The complexation of tetraphenylborate with organic *N*-heteroaromatic cations

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Received (in Cambridge, UK) 23rd January 2001, Accepted 18th October 2001
First published as an Advance Article on the web 14th November 2001

Complexation studies of eleven *N*-heteroaromatic cations with tetraphenylborate are reported. Tetraphenylborate forms complexes with five cations and reacts to form Lewis-base boranes with six cations. The complexes and the displacement reaction products were characterised by ^{1}H NMR spectroscopy, elemental analysis and crystallographic methods. In the complexes C–H ··· π or N–H ··· π hydrogen bonds are the principal intermolecular interactions. The stability constants for the complexes are determined by ^{1}H NMR titration in acetonitrile–methanol (1 : 1) solution. Crystal structures of four of the complexes and three of the Lewis-base triphenylborane products are reported.

Introduction

Complex formation of organic molecules typically requires multisite weak, non covalent host–guest interactions. This behaviour resembles closely the properties of the biological processes of the enzymes. The majority of the studies concerning the complexation of organic molecules are limited to neutral or cationic receptor molecules. Complexation of organic cations with anionic receptor molecules offers possibilities for complexation without additional counterions, which often make the systems complicated. Complexes with permanent opposite charges are called ion pairs.[1] Ion pairing and molecular recognition using Coulomb interactions have recently attracted considerable interest.[2–4]

The tetraphenylborate ion (BPh_4^-) has been widely used as a counterion in metal complexes.[5–10] Tetraphenylborate reacts with electrophilic species such as cations *via* metalation, phenyl group transfer or electron transfer[5] and is capable of decomposition by two general pathways: acidic and photolytic processes.[11] The tetraphenylborate ion can interact with metal centers *via* its phenyl groups. The metal center can for example be π-coordinated to one phenyl group[5–8] or the tetraphenylborate anion can bridge two or three metal centers.[9] Kruger *et al.* have prepared a compound in which a ruthenium ion is sandwiched between a cyclopentadienyl ring and one of the tetraphenylborate phenyl rings.[10] The interactions between tetraphenylborate ion and organic ammonium cations have been studied by Bakshi *et al.*[12,13] These investigations provide a classification of and numerous examples of N–H ··· π and O–H ··· π hydrogen bonds to the aromatic π-systems of tetraphenylborate in the crystalline state. Bakshi *et al.* have categorized hydrogen bonds into several types: *e.g.* normal X–H ··· π bonds as types A–D and bifurcated N–H ··· 2π as types E and F. In bipyridinium and 1,10-phenanthrolinium tetraphenylborates intracation N–H ··· N′ hydrogen bonds and in the latter also significant π–π-stacking interactions are observed.[13] Lindeman *et al.* have studied the arenediazonium tetraphenylborate [$ArN_2^+BPh_4^-$] cation anion pairs and have reported exceptionally short C–H ··· π hydrogen bonds in the crystalline state.[14] Recently, Zhu and Kochi have studied the methyl transfer from thermally or photochemically activated organoborate salts to pyridinium cations.[15]

In our previous studies we have investigated the complexation of crown ethers with tropylium,[16,17] five-[18,19] and six-membered *N*-heteroaromatic[20,21] and purinium[22] cations. Herein we report the complexation studies of five- and six-membered *N*-heteroaromatic cations with tetraphenylborate (Scheme 1). We also report seven X-ray crystal structures, four of which are of complexes and three of displacement reaction products.

Results and discussion

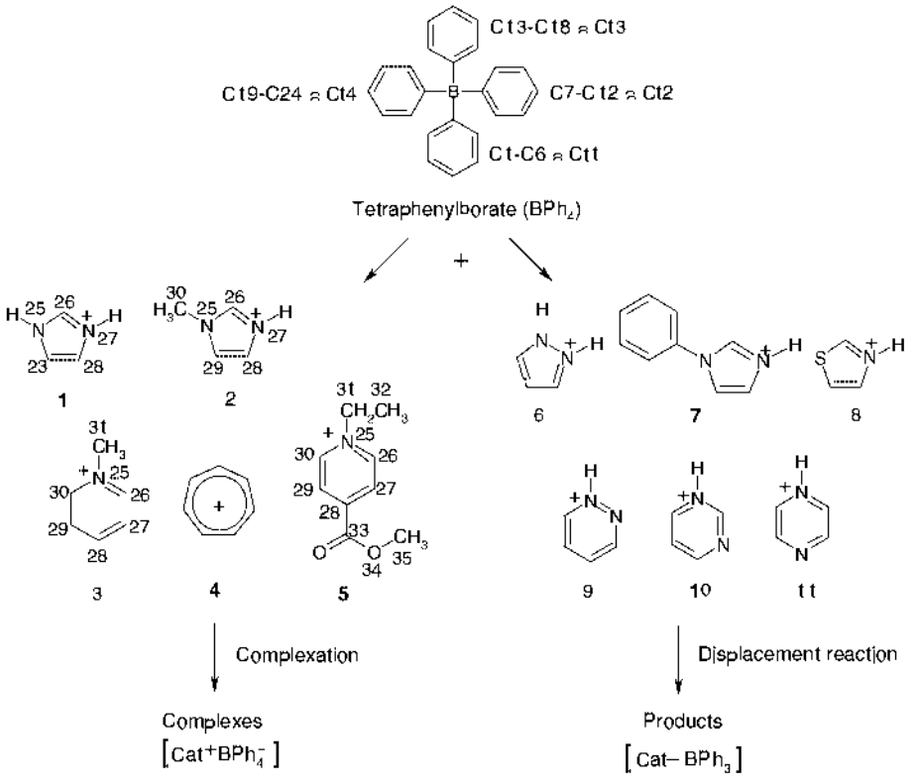
Studies in solution

Tetraphenylborate forms 1 : 1 complexes with five of the aromatic heterocyclic cations studied (**1**–**5**, Scheme 1). With the other cations (**6**–**11**) tetraphenylborate reacts to displace one phenyl group by a heterocycle. The complexes and the displacement reaction products have been characterised by ^{1}H NMR spectroscopy and elemental analysis.

The stability constants for the association of the cations and tetraphenylborate anion have been measured by ^{1}H NMR titration in acetonitrile–methanol (1 : 1) solution (Table 1). The complexation stoichiometry in solution was 1 : 1, since no deviations from the linear Benesi–Hildebrand plot were observed.[23] The complexation stoichiometry for **2**·BPh_4 was also determined by Job's method, which supported the 1 : 1 stoichiometry. Methanol was used to increase the solubility of the sodium tetraphenylborate, even though direct comparison with the stabilities of the respective crown ether complexes[18–22] could not be made. The stability constant of the tropylium tetraphenylborate complex (**4**·BPh_4) could not be measured because tropylium decomposes in the presence of alcohol.[24] In these kinds of organic complexes the solvent has a significant effect on complex formation. However, the more polar solvent used for the tetraphenylborates increases the solubility of the charged species, which decreases the degree of association of the complexes, leading to lower stability constants.

Imidazolium tetraphenylborate (**1**·BPh_4) has a stability constant (46 dm^3 mol^{-1}) that is more than twice that of 1-methylimidazolium tetraphenylborate (**2**·BPh_4, 19 dm^3 mol^{-1}). This kind of difference in the stabilities was also observed in the complexes of dibenzo-18-crown-6 (54 and 35 dm^3 mol^{-1}, respectively) and was explained by the ability of the imidazo-

 DOI: 10.1039/b100775k



Scheme 1 Structural formulae and crystallographic numbering of tetraphenylborate and complexed *N*-heteroaromatic cations.

Table 1 Stability constants (K) for the complexes between tetraphenylborate and cations **1**–**3** and **5** in 1 : 1 CD_3CN–CD_3OD solution at 30 °C determined by ^1H NMR titration

Complex	K/dm^3 mol^{-1}	$\Delta\delta_C$ (ppm)	r^2
1·BPh_4	46 ± 2	−0.25 ± 0.01	0.999
2·BPh_4	19 ± 4	−1.1 ± 0.4	0.995
3·BPh_4	17 ± 2	−0.43 ± 0.05	0.998
5·BPh_4	10 ± 1	−1.4 ± 0.1	0.997

lium cation to form two N–H ··· O hydrogen bonds.[18,19] Also, in the tetraphenylborate complexes imidazolium can use both of its N–H groups for N–H ··· π hydrogen bonding, while 1-Me-imidazolium can only use one. The stability of *N*-methylpyridinium tetraphenylborate (**3**·BPh_4) is equal to that of the *N*-methylimidazolium complex (**2**·BPh_4). So, the ring size of the cation does not have any effect on complexation strength in solution. The stability constant of the complex **5**·BPh_4, however, is almost half those of the complexes **2**·BPh_4 and **3**·BPh_4, possibly due to interactions between the polar groups of the guest and solvent molecules. Counter ions, ClO_4^- (heteroaromatics **1** and **2**) or I^- (heteroaromatics **3** and **5**), may have an effect on the stabilities, but the magnitude of these effects is difficult to estimate.

Lewis-base triphenylborane products are formed (Scheme 1) when the displacement of a phenyl ring from tetraphenylborate takes place. The loss of a phenyl ring and the formation of heterocycle–triphenylboranes occur at room temperature in good yields. The stronger Lewis base (heteroaromatic cation) drives out a weaker Lewis base (phenyl group). It is known that under acidic conditions the tetraphenylborate anion has limited stability, which produces triphenylboranes,[11] though at the same time the tricoordinated boron acts as an electrophile to establish a tetrahedral configuration. From previous studies it was observed that when heated with alkylammonium salts BPh_4^- can lose a phenyl ring and form a B–N bond with the ammonium compound.[12] This kind of displacement is also known to happen at room temperature, as was observed in our studies. The displacement takes place more easily with cations having lower pK_a values. Generally, the acidity constants of the reacting heteroaromatic cations (pK_a at 20 °C: pyrazine 0.51, pyrimidine 1.23, pyridazine 2.24, pyrazole 2.5 and thiazole 2.53)[25] are lower (pK_a < 3) than those of the complex-forming ones (imidazole 7.0,[22] methylimidazole 7.1[26]).

X-Ray crystallographic studies

The crystal structures of four 1 : 1 complexes and three displacement products were determined (Table 2). In imidazolium tetraphenylborate (**1**·BPh_4) and 1-methylimidazolium tetraphenylborate (**2**·BPh_4) complexes hydrogen bonding interactions to aromatic π-systems[12,13] can take place. In the other two complexes (**3**·BPh_4 and **5**·BPh_4) the possible interactions are mainly weaker C–H ··· π or electrostatic in nature. However, in the solid state other weak interactions also seem to have an important role in complexation.

In the unsubstituted imidazolium cation (**1**) there are two possible hydrogen bond donating sites. However, only one of them participates in complex formation while the other N–H group is weakly hydrogen bonded to the solvent acetonitrile [N(27) ··· N(100) = 3.125(3) Å]. The imidazolium cation is situated between two tetraphenylborate anions, being parallel to one host and perpendicular to the other host (Fig. 1). The perpendicular orientation is stabilised *via* normal N–H ··· π bond (type A according to the classification of Bakshi *et al*;[12] the same classification will also be used hereafter for the C–H ··· π interactions) and by simultaneous C–H ··· π bonding of the same type from the adjacent C(29) to the opposite phenyl ring. The distance between atom N(25) and the centroid of the phenyl ring C(7)–C(12) = Ct2 is 3.23 Å and the respective distance of atom C(29) to the closest phenyl ring is slightly longer [C(29) ··· Ct1 = 3.46 Å]. The interactions with the parallel host are symmetrical, bifurcated C–H ··· π interactions of type E[12] with the distances C(26) ··· Ct3* = 3.30 and C(26) ··· Ct4* = 3.31 Å.

The asymmetric unit of the crystal structure of 1-methylimidazolium·BPh_4 contains two crystallographically independent halves of the BPh_4, two cations and two acetonitrile molecules situated in the special position with an occupancy of

Table 2 Crystal data for tetraphenylborate complexes and displacement reaction products

Compound	**1**·BPh_4	**2**·BPh_4	**3**·BPh_4	**5**·BPh_4	**6**·BPh_3	**7**·BPh_3	**11**·BPh_3
Formula	$C_{24}H_{20}B^-C_3H_5N_2^+\cdot$ CH_3CN	$C_{24}H_{20}B^-C_4H_7N_2^+\cdot$ CH_3CN	$C_{24}H_{20}B^-C_6H_8N^+$	$C_{24}H_{20}B\cdot C_9H_{12}NO_2^+\cdot$ CH_3CN	$C_{21}H_{19}BN_2$	$C_{27}H_{23}BN_2$	$C_{22}H_{19}BN_2$
M_r	429.35	443.38	413.34	526.46	310.19	386.28	322.20
Crystal size/mm	0.05 × 0.30 × 0.30	0.30 × 0.30 × 0.30	0.20 × 0.20 × 0.40	0.20 × 0.20 × 0.35	0.20 × 0.40 × 0.50	0.20 × 0.20 × 0.25	0.15 × 0.20 × 0.55
Crystallisation solvent	CH_3CN–toluene	CH_3CN	CH_3CN	CH_3CN	CH_3CN–toluene	Ethanol	Acetone–propan-2-ol
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$ (No. 19)	$P2_1/m$ (No. 14)	$C2/m$ (No 12)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P2_1/a$ (No. 14)
a/Å	10.0245(3)	13.0490(5)	16.1480(5)	11.2280(6)	24.3436(8)	27.494(1)	7.1341(9)
b/Å	12.7797(4)	9.9316(4)	10.2577(3)	16.220(1)	11.0632(4)	9.4662(6)	15.305(2)
c/Å	19.0370(3)	19.1286(6)	13.9283(4)	16.2719(7)	16.4744(6)	20.009(1)	15.559(2)
β/°	90	91.065(2)	92.572(2)	98.991(3)	130.343(2)	127.672(3)	90.138(8)
V/Å^3	2438.8(1)	2478.6(2)	2304.8(1)	2927.0(3)	3381.7(2)	4121.9(3)	1698.8(4)
Z	4	4	4	4	8	8	4
D_c/Mg m^{-3}	1.169	1.188	1.191	1.195	1.219	1.245	1.260
μ/mm^{-1}	0.068	0.069	0.067	0.073	0.071	0.072	0.073
θ range/°	3.8–25.0	3.0–25.1	3.0–25.0	3.1–25.0	4.0–25.0	2.9–25	3.9–25.0
Reflections measured/unique	10987/4255	7917/4635	5895/2149	14479/5122	7416/2937	10097/3632	7443/2931
Parameters/reflections used in refinement [$I > 2\sigma(I)$]	299/3969	369/3961	169/1876	377/3261	217/2723	272/2349	226/2199
R_{int}	0.032	0.030	0.032	0.058	0.022	0.058	0.055
R/R_w [for data $I > 2\sigma(I)$]	0.042/0.110	0.087/0.199	0.043/0.105	0.082/0.203	0.036/0.085	0.050/0.096	0.075/0.162
GooF	1.055	1.163	1.062	1.036	1.100	1.021	1.153

Fig. 1 Crystal structure of the imidazolium·BPh_4 complex (**1**·BPh_4). Imidazolium is located between two hosts and interacts with them *via* N–H ··· π and C–H ··· π interactions (shown as broken bars). The other N–H is hydrogen bonded to the solvent acetonitrile.

Fig. 2 Crystal structure of the 1-methylimidazolium·BPh_4 complex (**2**·BPh_4). 1-Methylimidazolium interacts with three hosts *via* N–H ··· π and C–H ··· π interactions (shown as broken bars).

one half. The weak interactions between tetraphenylborate and the cation, however, remain the same as in **1**·BPh_4. Both cations are situated similarly between two hosts in a parallel position relative to one host and perpendicular to the other (Fig. 2). The type and the length of the interactions are also the same in both complexes **1**·BPh_4 and **2**·BPh_4 [interactions for the perpendicular orientations: N(27) ··· Ct3 = 3.29, C(26) ··· Ct2 = 3.42, N(27B) ··· Ct3B = 3.22, C(26B) ··· Ct2B = 3.42 Å; and for the parallel orientations 2 × C(28) ··· Ct1B = 3.33, 2 × C(28B) ··· Ct1* = 3.52 Å]. From to the similarity of the solid state interactions and the dissimilarity of the association constants of **1**·BPh_4 and **2**·BPh_4 it can be concluded that the N–H ··· π interactions play bigger role in solution, while in the crystalline state the efficiency of packing affects the complexation. In addition, there are C–H ··· π interactions of intermediate strength between the *N*-methyl group of the cations and the surrounding hosts [C(30) ··· Ct1′ = C(30B) ··· Ct1B′ = 3.58 Å]. Acetonitrile molecules fill the interstice with weak interactions to the cations.

In the *N*-methylpyridinium complex **3**·BPh_4 there is no possibility for N–H ··· π interactions. Therefore, only C–H ··· π interactions contribute to the complexation. The cation is located between three hosts with a type E bifurcated C–H ··· π interaction from C(26) to Ct1 and Ct1* (3.35 Å; the asymmetric unit comprises one half of the BPh_4 and the cation is located on a mirror plane) and a normal, type A C–H ··· π interaction from C(28) and methyl C(31) to two adjacent tetraphenylborates [C(28) ··· Ct2″ = 3.42, C(31) ··· Ct3′ = 3.55 Å]. The weak interactions of the guest with three different hosts give rise to an interesting strand-like packing in which there is no room for solvent as in **1**·BPh_4 and **2**·BPh_4 (Fig. 3).

1-Ethyl-4-(methoxycarbonyl)pyridinium (**5**) forms a solid state complex with tetraphenylborate *via* an unsymmetrical,

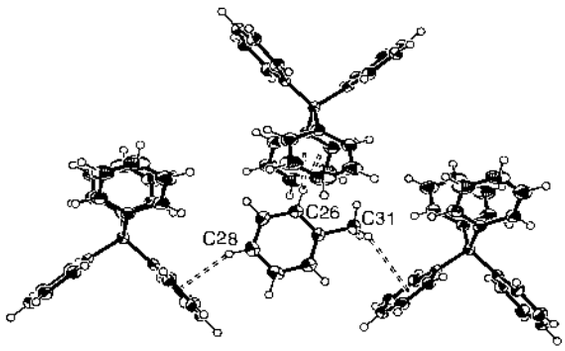


Fig. 3 *N*-Methylpyridinium (**3**) is situated between three hosts and interacts with them *via* C–H · · · π interactions (shown as broken bars). The strand-like packing leaves no room for solvents as in complexes **1**·BPh_4 and **2**·BPh_4.

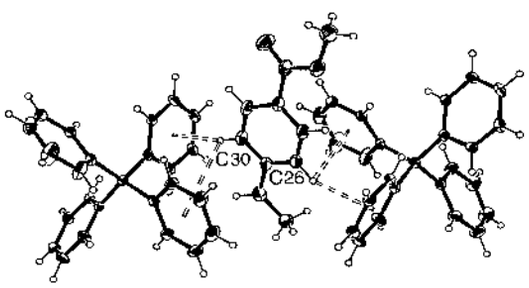


Fig. 4 Part of the crystal packing of complex **5**·BPh_4. C–H · · · π interactions are shown as broken bars and acetonitrile molecules are excluded for clarity.

bifurcated, type E C–H · · · π interaction to two anions [C(26) · · · Ct3 = 3.37, C(26) · · · Ct4 = 3.67, C(30) · · · Ct1* = 3.92 and C(30) · · · Ct2* = 3.30 Å]. The position of the cation between two tetraphenylborate molecules also shows weak π-stacking interactions between the edges of the aromatic rings thus stabilising the packing (Fig. 4). The methyl groups C(32) and C(35) also interact weakly with the edges of the aromatic rings of the nearby anions, the closest distances being C(32) · · · C(15) = 3.14 and C(35) · · · C22′ = 3.48 Å. Acetonitrile molecules fill the interstice in the crystal lattice.

The most interesting feature in the crystal structures of the displacement reaction compounds is the effect of the displacement on the B–C and B–N bond lengths compared to normal B–C and B–N bond lengths. In addition, the interactions between the molecules and the crystal packing are the points of interest. The average B–C bond length in BPh_4 is 1.643 Å and B–N length in B–N=C systems is 1.611 Å.[25] Phenylimidazole– and pyrazole–triphenylboranes (**7**–BPh_3 and **6**–BPh_3, respectively) resemble each other closely in respect of their B–N bonds, which are about the same length and slightly longer than usual [1.630(3) and 1.628(2) Å, respectively] and with their B–C bonds being shorter than usual (average length 1.631 Å). In addition, two of the B–C bonds are same length as the B–N bond while the third differentiates in that it is longer in pyrazole (**6**) and shorter in phenylimidazole–triphenylborane. In pyrazine–triphenylborane (**9**–BPh_3) all the bond lengths are different giving 1.637(4) Å for B–N and 1.616(4), 1.625(4) and 1.645(4) Å for the B–C bonds, *i.e.* two remarkably shortened B–C bonds and one average B–C bond.

The crystal packing of the pyrazole–triphenylborane (**6**–BPh_3) reveals the formation of dimeric pairs (Fig. 5a), while in the other two displacement products this is not observed. The reason for this is the ability of pyrazole–triphenylborane to form dual N–H · · · π hydrogen bonds [N(20) · · · Ct2* = 3.35 Å]. The other two displacement products organise themselves into chains in the crystalline state (Fig. 5b). The chain formation of the pyrazine–triphenylborane (**9**–BPh_3) is stabilised by a weak C–H · · · N interaction [C(5) · · · N(21) = 3.39 Å] and in phenylimidazole–triphenylborane (**7**–BPh_3) *via* weak π · · · π

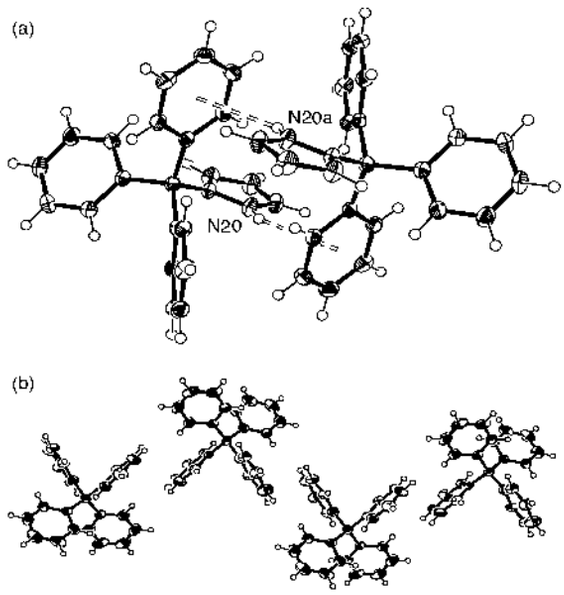


Fig. 5 The dimeric packing of compound **6**–BPh_3 is caused by a dual N–H · · · π interaction (a), while compound **11**–BPh_3 adopts chain-like packing (b).

interactions between the edges of the neighbouring aromatic rings [the closest distances are C(17) · · · C(17*) = 3.49 and C(23) · · · C(23*) = 3.47 Å].

Conclusions

Weak non-covalent interactions like C–H · · · π/N–H · · · π, stacking or electrostatic interactions stabilise the complexation between aromatic heterocyclic cations and tetraphenylborate. Four of the heterocyclic cations and the tropylium cation form complexes, which have been studied in solution and in the solid state. The stability constants of these complexes are low (10–50 $dm^3\ mol^{-1}$) correlating well with the corresponding crown ether complexes. Crystal structure studies of the complexes indicate that in solution weak interactions play a bigger role in complexation, while in the solid state the efficiency of packing can also affect the complexation.

Six of the aromatic heterocycles studied act as Lewis-bases replacing one phenyl group in the tetraphenylborate ion. The reaction occurs readily at room temperature giving good yields. Three crystal structures of these Lewis-base boranes have been determined.

Experimental

General

The analytical data and the preparation of heteroaromatic cation perchlorates (**1**, **2**, **6**–**11**) have been published earlier.[18,19,21] *N*-Methylpyridinium iodide (**3**) was prepared according to the literature procedure.[28] Tropylium tetrafluoroborate (**4**) and 1-ethyl-4-(methoxycarbonyl)pyridinium iodide (**5**) were commercially available and used without further purification. The solvents were dried and distilled according to the literature procedures.[29]

^{1}H NMR spectra were recorded on a Bruker Avance DPX200 spectrometer operating at 200.130 MHz. ^{1}H peak positions are reported relative to CD_3CN (δ = 1.94 ppm) and TMS (δ = 0 ppm). Elemental analysis was carried out with a Perkin-Elmer 2400.

Single crystals for X-ray diffraction studies † were obtained by

† CCDC reference numbers 156976–156982. See http://www.rsc.org/suppdata/p2/b1/b100775k/ for crystallographic files in .cif or other electronic format.

using either slow evaporation (**2**–**4**, **6**, **7**) or diffusion methods (**1**, **11**). X-Ray diffraction data were recorded on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation [λ(Mo-Kα) = 0.71073 Å] and a temperature of 173.0 ± 0.1 K. The structures were solved by direct methods (SHELXS-97[30]) and refined on F^2 by full-matrix least-squares technique (SHELXL-97[31]). The hydrogen atoms were calculated to their idealised positions with isotropic temperature factors (1.2 or 1.5 times the *C* temperature factor) except for the methyl hydrogens of complexes **2** and **3**, which were found from the difference Fourier and refined with isotropic temperature factors. Hydrogen atoms were located from the difference Fourier but in the final refinement calculated to their idealised positions with isotropic temperature factors (1.2 or 1.5 times *C* temperature factor). The methyl groups C(35) and C(52) in **3** are disordered over two positions with the occupancies of 0.559 : 0.441 and 0.744 : 0.256, respectively.

Synthesis

The preparation of the complexes and the displacement products is straightforward and the yields were high. Upon the addition of an aqueous solution of sodium tetraphenylborate to an aqueous solution of the cation salt an immediate precipitation was observed. The precipitates were filtered, washed with water and dried *in vacuo* to give pure complexes of cations **1**–**5** or substitution products of the cations **6**–**11**. The solid complexes were stable but when dissolved in *e.g.* acetonitrile the colour of the solution darkened gradually in several cases indicating decomposition.

Imidazolium tetraphenylborate (1·BPh$_4$). White solid. Yield 89%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 6.8 (4H, t, Ar-H), 7.0 (8H, t, Ar-H), 7.3 (8H, m, Ar-H), 7.4 (2H, d, imidazolium), 8.5 (1H, s, imidazolium). $C_{27}H_{25}BN_2$ (388.32): calcd C 83.51, H 6.49, N 7.21; found C 83.09, H 6.46, N 7.26%.

1-Methylimidazolium tetraphenylborate (2·BPh$_4$). White solid. Yield 76%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 3.8 (3H, s, N-CH_3), 6.9 (4H, t, Ar-H), 7.0 (8H, t, Ar-H), 7.3 (m, Ar-H, 8H; 1-Me-imidazolium, 2H), 8.3 (s, 1-Me-imidazolium, 1H). $C_{28}H_{27}BN_2$ (402.34): calcd C 83.59, H 6.76, N 6.96; found C 83.48, H 6.80, N 6.93%.

***N*-Methylpyridinium tetraphenylborate (3·BPh$_4$).** White solid. Yield 92%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 4.2 (3H, s, N-CH_3), 6.9 (4H, t, Ar-H), 7.0 (8H, t, Ar-H), 7.3 (8H, m, Ar-H), 8.0 (2H, t, Me-pyridinium), 8.5 (1H, t, Me-pyridinium), 8.6 (2H, d, Me-pyridinium). $C_{30}H_{28}BN$ (413.37): calcd C 87.17, H 6.83, N 3.39; found C 86.64, H 6.93, N 3.51%.

Tropylium tetraphenylborate (4·BPh$_4$). Orange solid. Yield 86%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 6.8 (4H, t, Ar-H), 7.0 (8H, t, Ar-H), 7.3 (8H, m, Ar-H), 9.2 (7H, s, tropylium). $C_{31}H_{27}B$ (410.46): calcd C 90.73, H 6.63; found C 90.22, H 6.44%.

1-Ethyl-4-(methoxycarbonyl)pyridinium tetraphenylborate (5·BPh$_4$). Pale yellow solid. Yield 87%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 1.6 (3H, t, N-$CH_2C\mathit{H}_3$), 4.0 (3H, s, -OCH_3), 4.6 (2H, q, N-$C\mathit{H}_2CH_3$), 6.8 (4H, t, Ar-H), 7.0 (8H, t, Ar-H), 7.3 (8H, m, Ar-H), 8.4 (2H, m), 8.8 (2H, d). $C_{33}H_{32}BNO_2$ (485,43): calcd C 81.65, H 6.64, N 2.89; found C 80.99, H 6.30, N 2.89%.

Pyrazole–triphenylborane (6–BPh$_3$). White solid. Yield 70%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 6.6 (1H, t, pyrazole), 7.2 (15H, m, Ar-H), 7.8 (2H, br, pyrazole). $C_{21}H_{19}BN_2$ (310.20): calcd C 81.31, H 6.17, N 9.03; found C 81.23, H 6.00, N 9.03%.

1-Phenylimidazole–triphenylborane (7–BPh$_3$). White solid. Yield 87%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 6.8–7.3 (15H, m, Ar-H), 7.56 (1H, m, Ph-imidazole), 7.63 (5H, m, Ph-imidazole), 7.8 (1H, m, Ph-imidazole), 8.8 (1H, m, Ph-imidazole). $C_{27}H_{23}BN_2$ (386.30): calcd C 83.95, H 6.00, N 7.25; found C 83.77, H 6.11, N 7.24%.

Thiazole–triphenylborane (8–BPh$_3$). White solid. Yield 82%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 6.8–7.7 (15H, m, Ar-H; 1H, thiazole), 7.9 (2H, m, thiazole), 9.0 (1H, m, thiazole). $C_{21}H_{18}NSB$ (327.45): calcd C 77.08, H 5.54, N 4.28, S 9.80; found C 77.26, H 5.54, N 4.25, S 9.70%.

Pyridazine–triphenylborane (9–BPh$_3$). Pale yellow solid. Yield 94%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 6.8–7.2 (15H, m, Ar-H), 8.0 (2H, m, pyridazine), 9.3 (2H, m, pyridazine). $C_{22}H_{19}BN_2$ (322.22): calcd C 82.01, H 5.94, N 8.69; found C 81.92, H 5.79, N 8.67%.

Pyrimidine–triphenylborane (10–BPh$_3$). Pale yellow solid. Yield 66%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 6.8–7.7 (15H, m, Ar-H; 1H, pyrimidine), 8.8 (2H, d, pyrimidine), 9.2 (1H, s, pyrimidine). $C_{22}H_{19}BN_2$ (322.22): calcd C 82.01, H 5.94, N 8.69; found C 81.84, H 5.68, N 8.58%.

Pyrazine–triphenylborane (11–BPh$_3$). Yellow solid Yield 77%. ^{1}H NMR (200 MHz; CD_3CN; Me_4Si): δ_H (ppm) 6.8–7.7 (15H, m, Ar-H), 8.7 (4H, s, pyrazine). $C_{22}H_{19}BN_2$ (322.22): calcd C 82.01, H 5.94, N 8.69; found C 82.05, H 5.79, N 8.43%.

Stability constant measurements

A standard solution of a cation in CD_3CN–CD_3OD (1 : 1) was prepared with a concentration of 1–2 × 10^{-3} M, just sufficient to give an observable ^{1}H NMR signal. Series of tetraphenylborate solutions (0.01–0.2 M) were made by weighing out an appropriate amount of $NaBPh_4$. A 1–2 ml portion of the standard solution of the guest was then added and the flask was re-weighed. The spectra were measured immediately at 30 °C after dissolving and mixing the samples. The stability constants for 1 : 1 complexation were calculated from the ^{1}H NMR chemical shifts using the Benesi–Hildebrand least-squares line-fitting procedure.[32] The stoichiometry of the complex **2**·BPh_4 was determined by Job's method. 3 × 10^{-3} M solutions of $NaBPh_4$ and 1-methylimidazolium perchlorate (**2**) in CD_3CN–CD_3OD (1 : 1 solution) were prepared. Portions of the solutions were mixed so that the total concentration was constant in each mixture and were then investigated by ^{1}H NMR.

Acknowledgements

Financial support by the Academy of Finland (SK) (Grant No. 40538) and the Ministry of Education of Finland (MN) is gratefully acknowledged. We thank the Trace Element Laboratory of the University of Oulu for the elemental analysis data.

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