) was added to a solution of 2,2′,6,6′-tetramethylpiperidyldichloroborane (4.10 g, 18.7 mmol) in 100 mL of CH_2Cl_2 at −30 °C. After stirring for 2 h the mixture was allowed to warm to 20 °C and the solvent was removed under vacuum. The product was washed with hexane and dried to give a colorless **2a**. Yield: 4.00 g (75%), m.p. 122 °C. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.15 (s, 12 H, CH_3), 1.60 (m, 4 H, CH_2), 1.85 (m, 2 H, CH_2), 7.04 (s, 2 H, CH=C*H*−N), 7.13 (s, 2 H, C*H*=CH−N), 7.79 (s, 2 H, N=CH−N). ^{11}B NMR (64.2 MHz, CD_2Cl_2): δ = 28.2. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 17.6 (CH_2*C*H$_2$CH$_2$), 32.2 (CH_3), 39.6 (*C*H$_2$CH$_2$*C*H$_2$), 56.5 [*C*(CH_3)$_2$], 121.9 (*C*H=CH−N), 131.4 (CH=*C*H−N), 142.8 (N=CH−N). EI-MS: *m*/*z* (%) = 285 (2) [M]$^+$, 270 (1) [M − CH_3]$^+$. HR EI-MS ($C_{15}H_{24}{}^{11}BN_5$): calcd. 285.2125; found 285.2111; Δ*m* = 1.4 mmu.

1,1′-Bis(4,5-dimethylimidazolyl)-1-(2,2′,6,6′-tetramethylpiperidyl)borane (2b): The synthesis of this compound was carried out analogously to **2a** with 4,5-dimethyl-1-trimethylsilylimidazole. Yield: 74%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.19 (s, 6 H, CH_3-TMP), 1.25 (s, 6 H, CH_3-TMP), 1.47 [s, 6 H, CH_3 (Im)], 1.55 (m, 2 H, CH_2), 1.83 (m, 4 H, CH_2), 2.08 [s, 6 H, CH_3 (Im)], 7.55 (s, 2 H, N=CH−N). ^{11}B NMR (64.2 MHz, CD_2Cl_2): δ = 28.5. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 9.0 [CH_3(Im)], 12.9 [CH_3(Im)], 17.0 (CH_2*C*H$_2$CH$_2$), 32.8 (CH_3-TMP), 35.3 (CH_3-TMP), 38.6 (*C*H$_2$CH$_2$*C*H$_2$), 56.3 [*C*(CH_3)$_2$], 125.2 (*C*Me=CMe−N), 138.2 (CMe=*C*Me−N), 140.3 (N=CH−N). EI-MS: *m*/*z* (%) = 341 (17) [M]$^+$, 326 (88) [M − CH_3]$^+$. HR EI-MS ($C_{19}H_{32}{}^{11}BN_5$): calcd. 341.2751; found 341.2738; Δ*m* = 1.4 mmu. $C_{19}H_{32}BN_5$ (341.3): calcd. C 66.86, H 9.45, N 20.52; found C 65.52, H 9.37, N 20.09.

1-(2,2′,6,6′-Tetramethylpiperidyl)-1,1′-bis(3-triethylborane-imidazolyl)borane (3a): Triethylborane (2.54 g, 25.9 mmol) was added dropwise to a solution of **2a** (3.71 g, 13.0 mmol) in 60 mL of CH_2Cl_2 at −60 °C. After warming to 20 °C the solution was stirred overnight. The solvent was removed under vacuum and the product washed with hexane. Recrystallization from CH_2Cl_2 at −20 °C yielded 3.06 g (49%) of a pale-yellow solid, m.p. 114 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.34 (q, $^3J_{H-H}$ = 7 Hz, 12 H, $C\mathit{H}_2CH_3$), 0.61 (t, $^3J_{H-H}$ = 7 Hz, 18 H, $CH_2C\mathit{H}_3$), 1.19 (s, 12 H, CH_3), 1.65 (m, 4 H, CH_2), 1.88 (m, 2 H, CH_2), 6.91 (s, 2 H, CH=C*H*−N), 7.28 (s, 2 H, C*H*=CH−N), 7.89 (s, 2 H, N=CH−N). ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 28.2 (br.,BN_3), −0.8 (br., N-BEt_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 9.6 ($CH_2\mathit{C}H_3$), 14.8 (br., $\mathit{C}H_2CH_3$), 16.9 ($CH_2\mathit{C}H_2CH_2$), 32.7 (CH_3), 39.2 ($\mathit{C}H_2CH_2\mathit{C}H_2$), 56.4 [$\mathit{C}(CH_3)_2$], 121.6 (*C*H=CH−N), 127.5 (CH=*C*H−N), 139.9 (N=CH−N).

1-(2,2′,6,6′-Tetramethylpiperidyl)-1,1′-bis(3-triethylborane-4,5-dimethylimidazolyl)borane (3b): Compound **3b** was prepared from **2b** analogously to **3a**. Yield: 57% colorless cubes. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.41 (q, $^3J_{H-H}$ = 7 Hz, 12 H, $C\mathit{H}_2CH_3$), 0.56 (t, $^3J_{H-H}$ = 7 Hz, 18 H, $CH_2C\mathit{H}_3$), 1.15 (s, 6 H, CH_3), 1.35 (s, 6 H, CH_3), 1.48 (s, 6 H, CH_3), 1.56 (m, 2 H, CH_2), 1.89 (m, 4 H, CH_2), 2.22 (s, 6 H, CH_3), 7.73 (s, 2 H, N=CH−N). ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 29.7 (br., BN_3), − 0.9 (br., N-BEt_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 8.5 [CH_3(Im)], 9.7 ($CH_2\mathit{C}H_3$), 10.9 [CH_3(Im)], 13.48 (br., $\mathit{C}H_2CH_3$), 15.4 ($CH_2\mathit{C}H_2CH_2$), 32.2 (CH_3-TMP), 35.1 (CH_3-TMP), 37.1 ($\mathit{C}H_2CH_2\mathit{C}H_2$), 60.0 [$\mathit{C}(CH_3)_2$], 126.1 (*C*Me=CMe−N), 135.0 (CMe=*C*Me−N), 138.6 (N=CH−N). EI-MS: *m/z* (%) = 341 (66) [M − $2BEt_3$]$^+$, 326 (100) [M − $2BEt_3$ − CH_3]$^+$.

1,1′-Bis(3-triethylboraneimidazolyl)methane (4a): Compound **4a** was prepared from 1,1′-bis(imidazolyl)methane in THF analogously to **3a**. Yield: 80% colorless crystals, m.p. 96 °C. ^1H NMR (200 MHz, CD_2Cl_2): δ = 0.30 (q, $^3J_{H-H}$ = 7 Hz, 12 H, $C\mathit{H}_2CH_3$), 0.58 (t, $^3J_{H-H}$ = 7 Hz, 18 H, $CH_2C\mathit{H}_3$), 6.09 (s, 2 H, CH_2), 7.06 (s, 2 H, CH=C*H*−N), 7.23 (s, 2 H, C*H*=CH−N), 7.91 (s, 2 H, N=CH−N). ^{11}B NMR (64.2 MHz, CD_2Cl_2): δ = −1.6 (br.). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 9.4 ($CH_2\mathit{C}H_3$), 14.4 (br., $\mathit{C}H_2CH_3$), 58.2 (CH_2), 118.6 (*C*H=CH−N), 126.9 (CH=*C*H−N), 134.6 (N=CH−N).

1,1′-Bis(3-boraneimidazolyl)methane (5a): A solution of 1,1′-bis(imidazolyl)methane (1.42 g, 9.58 mmol) in 50 mL of THF was cooled to −78 °C. At this temperature 19.2 mL of BH_3·thf (as a 1 M solution in THF) was added through a dropping funnel. The reaction mixture was allowed to warm and stirred for 4 h at 20 °C. During this period a precipitate was formed, which was filtered and washed with pentane. Yield: 1.65 g (98%) white solid. ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.10 (br., 6 H, BH_3), 6.32 (s, 2 H, CH_2), 7.10 (s, 2 H, CH=C*H*−N), 7.67 (s, 2 H, C*H*=CH−N), 8.64 (s, 2 H, N=CH−N). ^{11}B NMR (64.2 MHz, [D_6]DMSO): δ = −18.4 (br.). ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 56.8 (CH_2), 120.9 (*C*H=CH−N), 127.5 (CH=*C*H−N), 137.9 (N=CH−N). EI-MS: *m/z* (%) = 161 (1) [M − BH_3 − H]$^+$, 148 (16) [M − $2BH_3$ + 2H]$^+$.

1,1′-Bis(3-borane-4,5-dimethylimidazolyl)methane (5b): Compound **5b** was prepared from 1,1′-bis(4,5-dimethylimidazolyl)methane analogously to **5a**. Yield: 97%, white solid, m.p. 193 °C. ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.03 (s, 6 H, CH_3), 2.10 (s, 6 H, CH_3), 6.25 (s, 2 H, CH_2), 8.49 (s, 2 H, N=CH−N). ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 8.9 (CH_3), 9.9 (CH_3), 54.6 (CH_2), 125.1 (*C*Me=CMe−N), 131.4 (CMe=*CMe*−N), 137.2 (N=CH−N). ^{11}B NMR (64.2 MHz, [D_6]DMSO): δ = −20.3 (br.).

Cyclic Diboronium Dibromide 6: 1,1′-Bis(4,5-dimethylimidazolyl)methane (186 mg, 0.91 mmol) and tribromoborane (228 mg, 0.91 mmol) were each dissolved in 20 mL of CH_2Cl_2. Both solutions were added simultaneously within 45 min to 100 mL of CH_2Cl_2 through dropping funnels. After addition the suspension was stirred for 1 h, the precipitate was filtered off, washed with pentane and dried to yield 133 mg (32%) of **6** as a colorless solid. ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.21 (s, 12 H, CH_3), 2.23 (s, 12 H, CH_3), 6.70 (s, 4 H, CH_2), 9.38 (s, 4 H, N=CH−N). ^{11}B NMR (64.2 MHz, [D_6]DMSO): δ = −12.3. ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 8.0 (CH_3), 9.1 (CH_3), 55.7 (CH_2), 126.1 (*C*Me=CMe−N), 126.4 (CMe=*C*Me−N), 135.4 (N=CH−N). FAB-MS: *m/z* (%) = 749 (1) [M − H]$^+$, 579 (11) [M − BBr_2]$^+$.

1,1′-Methylene-(3-borane-4,5-dimethylimidazolyl)-2-diylidene (7): In a Teflon sealed NMR tube, 0.08 mL (0.20 mmol) of *n*BuLi (as a 2.5 M solution in hexane) were evaporated to dryness. At −78 °C 20 mg of **5b** (0.09 mmol) was added, followed by 1 mL of cold [D_8]THF. The yellow reaction mixture was shaken and the NMR spectrum measured directly (without warming to 20 °C). ^1H NMR (200 MHz, [D_8]THF): δ = −1.14 (br.), −0.15 (br.), 0.89 (br.), 1.26 (br.) (signals from BuH and BuLi), 1.79 (s, 6 H, CH_3), 1.92 (s, 6 H, CH_3), 6.00 (s, 2 H, CH_2).

[1,1′-Methylene-(3-borane-4,5-dimethylimidazolyl)-2-diylidene]dicyclopentadienyltitanium (8): Compound **5b** (220 mg, 0.95 mmol) in 30 mL of THF was treated with 0.8 mL (2.00 mmol) of *n*BuLi (2.5 M solution in hexane) at −78 °C to yield a solution of **7**. After 30 min this solution was added to a stirred mixture of Cp_2TiCl_2 (250 mg, 1.00 mmol) in 10 mL of THF at −78 °C with a transfer cannula. Within 4 h the reaction mixture was allowed to warm to 20 °C. Evaporation of the solvent, washing of the residue with hexane and drying yielded 291 mg (75%) of dark-red **8**. ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.02 (s, 6 H, CH_3), 2.10 (s, 6 H, CH_3), 6.08 and 6.31 (br., 2 H, CH_2), 6.45 (s, 5 H, C_5H_5), 6.53 (s, 5 H, C_5H_5). ^{11}B NMR (64.2 MHz, [D_6]DMSO): δ = −22.3 (br.). ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 8.9 (CH_3), 9.9 (CH_3), 42.1 (CH_2), 109.9 (C_5H_5), 111.8 (C_5H_5), 132.9 (*C*Me=CMe−N), 134.1 (CMe=*C*Me−N). EI-MS: *m/z* (%) = 407 (2) [M − H]$^+$, 395 (58) [M − BH_2]$^+$. HR EI-MS ($C_{21}H_{29}{}^{11}B_2N_4Ti$) [M − H]$^+$: calcd. 407.2058; found 407.2079; Δ*m* = 2.1 mmu.

[1,1′-Methylene-(3-borane-4,5-dimethylimidazol)-2-diylidene]dicyclopentadienylzirconium (9): Compound **9** was prepared analogously to **8** with Cp_2ZrCl_2. Yield: 80%, white solid. ^1H NMR (200 MHz, CD_2Cl_2): δ = 2.08 (s, 6 H, CH_3), 2.20 (s, 6 H, CH_3), 5.47 (s, 2 H, CH_2), 6.27 (s, 10 H, C_5H_5). ^{11}B NMR (64.2 MHz, [D_6]DMSO): δ = −17.8, −20.9. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 9.2 (CH_3), 9.3 (CH_3), 57.4 (CH_2), 110.8 (C_5H_5), 124.7 (*C*Me=CMe−N), 131.9 (CMe=*C*Me−N), 173.6 (N−C−N). EI-MS: *m/z* (%) = 384 (100) [M − Cp − H]$^+$.

Crystal Structure Determinations of 1, 3b, 4a, 5b, 8 and 9: Crystal data and details of the structure determinations are listed in Table 1 and 2. Intensity data were collected at 173 K (**3b**, **4a**), at 190 K (**1**, **8** and **9**) or at 293 K (**5b**) with a Bruker AXS area detector (Mo-K_α radiation λ = 0.71073 Å, graphite monochromator, ω-scan). The structures were solved by direct methods (SHELXS-86)[15] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97).[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference Fourier maps and refined.

CCDC-174038 (**1**), -174039 (**3b**), -174040 (**4a**), -174041 (**5b**), -174042 (**8**) and -174043 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of

Table 1. X-ray crystallographic data for compounds **1**, **3b** and **4a**

	1	**3b**	**4a**
Empirical formula	$C_8H_{18}B_2N_4Si$	$C_{31}H_{62}B_3N_5$	$C_{19}H_{38}B_2N_4$
Formula weight	219.97	537.29	344.15
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*P*2$P2_1/n$	$Pbcn$
a [Å]	16.370(2)	23.000(8)	11.0322(6)
b [Å]	6.3079(5)	11.363(6)	13.3381(8)
c [Å]	14.204(1)	26.98(1)	14.5648(8)
β [°]	117.210(2)	97.83(3)	90
Volume [$Å^3$]	1304.4(2)	6984(5)	2143.2(2)
Z	4	8	4
Density (calculated) [g/cm^3]	1.120	1.022	1.067
Absorption coefficient [mm^{-1}]	0.155	0.059	0.062
F(000)	472	2384	760
Crystal size [mm^3]	0.33 × 0.31 × 0.12	0.40 × 0.37 × 0.35	0.55 × 0.46 × 0.26
Theta range [°]	2.80 to 32.46	1.09 to 27.10	2.40 to 27.87
Index ranges	−24/+21, 0/+9, 0/+21	−29/+29, 0/+14, 0/+34	0/+14, 0/+17, 0/+18
Reflections collected	13086	58271	13498
Independent reflections	2209 [R(int) = 0.030]	15391 [R(int) = 0.040]	2462 [R(int) = 0.025]
Parameters	105	1196	190
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0367$	$R1 = 0.0543$	$R1 = 0.0367$
R indices (all data)	w$R2 = 0.1073$	w$R2 = 0.1632$	w$R2 = 0.1031$
Largest diff. peak and hole [e/$Å^3$]	0.428 and −0.191	0.760 and −0.313	0.314 and −0.172

Table 2. X-ray crystallographic data for compounds **5b**, **8** and **9**

	5b	**8**	**9**
Empirical formula	$C_{11}H_{22}B_2N_4$	$C_{21}H_{30}B_2N_4Ti\cdot 0.5CH_2Cl_2$	$C_{21}H_{30}B_2N_4Zr$
Formula weight	231.95	450.47	451.33
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$Pna2_1$
a [Å]	8.4793(9)	10.7849(12)	15.4843(8)
b [Å]	15.095(2)	14.693(2)	11.7675(6)
c [Å]	11.316(1)	14.753(2)	11.6797(6)
α [°]	90	90.661(2)	90
β [°]	107.601(2)	104.260(3)	90
γ [°]	90	93.631(2)	90
Volume [$Å^3$]	1380.5(3)	2260.4(4)	2128.2(2)
Z	4	4	4
Density (calculated) [g/cm^3]	1.116	1.324	1.409
Absorption coefficient [mm^{-1}]	0.067	0.513	0.530
F(000)	504	948	936
Crystal size [mm^3]	0.42 × 0.30 × 0.28	0.30 × 0.23 × 0.04	0.60 × 0.44 × 0.38
Theta range [°]	2.32 to 32.40	1.95 to 25.00	2.17 to 32.16
Index ranges	−12/+12, 0/+21, 0/+16	−12/+12, −17/+17, 0/+17	0/+23, 0/+17, −16/+16
Reflections collected	15064	25227	27203
Independent reflections	4572 [R(int) = 0.024]	7947 [R(int) = 0.091]	6995 [R(int) = 0.021]
Parameters	242	767	373
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0450$	$R1 = 0.0754$	$R1 = 0.0205$
R indices (all data)	w$R2 = 0.1315$	w$R2 = 0.2396$	w$R2 = 0.0569$
Largest diff. peak and hole [e/$Å^3$]	0.426 and −0.186	1.210 and −1.363	0.372 and −0.301

charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.ac.uk].

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