New Imidazabole Derivatives: Dimers of Carbene–Borane Adducts

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Received May 20, 1998

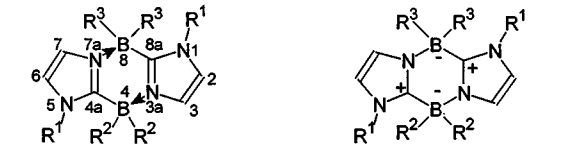
Keywords: Imidazaboles / Carbene–borane adducts / Azole–borane adducts

The preparation and characterization of five new imidazabole derivatives is reported: 1,5-dibenzyl-4,4,8,8-tetrahydroimidazabole (**2**), 4,4,8,8-tetrafluoro-1,5-dimethylimidazabole (**3**), 4,4-difluoro-8,8-dihydro-1,5-dimethylimidazabole (**4**), 4,4,8,8-tetrachloro-1,5-dimethylimidazabole (**5**), and 4,4,8,8-tetraethyl-1,5-dimethylimidazabole (**6**). The structures of compounds **2**–**6** as dimeric carbene–borane adducts rather than dimeric *N*-borane adducts are discussed on the basis of NMR (**2**–**6**) and X-ray diffraction data (**2**, **3**, **5** and **6**).

Introduction

Heterocyclic boron hydrides have found broad application in catalysis[1]. Examples of an important class of these compounds named pyrazaboles were first synthesized in 1966 and since then they have been exhaustively studied[2]. This class of compounds features two $-BR_2-$ moieties bridging two pyrazole rings through their nitrogen atoms. Recently, two series of related compounds have been synthesized, one incorporating pyridine derivatives[3] and the other five-membered azole rings with an N−C−X moiety (X = N, S)[4]. The common, distinguishing feature of both series is that the $-BR_2-$ moiety links the two heterocyclic rings via nitrogen and carbon atoms that are both highly nucleophilic, and hence the question arises as to whether they should be considered as aza- or carbene−borane adducts. The former compounds may be compared with pyridine derivatives[5], which are very stable, but there have been virtually no studies on the azole derivatives. In this paper, the synthesis of five new imidazabole derivatives **2**−**6** is reported with a view to delineating factors that might allow a distinction to be made between C−B and N−B donation. The molecular structures of these compounds based on NMR and X-ray diffraction data are strongly indicative that compounds **1**−**6** are dimers of carbene−borane adducts rather than dimers of *N*-borane adducts (Scheme 1)[*].

Scheme 1



1 $R^1 = CH_3$, $R^2 = R^3 = H$; **2** $R^1 = CH_2C_6H_5$, $R^2 = R^3 = H$
3 $R^1 = CH_3$, $R^2 = R^3 = F$; **4** $R^1 = CH_3$, $R^2 = F$, $R^3 = H$
5 $R^1 = CH_3$, $R^2 = R^3 = Cl$; **6** $R^1 = CH_3$, $R^2 = R^3 = CH_2CH_3$

Results and Discussion

Synthesis

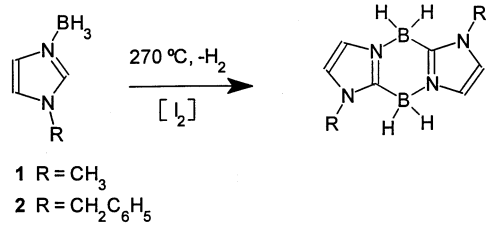
We have previously reported the synthesis of 4,4,8,8-tetrahydroimidazabole (**1**) from its *N*-methylimidazole−*N*-borane adduct[4]. The imidazabole **2** has been prepared from the 1-benzylimidazole−*N*-borane adduct in an analogous manner (Scheme 2). In order to examine the chemical stability and the molecular structures of imidazaboles (N−B−C fragment) and to compare them with pyrazaboles (N−B−N fragment), some derivatives of the parent imidazabole **1** have been synthesized (Scheme 3).

The chemical stabilities and reactivities of imidazaboles have been found to be very similar to those of pyrazaboles[2b][6]. Compounds **1**−**6** are very stable, even under the strongly acidic and oxidizing conditions of the reaction medium. Fluorination of **1** was performed with $BF_3 \cdot OEt_2$; formation of 4,4,8,8-tetrafluoro-1,5-dimethylimidazabole (**3**)

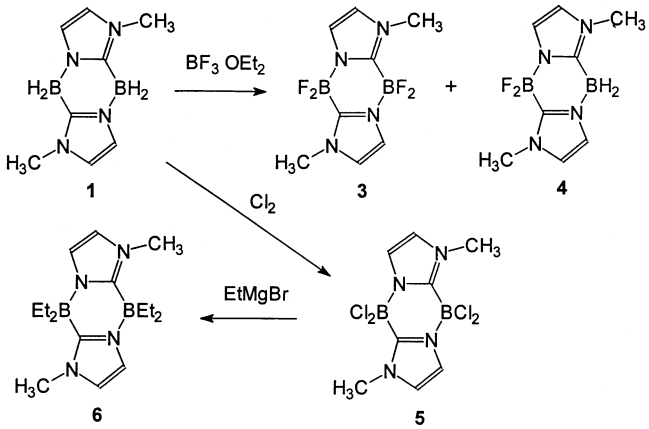
[*] Note added in proof (July 30, 1998): Other examples of carbene−boranes derived from imidazole have been recently reported: A. Wacker, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1998**, 843−849.

  1434−1948/98/1010−1547 $ 17.50+.50/0

Scheme 2

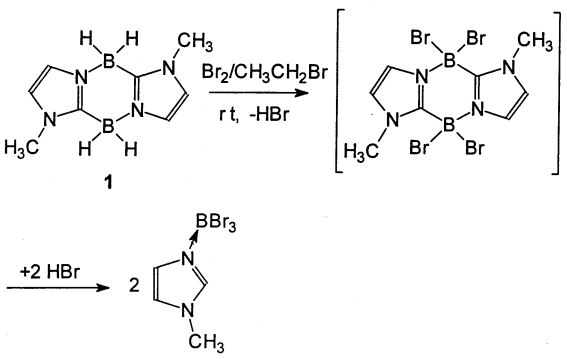


Scheme 3



and of the mixed compound 4,4-difluoro-8,8-dihydro-1,5-dimethylimidazabole (**4**) reveals that the reaction proceeds with opening of the central $C_2B_2N_2$ ring in a similar manner as in pyrazaboles[7]. Chlorination of **1** with molecular chlorine gave compound **5**, whereas bromination with Br_2 (Scheme 4) proceeded with central ring rupture via the 4,4,8,8-tetrabromo-1,5-dimethylimidazabole (observed by NMR) to give the 1-methylimidazole−tribromoborane adduct ($\delta^{11}B = -2.2$) by HBr addition. Reaction of compound **5** with MgEtBr in diethyl ether afforded **6** in good yield. The aforementioned reactions demonstrate the similar reactivity and stability of imidazabole compounds compared to pyrazabole compounds.

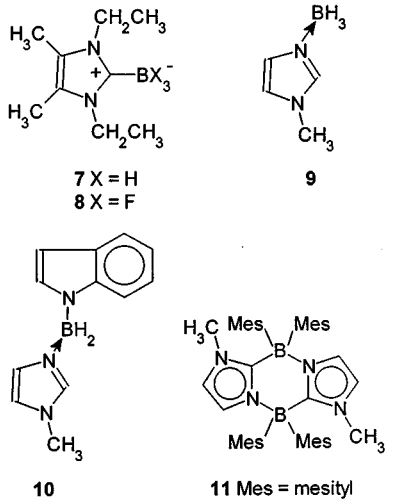
Scheme 4



Molecular Structures

The molecular structures of compounds **1**−**6** can be viewed as dimers of imidazole *N*-borane adducts with a simple N→B dative bond (structure **A**) or as dimers of a 2-ylidene−borane adduct (carbene adduct) with a C−B dative bond (structure **B**) (Scheme 1), similar to that described by Arduengo[8]. In order to establish the structures of the imidazaboles **2**−**6**, comparisons were made with the reported stable monomeric carbene−borane adducts 2-borane−1,2,3,4-tetramethylimidazoline (**7**) and 2-trifluoroborane−1,2,3,4-tetramethylimidazoline (**8**)[9], as well as with the N→B adducts *N*-borane−1-methylimidazole (**9**)[10] and indolylborane−*N*-methylimidazole (**10**)[11] (Scheme 5).

Scheme 5



NMR Studies

Compounds **2**−**6** have been characterized by their ^1H-, ^{11}B- and ^{13}C-NMR data (Table 1). The ^{11}B chemical-shift values are at lower frequencies relative to those of the pyrazabole analogues [$\delta^{11}B(H_2B$-μpz-$BH_2) = -8.8$, $\delta^{11}B(F_2B$-μpz-$BF_2) = 0.2$, $\delta^{11}B(Cl_2B$-μpz-$BCl_2) = 2.1$, $\delta^{11}B(Et_2B$-μpz-$BEt_2) = 2.2$, pz = pyrazabole][7a][12], in accordance with the change from the NBN to the NBC fragment. However, ^{11}B chemical shifts do not allow a distinction to be made between N→B coordination **A** and N−B covalent bonding **B** in tetracoordinated compounds (Scheme 1). If $\delta^{11}B$ values of similar N→B coordinated adducts and of N−B covalently-bonded borates are compared {$\delta^{11}B(Me_2HN{\rightarrow}BH_3) = -13.5$ vs. $\delta^{11}B(Me_2N{-}BH_3^-) = -14.7$; $\delta^{11}B(H_3N{\rightarrow}BMe_3) = -8.7$ vs. $\delta^{11}B(H_2N{-}BEt_3^-) = -9.8$; and $\delta^{11}B$[(*N*-methylimidazole)→BH_2−pyrrole] = −7.8 vs. $\delta^{11}B(pz_2{-}BH_2^-) = -7.4$}[11][12], no significant differences are apparent. On the other hand, coupling constants ^1J(B−X, X = F, C) appear to be more characteristic and do allow a distinction between N→B adducts and N−B covalently-bonded compounds. Coupling constants ^1J(B−F) for **3** and **4** are larger (43 and 54 Hz, respectively)

Table 1. $\delta^{11}B$, $\delta^{13}C$ and $\delta^{1}H$ in ppm, [^{1}J(B−X)], [^{1}J(C−H)] and [^{3}J(H−H)]] in Hz of imidazabole derivatives **2**−**6**[a], 2-borane−1,2,3,4-tetramethylimidazoline (**7**), 2-trifluoroborane−1,2,3,4-tetramethylimidazoline (**8**) and *N*-borane−1-methylimidazole (**9**)

Compd.	$\delta^{11}B$, [^{1}J(B−X)] X = H, F, C	$\delta^{13}C$(8a)	$\delta^{13}C$(2)	$\delta^{13}C$(3)	$\delta^{13}C$(R)	$\delta^{1}H$(2)	$\delta^{1}H$(3)	$\delta^{1}H$(R)
2[b]	−18.6, $h_{1/2}$ = 265	164.0 (br.)	124.3	119.1	50.7	6.96 [1.9]	6.78 [1.9]	5.11
3	0.5 [43]	[c]	123.7 [197]	119.7 [197]	34.2	7.47 [1.7]	7.34 [1.7]	3.96
4[d]	0.9 [54] (BF_2)	[c]	123.1 (C2)	118.7 (C3)	34.4 (N1)	7.43 [1.8]	7.41 [1.8]	3.83 (N1)
	−18.3 [101] (BH_2)		123.6 (C6)	122.5 (C7)	33.5 (N3a)	7.44 [1.5]	7.17 [1.5]	3.60 (N3a)
5	−1.6	[c]	121.4 [199]	126.5 [203]	35.4	7.78 [1.8]	7.67 [1.8]	4.02
6[e]	−6.3 [54]	164.0 (br.)	121.1 [190]	120.4 [192]	34.3	6.88 [1.7]	6.08 [1.7]	3.12
7[f]	−34.9 [86]	167.3 (C2) [51.5]	122.9 (C5)	122.9 (C4)	32.1			3.50
8[g]	1.48 [38]	[c]	125.7 (C5)	125.7 (C4)	32.8			3.71
9[h]	−18.4 [98]	136.9 (C2)	121.5 (C5)	127.1 (C4)	34.9	6.95	6.97	3.75

[a] **2**−**4** and **5** in $CDCl_3$ and **6** in C_6D_6. − [b] Phenyl protons as a multiplet at δ = 7.28; $\delta^{13}C$ = 128.8 (*o*-C), 127.9 (*m*-C), 128.0 (*p*-C) and 136.4 (*i*-C). − [c] Not observed. − [d] Mixed with signal of **3**. − [e] Ethyl: CH_2: $\delta^{13}C$ = 17.9 (br.), $\delta^{1}H$ = 0.95 (m); CH_3: $\delta^{13}C$ = 11.4, $\delta^{1}H$ = 0.80 [7.3]. − [f] CD_2Cl_2[9]. − [g] CD_2Cl_2[9]. − [h] $CDCl_3$[11].

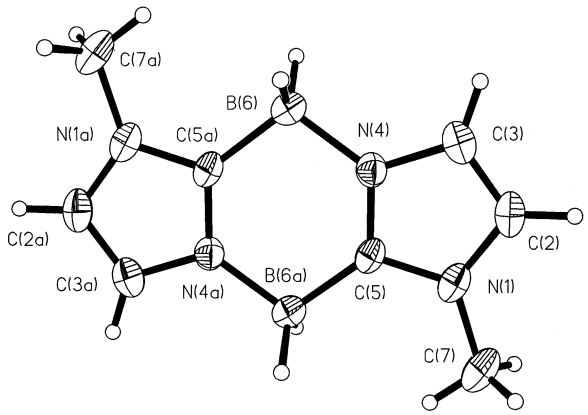
than in the pyrazabole analogues (23 and 22 Hz)[7a] and are intermediate between that in the adduct $Me_3N{\rightarrow}BEtF_2$ (65 Hz)[7a] and the reported value (37.6 Hz) for the carbene adduct 2-trifluoroborane−1,2,3,4-tetramethylimidazoline (**8**)[9]. Moreover, the value of the coupling constant ^{1}J(B−C) found for **6** (54 Hz) is close to that of the 2-ylidene adduct 2-borane−1,2,3,4-tetramethylimidazoline (**7**) (51.5 Hz)[9].

^{13}C chemical-shift values have proved to be a useful tool in establishing the nature of the N→B coordinative bond and to distinguish it from N−B covalent bonding[10]. The ^{13}C signal of C4 of 1-methyl imidazole (δ = 129.2) is shifted upon coordination to δ = 127.1 in the $N{\rightarrow}BH_3$ adduct **9** and to δ = 122.4 in the 1,3-dimethylimidazolium cation[10]. The ^{13}C signal of C3 (C4 in imidazoles) in compounds **2**−**6** is shifted to lower frequencies (Δδ ≈ 7−10 ppm), which is clearly indicative of N−B covalent bond formation. $\delta^{13}C$ values for C3 of **2**−**6** are in agreement with $\delta^{13}C$ values reported for C4 and C5 of the carbene adducts **7** and **8**. $\delta^{13}C$ signals for C8a of **2**−**6** are either extremely broad or are not observed at all as a result of the partially relaxed scalar $^{13}C-^{11}B$ spin-spin coupling[12]. When present, these are found in the range reported for **7**. On the other hand, $^{1}J(^{13}C,1H)$ values of C2 and C3 lie in the typical range for a neutral imidazole ring[10], in spite of the development of a positive charge delocalized over the whole ring. The C−H coupling pattern helped to unequivocally assign the ^{13}C signals for C2 and C3 in **3**, **5** and **6**. The signal for C2 appears as a double multiplet due to coupling with the 2-H, 3-H and CH_3 hydrogen atoms. These findings confirm that the canonical form with N−B covalent bonding makes the principal contribution to the structures of compounds **2**−**6**.

X-ray Structure Analysis

The molecular structure of the imidazabole **1** found by X-ray diffraction analysis was previously reported to have the space group $P2_1$ (monoclinic)[4]. However, the structure has since been resolved in space group $P2_1/n$ and this resulted in better parameters. The corrected molecular structure of imidazabole **1** is shown in Figure 1. Molecular structures of the imidazaboles **2**, **3**, **5** and **6** are shown in Figures 2−5 and selected bond lengths and angles are summarized in Table 2 (those pertaining to the central ring $C_2B_2N_2$) and Table 3 (those of the imidazole ring). Compounds **1**−**3**, **5** and **6** have a crystallographic centre of inversion. Thus, only one half of the "dimeric" molecule occupies the asymmetric unit.

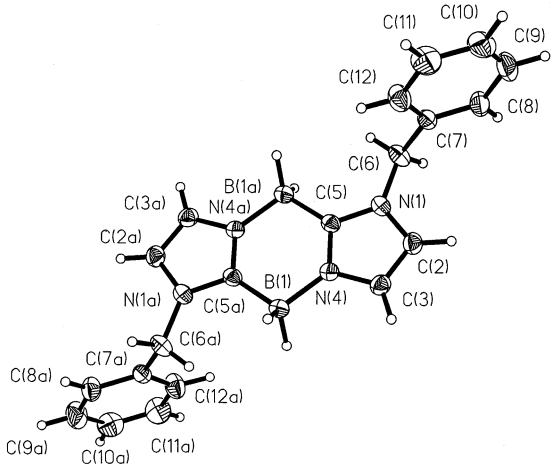
Figure 1. Molecular structure of imidazabole **1**[a]



[a] Selected bond lengths [pm] and angles [°]: B(6)−N(4) 155.4(4), B(6A)−C(5) 159.0(4), N(1)−C(2) 136.7(4), C(2)−C(3) 133.3(4), C(3)−N(4) 138.5(3), N(4)−C(5) 134.6(3), C(5)−N(1) 135.5(3), N(1)−C(7) 145.2(3); B(6A)−C(5)−N(4) 127.7(2), N(4)−B(6)−C(5A) 106.8(2), B(6)−N(4)−C(5) 125.5(2), N(1)−C(5)−B(6A) 125.8(2), C(3)−N(4)−B(6) 125.6(2), N(1)−C(2)−C(3) 107.5(3), C(2)−C(3)−N(4) 107.5(3), C(3)−N(4)−C(5) 108.9(2), N(1)−C(5)−N(4) 106.4(2), C(2)−N(1)−C(5) 109.6(2), C(2)−N(1)−C(7) 126.1(2), C(5)−N(1)−C(7) 124.4(3).

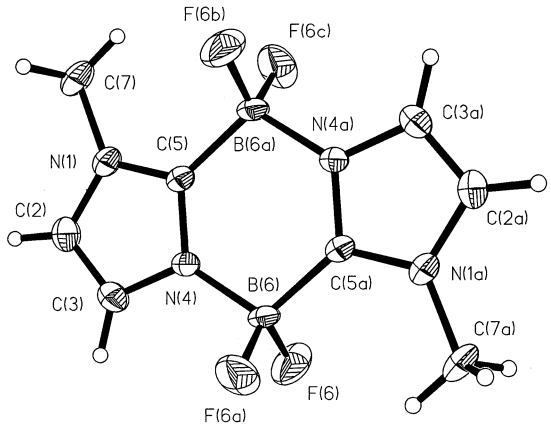
The geometry around the boron atoms in **1**−**3** and **5** is of a slightly distorted tetrahedron (92% tetrahedron character, THC)[13], whereas in compound **6** it is a highly distorted tetrahedron (41% THC), probably due to steric effects. The central $C_2B_2N_2$ ring is almost planar, in contrast with the pyrazabole analogues, which are observed in chair, boat or planar conformations. The mean B−N(4) length in compounds **1**−**3** and **5** is intermediate between that of a coordinate bond $N(sp^2)-B(sp^3)$ [157.8(8) pm][11] and a covalent bond $N(sp^2)-B(sp^3)$ [151.3(2) pm][11]. This bond is significantly elongated [158.6(5) pm] in **6**, probably due to steric

Figure 2. Molecular structure of imidazabole **2**[a]



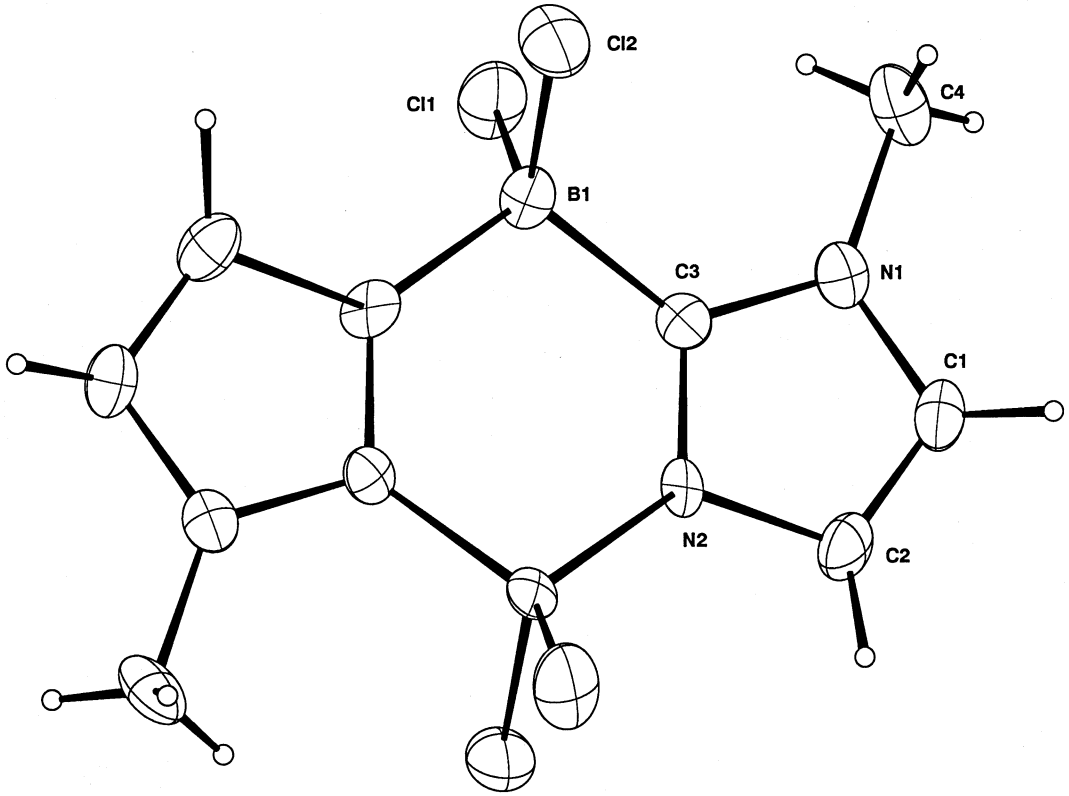
[a] Selected bond lengths [pm] and angles [°]: B(1)−N(4) 155.5(2), B(1A)−C(5) 158.6(2), N(1)−C(2) 137.3(2), C(2)−C(3) 133.7(2), C(3)−N(4) 137.8(2), N(4)−C(5) 133.7(2), C(5)−N(1) 134.9(2), N(1)−C(6) 146.0(2); B(1A)−C(5)−N(4) 126.7(1), N(4)−B(1)−C(5A) 107.4(1), B(1)−N(4)−C(5) 125.9(1), N(1)−C(5)−B(1A) 126.4(1), C(3)−N(4)−B(1) 125.3(1), N(1)−C(2)−C(3) 106.6(2), C(2)−C(3)−N(4) 108.1(2), C(3)−N(4)−C(5) 108.8(1), N(1)−C(5)−N(4) 106.9(1), C(2)−N(1)−C(5) 109.7(1), C(2)−N(1)−C(6) 124.9(1), C(5)−N(1)−C(6) 125.4(1).

Figure 3. Molecular structure of imidazabole **3**[a]



[a] Selected bond lengths [pm] and angles [°]: (B6)−N(4) 155.2(4), B(6A)−C(5) 161.1(5), N(1)−C(2) 137.1(5), C(2)−C(3) 133.0(5), C(3)−N(4) 137.9(4), N(4)−C(5) 134.3(4), C(5)−N(1) 133.8(4), N(1)−C(7) 146.7(4), B(6)−F(6) 137.9(3), B(6)−F(6B) 137.9(3); B(6A)−C(5)−N(4) 126.1(3), N(4)−B(6)−C(5A) 108.2(2), B(6)−N(4)−C(5) 125.7(3), N(1)−C(5)−B(6A) 126.6(3), C(3)−N(4)−B(6) 126.0(3), N(1)−C(2)−C(3) 107.3(3), C(2)−C(3)−N(4) 107.8(3), C(3)−N(4)−C(5) 108.3(3), N(1)−C(5)−N(4) 107.3(3), C(2)−N(1)−C(5) 109.2(3), C(2)−N(1)−C(7) 125.8(3), C(5)−N(1)−C(7) 125.0(3), F(6B)−B(6)−F(6) 109.4(3), F(6)−B(6)−N(4) 108.7(2), F(6)−B(6)−C(5A) 110.9(2).

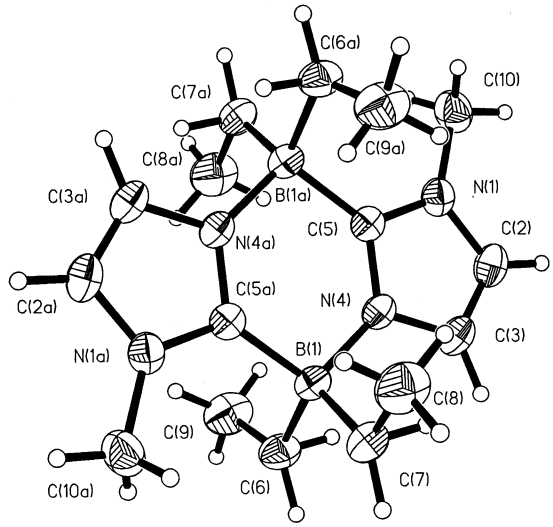
Figure 4. Molecular structure of imidazabole **5**[a]



[a] Selected bond lengths [pm] and angles [°]: (B1)−N(2) 153.4(8), B(1)−C(3) 159.3(9), N(1)−C(1) 137.0(8), C(1)−C(2) 133.3(9), C(2)−N(2) 139.8(8), N(2)−C(3) 134.0(7), C(3)−N(1) 134.6(7), N(1)−C(4) 147.3(8), B(1)−Cl(1) 184.6(4); B(1)−C(3)−N(2) 125.3(5), N(2)−B(1)−C(3) 108.4(5), B(1)−N(2)−C(3) 126.3(5), N(1)−C(3)−B(1) 126.7(5), C(2)−N(2)−B(1) 125.4(5), N(1)−C(1)−C(2) 108.6(5), C(1)−C(2)−N(2) 106.7(6), C(2)−N(2)−C(3) 108.3(5), N(1)−C(3)−N(2) 107.9(5), C(1)−N(1)−C(3) 108.4(5), C(1)−N(1)−C(4) 126.3(5), C(3)−N(1)−C(4) 125.3(5), Cl(1)−B(1)−Cl(2) 111.1(4), Cl(1)−B(1)−N(2) 108.6(3), Cl(1)−B(1)−C(3) 110.0(3).

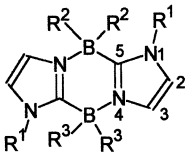
effects, but it is shorter than that in the analogous pyrazabole [167(6)−172(6) pm][14]. The B−C(5) bonds lie in the typical range for a B(sp^3)−C(Ar) linkage of 160.3(8) pm[15]. The B−C(5) bond length in **3** [161.1(5) pm] is slightly longer than in 2-trifluoroborane−1,2,3,4-tetramethylimidazoline (**8**) [160.3(3) pm]. These figures suggest that the molecular structures of imidazaboles **1**−**6** should be considered as carbene−borane dimers.

Figure 5. Molecular structure of imidazabole **6**[a]



[a] Selected bond lengths [pm] and angles [°]: B(1)−N(4) 158.6(5), B(1A)−C(5) 161.4(5), N(1)−C(2) 136.0(5), C(2)−C(3) 131.9(5), C(3)−N(4) 138.3(4), N(4)−C(5) 133.7(4), C(5)−N(1) 135.9(4), N(1)−C(10) 145.7(5), B(1)−C(6) 162.8(5), B(1)−C(7) 162.6(5); B(1A)−C(5)−N(4) 127.2(3), N(4)−B(1)−C(5A) 104.2(2), B(1)−N(4)−C(5) 128.5(3), N(1)−C(5)−B(1A) 126.5(3), C(3)−N(4)−B(1) 122.9(3), N(1)−C(2)−C(3) 107.4(3), C(2)−C(3)−N(4) 108.2(3), C(3)−N(4)−C(5) 108.6(3), N(1)−C(5)−N(4) 106.3(3), C(2)−N(1)−C(5) 109.5(3), C(2)−N(1)−C(10) 123.8(3), C(5)−N(1)−C(10) 126.6(3), C(6)−B(1)−C(7) 109.3(3), C(6)−B(1)−N(4) 109.3(3), C(6)−B(1)−C(5A) 111.3(3), C(6)−B(1)−N(4) 109.3(3), C(6)−B(1)−C(5A) 111.3(3).

Table 2. Selected bond lengths [pm] and angles [°] of the central $C_2B_2N_2$ ring of imidazaboles **1**−**3**, **5** and **6**



1 $R^1 = CH_3$, $R^2 = R^3 = H$; **2** $R^1 = CH_2C_6H_5$, $R^2 = R^3 = H$
3 $R^1 = CH_3$, $R^2 = R^3 = F$; **5** $R^1 = CH_3$, $R^2 = R^3 = Cl$;
6 $R^1 = CH_3$, $R^2 = R^3 = CH_2CH_3$

	1	**2**	**3**	**5**[a]	**6**
B−R			137.9(3)	184.6(4)	162.8(5), 162.6(5)
B−N(4)	155.4(4)	155.5(2)	155.2(4)	153.4(8)	158.6(5)
B−C(5)	159.0(4)	158.6(2)	161.1(5)	159.3(9)	161.4(5)
R−B−R			109.4(3)	111.1(4)	109.3(3)
N(4)−B−C(5)	106.8(2)	107.4(1)	108.2(2)	108.4(5)	104.2(2)
B−N(4)−C(5)	125.5(2)	125.9(1)	125.7(3)	126.3(5)	128.5(3)
B−C(5)−N(4)	127.7(2)	126.7(1)	126.1(3)	125.3(5)	127.2(3)

[a] The numbering scheme is as that used for imidazaboles **1**−**3** and **6**.

The most categorical evidence for this conclusion comes from a comparison of the molecular structures of **1**−**3** and **5** with that of 4,4,8,8-tetramesityl-1,5-dimethylimidazabole **11**[16], the latter being characteristic of an imidazole *N*-borane adduct dimer. This compound exhibits a boat conformation of the central $C_2B_2N_2$ ring, with an angle between the two imidazole rings of 128°, in contrast with the fully planar structure found in imidazaboles **1**−**6**. The B−N bond length [163.8(4) pm] is larger than the corresponding bond lengths in imidazaboles **1**−**3**, **5** and **6**, which lie in the typical range for weak N→B adducts[17]. The marked contrast between these structures confirms that compounds **1**−**6** have to be considered as 2-ylidene−borane adducts (carbene−boranes).

The geometry of the imidazole ring is strongly modified when 2-ylidene adducts are formed. Table 3 shows bond lengths and angles related to the imidazole ring for compounds **1**−**3**, **5** and **6**, 2-trifluoroborane−1,3,4,5-tetramethylimidazoline (C−B coordination) (**8**)[9], and indolylborane−*N*-methylimidazole adduct (N→B coordination) (**10**)[11]. The main difference between the latter two lies in the N−C−N fragment. The bond length N(4)−C(5) [130.1(5) pm] is shorter than C(5)−N(1) [132.0(6) pm] in the N→B adduct **10**, whereas both have the same large value [135.2 (2) pm] in the C−B adduct **8**. These bonds in **1**−**3**, **5** and **6** are practically equivalent and have the same value as that in the C−B adduct **8**. The angle N(1)−C(5)−N(4) is wider in the C−B adduct **8** [104.7(1)°] than in the N−B adduct **10** [111.2(4)°]. In the opposite sense, the angles C(3)−N(4)−C(5) and C(2)−N(1)−C(5) become equal and are wider in the C−B adduct **8** [111.2(1)°] than in the N−B adduct **10** [106.2(4)° and 106.3(4)°, respectively]. Both these angles in **1**−**3**, **5** and **6** have a value intermediate between those found in the N−B and C−B adducts. These findings and the planarity found for all the structures reported here strongly support a significant contribution from the C−B adduct to the resonance structure and indicate that the positive charge is delocalized over the fragment N−C−N according to structure **C**, instead of over the fully delocalized resonance structure **D** (Scheme 6).

It follows from the aforementioned changes that as the groups attached to boron become bulkier, the resulting structure resembles more the N→B adduct. On the other hand, the B−C(5) length becomes longer (Table 2) as the electronegativity of the boron substituent increases (Pauling values: H 2.20, C 2.55, Cl 3.16, F 3.98)[18]. These observations demonstrate that both steric and electronic effects on the boron atom determine the degree of carbene−borane or *N*-borane dimer character of the structure.

Conclusion

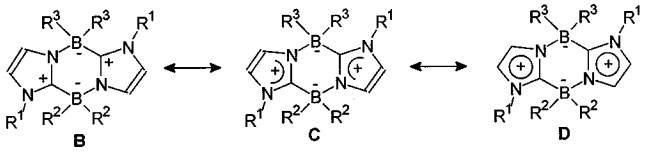
NMR and X-ray diffraction experiments confirm that compounds **1**−**6** are dimers of carbene−borane adducts rather than *N*-borane adducts. The main differences between these structures are most clearly apparent in the imidazole

Table 3. Selected bond lengths [pm] and bond angles [°] of the imidazole ring in imidazaboles **1**−**3**, **5** and **6**, 2-trifluoroborane−1,2,3,4-tetramethylimidazoline (**8**) (C−B adduct)[9], and pyrrolylborane−*N*-methylimidazole adduct (**10**) (N−B adduct)[11]; the numbering scheme is as that used in Table 2

	8[a]	**1**	**2**	**3**	**5**	**6**	**10**[a]
N(1)−C(2)	139.2(2)	136.7(4)	137.3(2)	137.1(5)	137.4(4)	136.0(5)	135.4(7)
C(2)−C(3)	135.0(2)	133.3(4)	133.7(2)	133.0(5)	133.7(4)	131.9(5)	132.0(8)
C(3)−N(4)	139.3(2)	138.5(3)	137.8(2)	137.9(4)	136.9(4)	138.3(4)	135.7(6)
N(4)−C(5)	135.2(2)	134.6(3)	133.7(2)	134.3(4)	134.0(3)	133.7(4)	130.1(5)
C(5)−N(1)	135.2(2)	135.5(3)	134.9(2)	133.8(4)	133.8(4)	135.9(4)	132.0(6)
N(1)−C(5)−N(4)	104.7(1)	106.4(2)	106.8(1)	107.3(3)	107.3(2)	106.3(3)	111.2(4)
C(3)−N(4)−C(5)	111.2(1)	108.9(2)	108.8(1)	108.3(3)	108.7(2)	108.6(3)	106.2(4)
C(2)−N(1)−C(5)	111.1(1)	109.6(2)	109.7(1)	109.2(3)	108.4(5)	109.5(3)	106.3(4)

[a] For comparison purposes, the numbering scheme has been changed to the ring numbering followed in imidazaboles.

Scheme 6



N−C−N fragment bond lengths and angles and in the N−B bond lengths. The $C_2B_2N_2$ ring in compounds **1**−**6** is quite stable, even under the strongly acidic and oxidizing conditions used for the synthesis of such species. Imidazabole compounds **1**−**6** are the first examples of cyclic dimers of carbene−borane adducts to be reported.

We thank Professor *M. J. Rosalez-Hoz*, Mr. *F. Roberts* and Mr. *M. A. Leyva-Ramírez* for performing the X-ray diffraction studies

Experimental Section

General Remarks: All solvents were freshly distilled and dried before use according to established procedures. *N*-Methylimidazole, $BF_3 \cdot OEt_2$, Cl_2, Br_2 and Mg (granules) were commercial products. $BH_3 \cdot THF$ solution was prepared according to reported methods[19]. − Melting points (uncorrected): Gallenkamp apparatus. − IR (KBr): Perkin-Elmer 16F, PC spectrometer. − $^1H/^{13}C$ NMR: Jeol GXS 270 (270.67/67.94 MHz), TMS as external standard. − ^{11}B NMR: Jeol GXS 270 (86.84 MHz), $Et_2O \cdot BF_3$ as external standard ($\Xi^{11}B$ = 32.083971 MHz). − Elemental analyses were performed by Oneida Research Services, Whitesboro, N.Y. − The X-ray diffraction studies were performed with an Enraf-Nonius CAD4 diffractometer [λ(Mo-K_α) = 71.069 pm, monochromator: graphite, T = 293 K, ω-2θ scan]. Cell parameters were determined by least-squares refinement on diffractometer angles for 24 automatically centered reflections. Absorption corrections were not necessary; corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for

Table 4. Crystallographic data for imidazaboles **1**−**3**, **5** and **6**

	1[a]	**2**[a]	**3**[a]	**5**[b]	**6**[a]
formula	$C_8H_{14}B_2N_4$	$C_{20}H_{22}B_2N_4$	$C_4H_7BF_2N_2$	$C_8H_{10}B_2Cl_4N_4$	$C_{16}H_{30}B_2N_4$
molecular mass [g/mol]	187.85	340.04	131.93	325.62	300.06
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P1$	$I2/m$	$C2/m$	$P2_1/n$
a [pm]	867.2(2)	644.90(10)	752.0(2)	1230.5(9)	788.2(2)
b [pm]	632.50(10)	791.6(2)	693.60(10)	711.5(4)	1031.0(2)
c [pm]	978.0(2)	698.8(2)	1125.6(2)	817.4(4)	1127.7(2)
α [°]	90.00	108.85(3)	90.00	90.00	90.00
β [°]	100.70(3)	101.33(3)	109.37 (3)	108.38(6)	93.47(3)
γ [°]	90.00	93.47(3)	90.00	90.00	90.00
V 10^3 [nm^3]	527.1(2)	464.2(2)	553.9(2)	679.1(7)	914.7(3)
Z	2	1	4	2	2
$d_{calcd.}$ [g cm^{-3}]	1.184	1.216	1.582	1.59	1.089
2θ range [°]	6.96−49.92	4.48−51.92	5.76−52.58		5.36−51.94
reflections measured	984	1916	1237	702	1884
unique reflections	927	1806	618	655	1795
reflns. used with $(F_o)^2 > 4\sigma(F_o)^2$	709	1356	548	548 $(F_o)^2 > 3\sigma(F_o)^2$	1047
R (int)	0.0338	0.0176	0.0674	0.024	0.0191
no. of variables	64	127	52	52	100
final R indices [$F > 4\sigma(F)$]	0.0618	0.0417	0.0685	0.045 [$F > 3\sigma(F)$]	0.0722
Rw	0.1808	0.1210	0.2217	0.047 $w = 1/\sigma^2$	0.2368
goodness of fit	1.114	0.992	1.156	5.4	1.093
min. res. density [10^{-6} e/pm^{-3}]	−0.317	−0.175	−0.645	−0.38	−0.386
max. res. density [10^{-6} e/pm^{-3}]	0.340	0.200	0.351	0.47	0.406

[a] Program for structure solution and refinement: SHELXL-93[20]. − [b] Program for structure solution and refinement: CRYSTALS[21].

structure solution. The SHELXL[20] and CRYSTALS (version 9, **1994**)[21] software packages were used for refinement and data output. All hydrogen atoms in structures **1**, **3**, **5** and **6** were refined as riding atoms. Experimental parameters are listed in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101913 (**1**), -101909 (**2**), -101910 (**3**), -101912 (**5**), -101911 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

1,5-Dibenzyl-4,4,8,8-tetrahydroimidazabole (**2**): 2.00 g (11.6 mmol) of 2-borane−1-benzylimidazole, prepared as described previously[11], was left to stand overnight at 0 °C in the presence of a solution of one small I_2 crystal in 1 ml of dry benzene. The mixture was then heated in a sand bath at 290 °C until hydrogen evolution had ceased. Crystallization from a saturated solution in toluene at −20 °C gave 0.637 g of **2** (32%) as a white, crystalline powder, m.p. 204−205 °C. Crystals suitable for X-ray structure analysis were obtained from a CH_2Cl_2 solution at −17 °C. − IR (KBr): $\tilde{\nu}_{max}$ = 2354 cm^{-1} (B−H), 1636 (C=N), 1206 (B−N). − $C_{20}H_{22}N_4B_2$ (340.04): calcd. C 70.64, H 6.52, N 16.49; found C 70.92, H 6.88, N 16.67.

4,4,8,8-Tetrafluoro-1,5-dimethylimidazabole (**3**) *and 4,4-Difluoro-8,8-dihydro-1,5-dimethylimidazabole* (**4**): To 10 ml of $BF_3 \cdot OEt_2$ was added 1.0 g of **1** and the mixture was stirred for a week. Excess $BF_3 \cdot OEt_2$ was then distilled off in vacuo, and the residual solid was washed with CH_2Cl_2 and then with THF to give 262 mg of a white solid composed of 95 parts of **3** (36% overall yield) and 5 parts of **4** (2.2% overall yield). Suitable crystals of **3** for X-ray structure analysis were obtained from acetone solution; m.p. 277 °C. − IR (KBr): $\tilde{\nu}_{max}$ = 1684 cm^{-1} (C=N), 1162 (B−N), 842 (B−F). − $C_8H_{10}N_4B_2F_4$ (259.81): calcd. C 36.98, H 3.88, N 21.56; found C 37.69, H 4.13, N 21.39. − The THF solution was found to contain a 1:1 mixture of **3** and **4**, from which the NMR spectra of **4** were obtained.

4,4,8,8-Tetrachloro-1,5-dimethylimidazabole (**5**): 2.00 g (10.6 mmol) of imidazabole **1** was dissolved in 30 ml of CH_2Cl_2. Molecular chlorine was bubbled through this solution until a yellow-green color persisted. After stirring for 1 h, the product formed was filtered off to afford 2.8 g (81%) of **5** as a white, crystalline solid, m.p. > 310 °C. − IR (KBr): $\tilde{\nu}_{max}$ = 1628 cm^{-1} (C=N), 1096 (B−N), 770 (B−Cl). − $C_8H_{10}N_4B_2Cl_4$ (325.63): calcd. C 29.51, H 3.10, N 17.21; found C 29.41, H 3.15, N 17.32.

4,4,8,8-Tetraethyl-1,5-dimethylimidazabole (**6**): A suspension of 124 mg of magnesium and a small amount of iodine in 10 ml of diethyl ether was stirred for 2 h. Then, 0.40 ml (5.1 mmol) of ethyl bromide was added and, after 1 h, a solution of 331 mg (1.02 mmol) of **5** in 100 ml of diethyl ether. The resulting mixture was refluxed under nitrogen for 4 h. After cooling overnight, 295 mg (96%) of crystals suitable for X-ray structure analysis were obtained; m.p. 200 °C. − IR (KBr): υ_{max} = 1684 cm^{-1} (C=N), 1074 (B−N). − $C_{16}H_{30}N_4B_2$ (300.06): calcd. C 64.05, H 10.08, N 18.67; found C 64.64, H 9.72, N 18.83.

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