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Lewis-base adducts of the diborane(4) compounds $B_2(1,2\text{-}E_2C_6H_4)_2$ (E = O or S)

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The reactivity of the diborane(4) compounds $B_2(1,2\text{-}E_2C_6H_4)_2$ (E = O or S) have been studied with respect to their ability to co-ordinate Lewis bases, specifically 4-methylpyridine (mpy) and the phosphines PMe_2Ph and PEt_3. Four monoadducts have been characterised by X-ray crystallography, namely $B_2(1,2\text{-}O_2C_6H_4)_2(mpy)$, $B_2(1,2\text{-}S_2C_6H_4)_2$-(mpy), $B_2(1,2\text{-}S_2C_6H_4)_2(PMe_2Ph)$ and $B_2(1,2\text{-}S_2C_6H_4)_2(PEt_3)$, together with three bis adducts $B_2(1,2\text{-}O_2C_6H_4)_2$-$(mpy)_2$, $B_2(1,2\text{-}S_2C_6H_4)_2(mpy)_2$ and $B_2(1,2\text{-}S_2C_6H_4)_2(PMe_2Ph)_2$. In the former set of compounds the one base is co-ordinated to one boron centre which adopts a tetrahedral geometry, the remaining boron being trigonal planar as in the structure of the parent compound. For the bis adducts each of the two borons is co-ordinated to a mpy or phosphine with both borons tetrahedral. Bond-length changes associated with ligand co-ordination are discussed. Multinuclear solution-state NMR studies have also been performed for solutions containing $B_2(1,2\text{-}O_2C_6H_4)_2$ and mpy, $B_2(1,2\text{-}S_2C_6H_4)_2$ and mpy and $B_2(1,2\text{-}S_2C_6H_4)_2$ and PEt_3. All of these studies indicate that intermolecular exchange of base between the parent compound, the mono- and the bis-adducts occurs in solution together with intramolecular exchange between the two boron centres in the monoadducts. The various rates of these processes, inasmuch as they have been determined accurately, are discussed and rationalised. The monoadducts $B_2(1,2\text{-}O/S_2C_6H_4)_2(mpy)$ are nominally isoelectronic with the phenonium cation.

Introduction

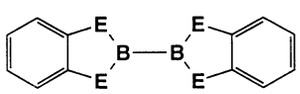
Transition-metal-catalysed diboration reactions involving the addition of the B–B bond in diborane(4) compounds to alkenes or alkynes is a topic of considerable current interest. Thus, whilst the diboron tetrahalides, B_2X_4, will undergo uncatalysed reactions with C=C or C≡C bonds,[1] addition of the much more stable and easily prepared tetraalkoxydiborane(4) compounds $B_2(OR)_4$ requires the presence of a catalyst, recent examples of which include rhodium- and gold-catalysed B–B bond addition to alkenes[2] and platinum-catalysed addition to alkynes.[3] In addition, a recent report of the palladium-catalysed syntheses of aryl boronate esters from aryl halides and a diborane(4) compound has attracted much attention.[4]

Two of the diborane(4) compounds which have been most studied with regard to these reactions are the catecholate species $B_2(1,2\text{-}O_2C_6H_4)_2$ **1**[5] and the pinacol derivative B_2-$(OCMe_2CMe_2O)_2$.[6] During these studies it became clear that the nature of the solvent had a marked influence on the course of the metal-catalysed reactions and it was assumed that the Lewis-acidic nature of the boron centre and its interaction with the solvent might be a factor of some importance. With this in mind we undertook a study of the reactivity of the diborane(4) compound **1** and the thiocatecholate species $B_2(1,2\text{-}S_2C_6H_4)_2$ **2**[5] towards a range of pyridines and phosphines and describe herein the results of both solid- and solution-state studies; part of this study has already been published as a preliminary communication.[7]

Results and Discussion

Structural studies

In ref. 7 we described the reaction between compound **1** and 1 and 2 equivalents of 4-methylpyridine (mpy) which resulted in the formation of the colourless, crystalline mono- and bis-adducts $B_2(1,2\text{-}O_2C_6H_4)_2(mpy)$ **3** and $B_2(1,2\text{-}O_2C_6H_4)_2$-$(mpy)_2$ **4** both of which were characterised by X-ray crystallography. The structures will not be reported again in detail here (views of both are presented in ref. 7 with selected bond lengths and angles), but important structural features in comparison with **1**[5b] will be briefly reiterated. Thus, the B–B bond lengths for **3** [1.706(3)] and **4** [1.713(4) Å] are somewhat longer than that in **1** [1.678(3) Å][5b] consistent with both the larger co-ordination numbers around one or both borons and the change in hybridisation from sp^2 to sp^3 at the co-ordinated boron centre. In **4** the average B–O distances are about 0.1 Å longer than those in **1** for similar reasons together with the fact that any B–O π bonding present in **1** is likely to be much reduced in **4**. This change in circumstances at the oxygen atoms in **4** is also reflected in a shortening of the C–O distances by about 0.02 Å compared to **1**, and a noticeable change is apparent in the C(3)–C(4) bond lengths: 1.378(4) Å for **4** and 1.393(2) Å for **1**. The structure of **3** is essentially a composite of those for **1** and **4** and the B–N distances are 1.644(2) and 1.659(2) Å for **3** and **4** respectively.



1, E = O; **2**, E = S

Compounds **3** and **4** are the first examples of adducts of $B_2(OR)_4$ type compounds and the only previous examples of structurally characterised adducts of diborane(4) compounds in general, of which we are aware, are $B_2H_4(PPh_3)_2$,[8] B_2Cl_4-$(NMe_3)_2$,[9] $B_2(pz)_4(Hpz)_2$[10] (Hpz = pyrazole) and BCl_2BCl-$[N(Me)CH_2CH_2NMe_2]$[11] for which B–B distances are in the range 1.698(4)–1.769(6) Å. We have also reported the structure of $B_2Cl_4(NHMe_2)_2$ for which the B–B distance (average of three independent molecules) is 1.736 Å.[5b]

The thiocatecholate compound **2** also forms colourless, crystalline mono- and bis-adducts $B_2(1,2\text{-}S_2C_6H_4)_2(mpy)$ **5** and

Table 1 Selected bond lengths (Å) and angles (°) for compounds **5**–**9**

5		**6**[a]		**7**		**8**[b]		**9**	
B(1)–B(2)	1.701(7)	B(1)–B(1A)	1.715(10)	B(1)–B(2)	1.689(5)	B(1)–B(1A)	1.750(4)	B(1)–B(2)	1.707(3)
B(1)–S(1)	1.915(5)	B(1)–S(1)	1.913(5)	B(1)–S(1)	1.910(4)	B(1)–S(1)	1.928(2)	B(1)–S(1)	1.929(2)
B(1)–S(2)	1.899(5)	B(1)–S(2)	1.910(5)	B(1)–S(2)	1.921(4)	B(1)–S(2)	1.930(2)	B(1)–S(2)	1.924(2)
B(1)–N(1)	1.648(5)	B(1)–N(1)	1.645(6)	B(1)–P(1)	1.979(4)	B(1)–P(1)	1.974(2)	B(1)–P(1)	1.967(2)
B(2)–S(3)	1.792(5)			B(2)–S(3)	1.798(4)			B(2)–S(3)	1.800(2)
B(2)–S(4)	1.798(5)			B(2)–S(4)	1.796(4)			B(2)–S(4)	1.801(2)
B(2)–B(1)–S(1)	111.0(3)	B(1A)–B(1)–S(1)	114.6(4)	B(2)–B(1)–S(1)	113.1(2)	B(1A)–B(1)–S(1)	109.04(7)	B(2)–B(1)–S(1)	106.7(1)
B(2)–B(1)–S(2)	113.5(3)	B(1A)–B(1)–S(2)	113.2(4)	B(2)–B(1)–S(2)	115.0(2)	B(1A)–B(1)–S(2)	120.2(1)	B(2)–B(1)–S(2)	111.4(1)
B(2)–B(1)–N(1)	110.2(3)	B(1A)–B(1)–N(1)	108.4(4)	B(2)–B(1)–P(1)	109.2(2)	B(1A)–B(1)–P(1)	111.2(2)	B(2)–B(1)–P(1)	114.4(1)
S(1)–B(1)–S(2)	104.3(2)	S(1)–B(1)–S(2)	104.0(2)	S(1)–B(1)–S(2)	105.9(2)	S(1)–B(1)–S(2)	104.3(1)	S(1)–B(1)–S(2)	104.5(1)
S(1)–B(1)–N(1)	108.5(3)	S(1)–B(1)–N(1)	108.2(3)	S(1)–B(1)–P(1)	106.2(2)	S(1)–B(1)–P(1)	106.9(1)	S(1)–B(1)–P(1)	110.2(1)
S(2)–B(1)–N(1)	109.1(3)	S(2)–B(1)–N(1)	108.1(3)	S(2)–B(1)–P(1)	106.9(2)	S(2)–B(1)–P(1)	104.3(1)	S(2)–B(1)–P(1)	109.3(1)
B(1)–B(2)–S(3)	124.6(3)			B(1)–B(2)–S(3)	124.9(3)			B(1)–B(2)–S(3)	128.3(2)
B(1)–B(2)–S(4)	124.2(3)			B(1)–B(2)–S(4)	124.0(3)			B(1)–B(2)–S(4)	120.1(2)
S(3)–B(2)–S(4)	111.2(3)			S(3)–B(2)–S(4)	111.1(2)			S(3)–B(2)–S(4)	111.3(1)

Symmetry transformations used to generate equivalent atoms: [a] A: $-x, -y+1, -z+1$; [b] A: $-x+2, y, -z+\frac{1}{2}$.

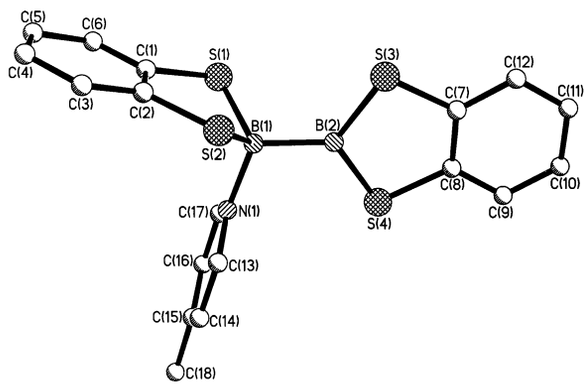
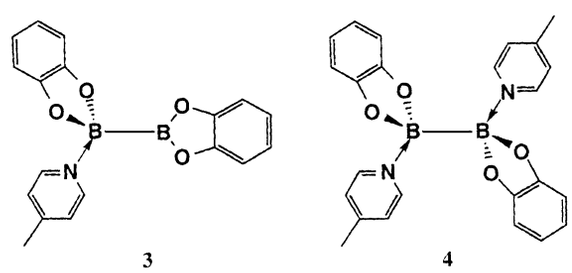


Fig. 1 View of the molecular structure of compound **5** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius



$B_2(1,2\text{-}S_2C_6H_4)_2(mpy)_2$ **6** analogous to **3** and **4**, both of which were characterised by X-ray crystallography. Views of **5** and **6** are shown in Figs. 1 and 3 with selected bond lengths and angles given in Table 1, and the packing of molecules of **5** in the crystal is shown in Fig. 2.

Crystals of compound **5** are not isomorphous with those of **3** but the molecular structures are similar in all respects. Thus, the two boron centres in **5** (and **3**) have approximately idealised tetrahedral and trigonal co-ordination geometries [B(1) and B(2) respectively], the only significant deviations arising due to constraints of the thiocatecholate (catecholate for **3**) groups. The structures are also similar with respect to the conformations about the B–B bonds. Thus in **5** the angle which the B(1)–N(1) bond makes to the plane defined by atoms B(1), B(2), S(3) and S(4) is 2.9°, the corresponding angle in **3** being a little larger (23.0°). Comparisons between **5** and **2**[5b] reveal a longer B–B bond length for **5** [1.701(7) *vs.* 1.673 Å (average) for two independent molecules of **2**]. The B–S bond lengths to B(2) in **5** (average 1.794 Å) are essentially identical to the B–S distances in **2** (average 1.794 Å), whereas those to B(1) (average

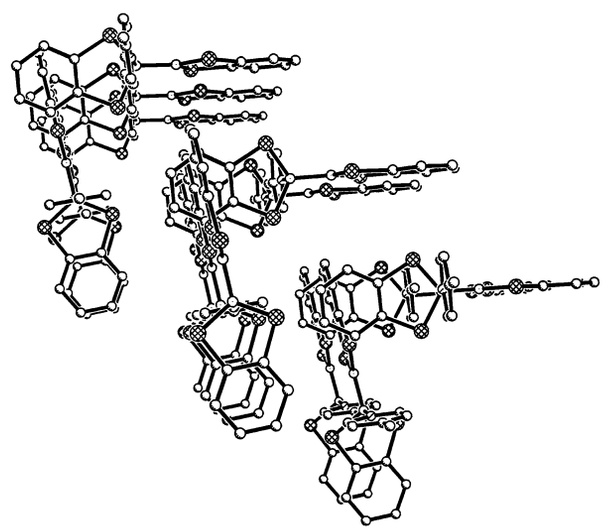


Fig. 2 Packing of molecules of compound **5** in the crystal

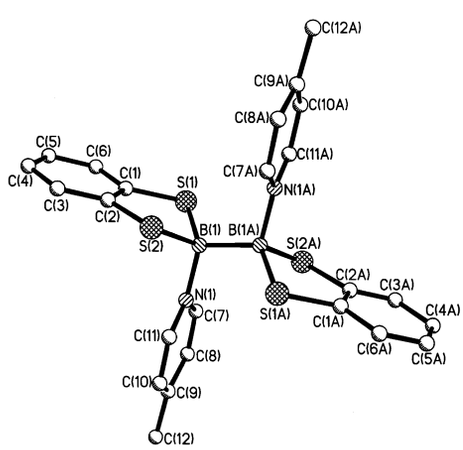


Fig. 3 Molecular structure of compound **6** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Those labelled A are related by the symmetry operation $-x, -y+1, -z+1$

1.907 Å) are somewhat longer as expected (see above). Significant changes are also evident in the C–S and C–C distances in the thiocatecholate group attached to B(1). Thus for **2** the average C–S, C^1–C^2, C^2–C^3, C^3–C^4 and C^5–C^6 bond lengths (using a generalised numbering scheme where C^1 and C^2 are bonded to sulfur, rather than the crystallographic scheme) are 1.757, 1.398, 1.398, 1.379 and 1.392 Å. The corresponding distances associated with B(2) in **5** are 1.764, 1.382, 1.394, 1.382 and

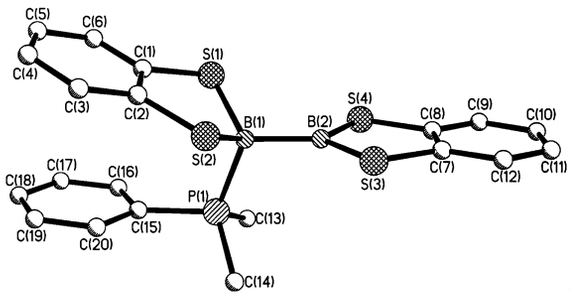


Fig. 4 Molecular structure of compound **7** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius

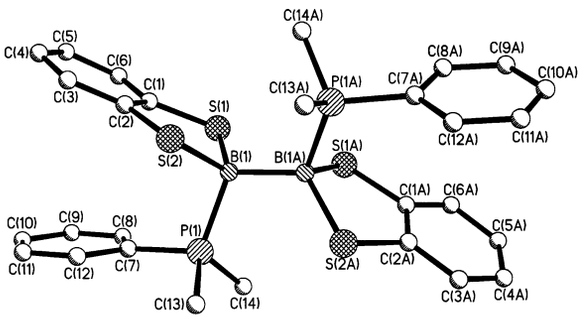


Fig. 5 Molecular structure of compound **8** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Those labelled A are related by the symmetry operation $-x + 2, y, -z + \frac{1}{2}$

1.394 Å, which differ significantly only in the C^1–C^2 value, but those for B(1) (1.768, 1.399, 1.386, 1.398 and 1.385 Å) show somewhat greater differences. These data could be interpreted as indicating that B–S π bonding at the trigonal boron centres in **2** and **5** is significant and that, on addition of mpy, this is disrupted resulting in noticeable changes in the π-bonding structure of the associated thiocatecholate group. However, the corresponding bond lengths for **6** are 1.764, 1.401, 1.394, 1.385 and 1.382 Å which do not match either of the sets of values for **5**. Thus, whilst B–S π bonding may well be appreciable, we are in danger of overinterpreting any changes that arise in the thiocatecholate distances resulting from the co-ordination of 4-methylpyridine (mpy).

In crystals of compound **6** molecules of the bis(mpy) adduct of **2** reside on crystallographic centres of symmetry. The structure is therefore constrained to have an *anti* conformation about the B–B bond with respect to the mpy ligands (as is also the case for **4**). Crystals of **4** and **6** are not isomorphous, however, since in **6** there is also one molecule of thf (tetrahydrofuran) per asymmetric unit (for **4**, mpy of crystallisation is present). The B–B distance for **6** [1.715(10) Å] is slightly lengthened with respect to **5**, but the B–S (average 1.912 Å) and B–N [1.645(6) Å] bond lengths are similar to those in **5** [B–N 1.648(5) Å] and, in the latter case, to those in **3** and **4**.

Whilst compound **1** readily co-ordinates mpy, it shows no evidence for co-ordinating phosphines (see later).[7] In contrast, **2** reacts with the phosphine PMe_2Ph affording, after work-up, a colourless, crystalline mixture of both the mono- and bis-phosphine adducts $B_2(1,2\text{-}S_2C_6H_4)_2(PMe_2Ph)$ **7** and $B_2(1,2\text{-}S_2C_6H_4)_2(PMe_2Ph)_2$ **8** both of which have been characterised by X-ray crystallography. The structures are shown in Figs. 4 and 5 respectively and a view of the packing of molecules of **8** is in Fig. 6; selected bond lengths and angles for both structures are given in Table 1. Much of the discussion for both **5** and **6** is also appropriate for **7** and **8**. Thus, important metrical parameters are, for **7**, B–B [1.689(5) Å], B(1)–S (average 1.915 Å), B(2)–S (average 1.797 Å) and B–P [1.979(4) Å] and, for **8**, B–B [1.750(4) Å], B–S (average 1.929 Å) and B–P [1.974(2) Å] (molecules of **8** reside on a crystallographic two-fold axis) which show an increase in B–B bond length in the order **2** < **7** < **8** and

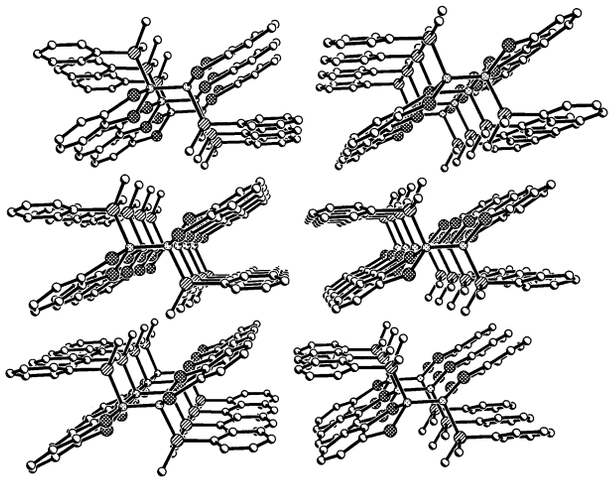


Fig. 6 Packing of molecules of compound **8** in the crystal

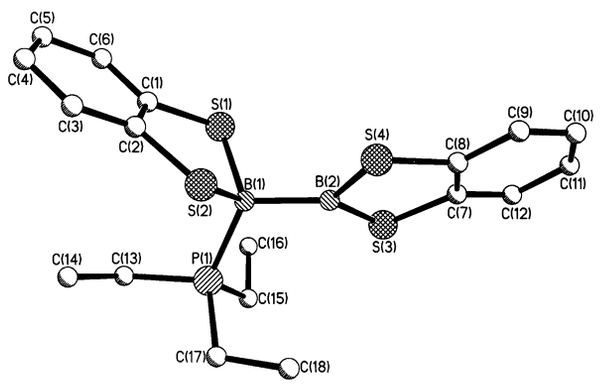


Fig. 7 Molecular structure of compound **9** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius

a marked increase in the B–S distances on co-ordination of a phosphine to the boron centre. With regard to the conformations about the B–B bonds, the angle between the B(1)–P(1) bond and the plane defined by B(1), B(2), S(3) and S(4) for **7** is 79.9° which is quite different to the corresponding angle found in **5** (and **3**). Thus in **7** the unco-ordinated, trigonal boron centre is almost orthogonal to the boron–ligand bond whereas in **5** (and **3**) this bond lies almost in the plane of the trigonal boron centre. In **8** the phosphines are *anti*, but there is no crystallographic constraint on the P–B–B–P torsion angle which is 153.1°, somewhat less than 180°; for **6** the corresponding N–B–B–N torsion angle is exactly 180° by symmetry.

Compound **2** also reacted with PEt_3 and, after work-up, afforded colourless crystals which were shown by X-ray crystallography to be the monophosphine complex $B_2(1,2\text{-}S_2C_6H_4)_2(PEt_3)$ **9**; we were not able to isolate crystals of the bis(phosphine) adduct although NMR evidence for the presence of such a compound was obtained (see later). A view of the structure of **9** is shown in Fig. 7 with selected bond lengths and angles in Table 1. Relevant parameters include the distances B–B [1.707(3) Å], B(1)–S (average 1.927 Å), B(2)–S (average 1.800 Å) and B–P [1.967(2) Å]. The angle between the B(1)–P(1) bond and the B(1), B(2), S(3), S(4) plane is 39.6° which is significantly different from that of either **5** or **7**, but rotation about the B–B bonds in these complexes is expected to be a very low-energy process and significant differences due to crystal-packing effects are therefore not unexpected. The differences in ligand–B–B–ligand torsion angles for **6** and **8** mentioned above provide further evidence for this assertion.

For all of the structures described above there are no particularly short intermolecular contacts between molecules or solvent of crystallisation although in two cases the crystal packing

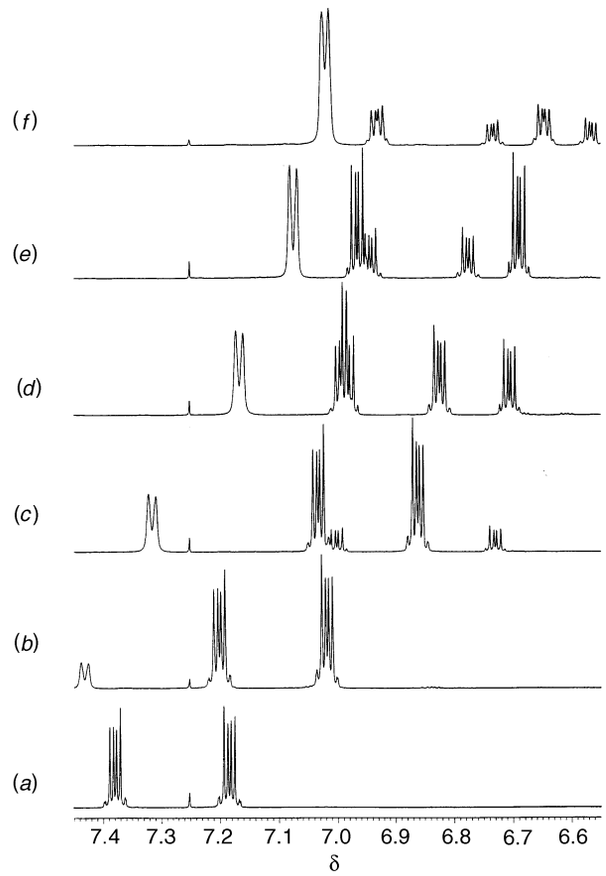


Fig. 8 The 500 MHz ^{1}H NMR spectra showing the aromatic region for each of six solutions at room temperature containing compound **1** and 0 (*a*), 0.5 (*b*), 1.0 (*c*), 1.5 (*d*), 2.0 (*e*) and 5.0 equivalents (*f*) of mpy in $CDCl_3$. The small singlet at δ 7.25 is due to $CHCl_3$

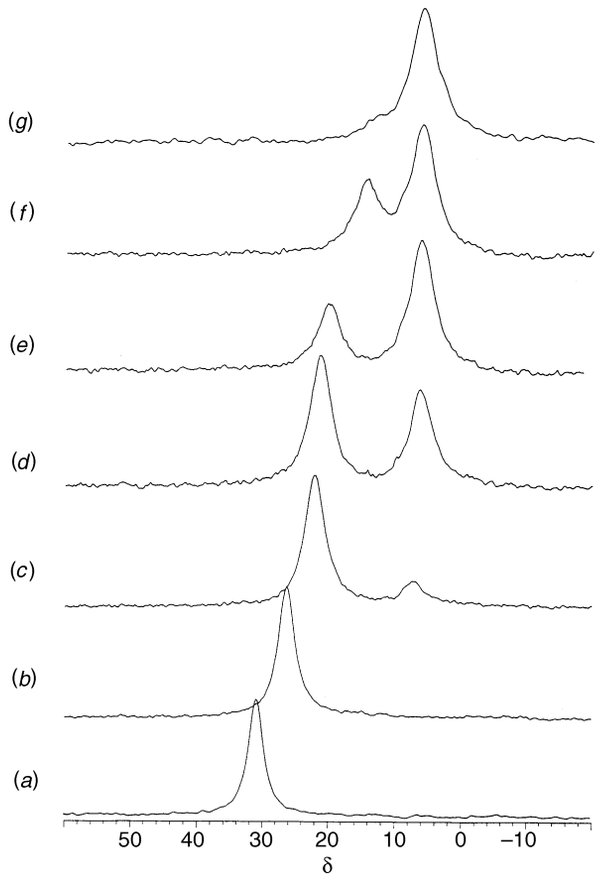


Fig. 9 The 160 MHz ^{11}B-{^{1}H} NMR spectra for each of seven solutions at room temperature containing compound **1** and 0 (*a*), 0.5 (*b*), 1.0 (*c*), 1.5 (*d*), 2.0 (*e*), 5.0 (*f*) and 10.0 equivalents (*g*) of mpy in $CDCl_3$

is sufficiently interesting to warrant illustrative views (Figs. 2 and 6 for **5** and **8** respectively). As in the structure of **2**,[5b] however, there are some intermolecular C–H · · · S (2.877 Å) and S · · · S (3.583 Å) contacts in the case of **7** worthy of mention.

Solution studies

In ref. 7 we reported preliminary data on the solution-state properties of compounds **3** and **4** *vis-à-vis* inter- and intramolecular exchange of mpy ligands between boron centres. Herein we describe a series of more detailed ^{1}H and ^{11}B-{^{1}H} NMR studies, involving both variable molar ratios of **1** to mpy and a variable-temperature study of a 1:1 mixture of **1** and mpy, together with related studies concerning **2**.

Fig. 8 shows part of a ^{1}H NMR spectrum, specifically the aromatic region, for each of six solutions at room temperature containing compound **1** and 0, 0.5, 1.0, 1.5, 2.0 and 5.0 equivalents of mpy in $CDCl_3$ [Fig. 8(*a*)–8(*f*) respectively]. In Fig. 8(*b*)–8(*f*) only one of the pair of mpy aromatic resonances is shown (a broad doublet in each case) and the small singlet at δ 7.25 is due to $CHCl_3$. The spectrum shown in Fig. 8(*a*) is of **1** itself and comprises two multiplets at δ 7.38 and 7.18 due to the $O_2C_6H_4$ (catecholate) groups (an AA′BB′ system). On addition of 0.5 equivalent of mpy [Fig. 8(*b*)] there is a marked upfield shift of this pair of multiplets (δ 7.20, 7.02), but the fact that only one pair is present indicates that intermolecular exchange between **1** and **3** (which must both be present in solution at this ratio of reactants), and probably intramolecular exchange between the inequivalent boron centres in **3**, is fast at this temperature on the NMR time-scale. When 1.0 equivalent of mpy is present [Fig. 8(*c*)] a further upfield shift of these two multiplets is apparent (δ 7.03, 6.86), but in addition a second pair of multiplets is now observed at δ 7.00 and 6.73 revealing that a second species is present. This species we assume to be the bis(mpy) adduct **4**. Fig. 8(*d*)–8(*f*) shows the result of adding further equivalents of mpy such that after 5 equivalents have been added [Fig. 8(*f*)] the original pair of multiplets has moved further upfield to δ 6.74 and 6.57 whilst the second set of multiplets, first seen in Fig. 8(*c*), has not changed greatly (δ 6.94, 6.65) but it now represents the predominant species present (the major species present after addition of 10.0 equivalents of mpy: spectrum not shown).

The simplest explanation for these data is that intermolecular exchange of mpy between compounds **1** and **3** is fast, as mentioned above, but that intermolecular exchange involving the bis adduct **4** is substantially slower. Inasmuch as **3** can be distinguished as a separate species, intramolecular exchange between the two different boron centres would also seem to be fast (see below). We note, however, that at this temperature only one set of mpy resonances is observed regardless of the amount present, and that the aromatic resonances, one of which is shown in Fig. 8(*b*)–8(*f*), show a marked upfield shift as the amount of mpy present increases.

Further data in support of this explanation were obtained by examining the ^{11}B-{^{1}H} NMR spectra of a series of solutions identical to those described above (Fig. 9); Fig. 9(*a*) shows the ^{11}B-{^{1}H} spectrum of compound **1** itself (δ 32). After addition of 0.5 equivalent of mpy [Fig. 9(*b*)] a single resonance is observed at higher field (δ 26) which continues to shift upfield (δ 22) after addition of 1.0 equivalent of mpy, although a new resonance at δ 8 is now also seen. As successive amounts of mpy are added the original resonance continues to move upfield [δ 14 at 5.0 equivalents, Fig. 9(*f*)], whilst the second resonance remains in the same position but grows in intensity. After addition of 10.0 equivalents of mpy to **1** [Fig. 9(*g*)] the second resonance dominates the spectrum. As with the ^{1}H NMR spectra, the original resonance which moves upfield is assumed to be

due to rapidly exchanging **1** and **3**, whilst that at δ 8 results from **4** for which exchange is slower. Confirmation that the latter resonance is due to **4** was provided by a solid-state ^{11}B NMR spectrum of isolated, pure crystalline **4**.

In order to probe these exchange processes in more detail a variable-temperature study was carried out on a 1:1 mixture of compound **1** and mpy in CD_2Cl_2, the results of which, for the aromatic region, are shown in Fig. 10. At 283 K [Fig. 10(*a*)] a broad pair of resonances is seen for the mpy ligands (δ 8.54 and 7.38) together with a predominant AA′BB′ multiplet corresponding to **1**/**3** at δ 7.02 and 6.87 and a minor AA′BB′ multiplet, due to **4**, one part of which lies under the aforementioned signal centred at δ 6.87 and the other part of which is centred at δ 6.70. As the temperature is lowered the mpy signals broaden considerably [Fig. 10(*b*), δ 263 K], but beginning at 253 K [Fig. 10(*c*)], and readily seen by 243 K [Fig. 10(*d*)], a second pair of mpy resonances have appeared at δ 8.08 and 7.13. As the temperature is further lowered to 233 K [Fig. 10(*e*)] both pairs of mpy resonances begin to sharpen and resolve into doublets, but at the same time the AA′BB′ multiplet due to **1**/**3** starts to broaden; both features are more marked at 228 K [Fig. 10(*f*)]. At 218 K [Fig. 10(*g*)] the broadening of this AA′BB′ multiplet is very marked, but in addition a new pair of signals is just apparent at δ 7.40 and 7.20 which correspond to uncomplexed **1** [Fig. 8(*a*)]. As the temperature is further lowered to 208 K [Fig. 10(*h*)] the signals due to **4** remain sharp and well resolved and those due to **1** become more prominent, but the catecholate resonances for **3** become very poorly resolved. Thus at this point the intermolecular exchange of mpy between **1** and **3** has been effectively frozen out but intramolecular exchange of mpy between the two boron sites in **3** is apparently still resonably fast. However by 183 K [Fig. 10(*j*)] this intramolecular exchange has now also been almost frozen out since four resonances of equal intensity are now seen at δ 7.20, 7.04, 6.77 and 6.63, the first two being presumably associated with the uncomplexed boron centre and the latter two, at higher field, with the mpy-ligated boron. Resonances due to **4** remain sharp and are clearly visible at δ 6.83 and 6.85 and those due to **1** are also clearly present although only the one at δ 7.40 is observed as the other at δ 7.20 is masked by one of the signals due to **3**. Also at this lowest temperature the higher-field pair of mpy resonances (δ 8.00 and 7.12) integrate correctly with the catecholate resonances due to **4** and are, therefore, themselves most likely associated with **4**, while the predominant and lower-field set of mpy resonances (δ 8.62 and 7.49) integrate correctly with the four catecholate signals for **3**.

Thus, in summary, all of these NMR data for the interaction between compound **1** and mpy indicate that intermolecular exchange of mpy involving **4** is slow whereas that between **1** and **3** is much faster, and also that intramolecular exchange between the boron centres in **3** is faster still. This information is summarised in Scheme 1.

We also examined the interaction between compound **2** and mpy in $CDCl_3$ solution. Resonances for **2** itself occur at δ 7.93 and 7.38 and comprise a pair of multiplets characteristic of the expected AA′BB′ system. On addition of 0.5 equivalent of mpy this pair of thiocatecholate resonances shifts upfield to δ 7.74 and 7.23 and a pair of mpy signals appear as doublets at δ 9.03 and 7.37. Further addition of mpy up to 5.0 equivalents gives rise to a spectrum which still contains only one pair of thiocatecholate resonances, now at δ 7.19 and 6.76, together with one pair of mpy aromatic signals at δ 8.55 and 7.11, the lower-field component of which is rather broad. The main difference between the interactions of **2** and mpy and that of **1** and mpy is, therefore, that at room temperature, all exchange processes would seem to be fast since no separate resonances are observed for the bis(mpy) adduct **6**.

A variable-temperature study of a solution of compound **2** and 1.0 equivalent of mpy was also carried out to see to what extent the various exchange processes could be frozen out. At room temperature a single set of thiocatecholate resonances was observed which had broadened significantly by 273 K. By 223 K the spectrum was reasonably well resolved and indicated that all exchange processes had indeed been frozen out showing

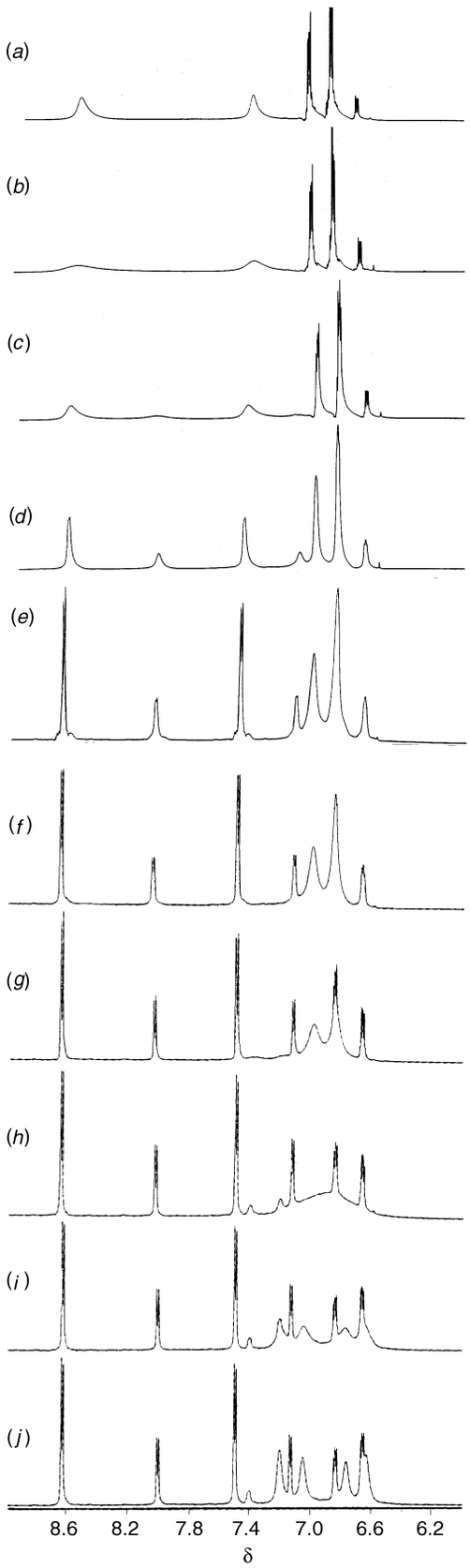
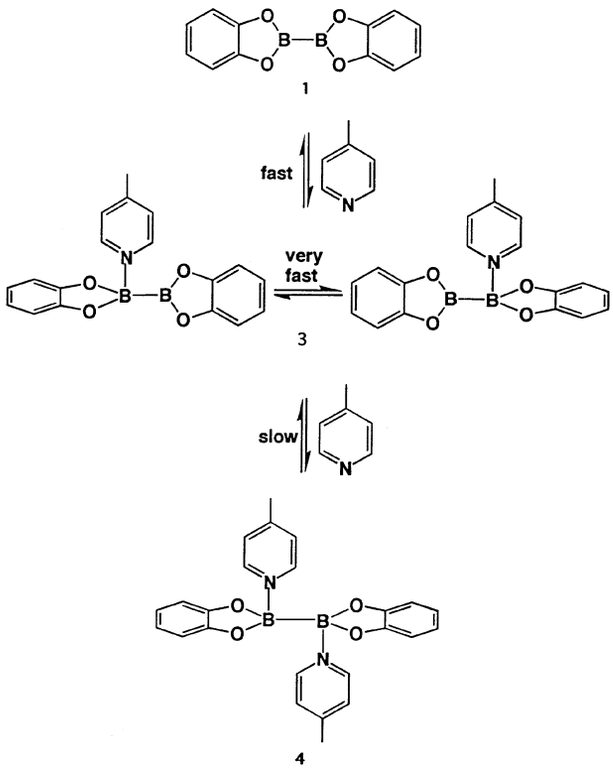


Fig. 10 The 500 MHz ^{1}H NMR spectra showing the aromatic region for a solution of compound **1** and 1.0 equivalent of mpy in CD_2Cl_2 at (*a*) 283, (*b*) 263, (*c*) 253, (*d*) 243, (*e*) 233, (*f*) 228, (*g*) 218, (*h*) 208, (*i*) 198 and (*j*) 183 K



Scheme 1

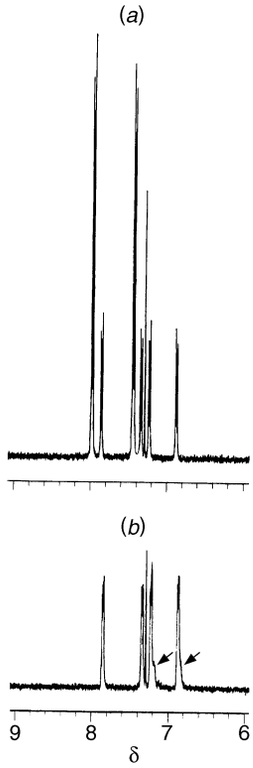


Fig. 11 The 400 MHz ^{1}H NMR spectra in $CDCl_3$ solution showing the aromatic region at 223 K for (*a*) **2** and 0.5 equivalent of PEt_3 and (*b*) **2** and 1.5 equivalents of PEt_3. In both spectra the singlet at δ 7.3 is due to $CHCl_3$. In (*b*) the arrows indicate resonances due to **10**

a pair of resonances at δ 7.90 and 7.35 due to **2**, a smaller pair at δ 7.17 and 6.76 corresponding to **6** and, as the major component, a set of four multiplets of equal intensity at δ 7.71, 7.32, 7.23 and 6.91 due to **5** for which the two thiocatecholate groups are inequivalent. As with the low-temperature spectrum of **1** and mpy, two sets of mpy resonances with correct integrations were seen corresponding to **5** (δ 8.94 and 7.41) and **6** (δ 9.09 and ≈7.3). A second experiment using almost 2 equivalents of mpy gave rise to a similar spectrum at 223 K but one in which signals due to **6** were the major component and those due to **2** were absent.

The interaction between compound **2** and PEt_3 was also studied in some detail by NMR spectroscopy. At room temperature in $CDCl_3$ addition of 0.5 equivalent of PEt_3 to **2** gave a 500 MHz ^{1}H NMR spectrum in which a single pair of thiocatecholate resonances was observed at δ 7.75 and 7.23 (upfield of **2**) both of which, however, were very broad (approximately 0.15 ppm at 500 MHz). A single set of PEt_3 signals was observed as multiplets at δ 1.92 and 1.11. As successive amounts of PEt_3 were added the PEt_3 resonances broadened slightly whereas the thiocatecholate signals sharpened and moved upfield such that after addition of 5.0 equivalents one pair of signals was seen at δ 7.37 and 6.95.

In terms of only one pair of thiocatecholate resonances being observed, the situation here is similar to what was found for compound **2** and mpy, but the fact that the thiocatecholate resonances were very broad suggested that any coalescence point was close to room temperature. This was confirmed by a variable-temperature study of a solution of **2** and 0.5 equivalent of PEt_3 in $CDCl_3$ at 400 MHz. Thus by 253 K the signals due to **2** were well resolved and four slightly less well resolved multiplets of equal intensity at δ 7.86, 7.33, 7.23 and 6.87 were present corresponding, most likely, to the mono(PEt_3) adduct **9**; at 233 K the resonances due to **9** were fully resolved [Fig. 11(*a*)]. A similar experiment carried out using 1.5 equivalents of PEt_3 [Fig. 11(*b*)] showed that at 233 K the major species present was **9** with no sign of **2**, but that a second species with one pair of thiocatecholate resonances at δ 7.18 and 6.85 was present which was most probably due to a bis(PEt_3) adduct $B_2(1,2\text{-}S_2C_6H_4)_2(PEt_3)_2$ **10**.

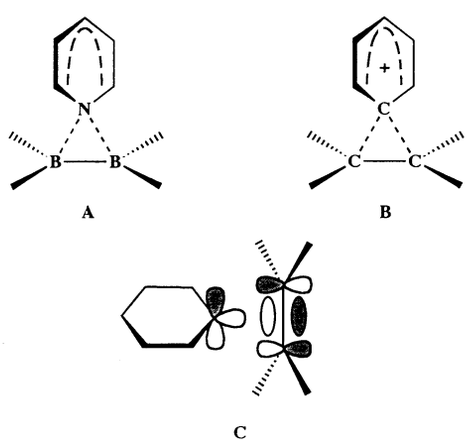
The ^{11}B-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of solutions of compound **2** and PEt_3 were also acquired. In the case of the former, a set of spectra for both **2** and 0.5 equivalent of PEt_3 and for **2** and 1.5 equivalents of PEt_3 were examined. These spectra all showed broad resonances at about δ 64, 56 and −13 which varied little with temperature, the first two corresponding to unligated boron centres in **9** and **2**,[4] and the latter to the PEt_3-ligated borons in **9** and **10**. For the solution with 1.5 equivalents of PEt_3 the signal at δ −13 was more intense. The ^{31}P-{^{1}H} spectra for the solution with 1.5 equivalents of PEt_3 showed a broad singlet at about δ −3 at room temperature which was resolved into two sharper singlets at δ 1.7 and 0.2 at 223 K these presumably corresponding to the two phosphorus environments in **9** and **10**.

The situation for the interaction between compound **2** and PEt_3 is thus broadly similar to that between **2** and mpy in that all exchange processes would seem to occur at similar rates but differs in that the rates are somewhat slower in the case of PEt_3. As with the spectra for the mpy adducts, we have not sought to do a detailed analysis in order to calculate precise rate constants as there were problems with compound precipitation at the lower temperatures and we cannot therefore be certain as to how much material was actually in solution.

In summarising all of the solution-state results described above it is clear that for compound **2** and mpy both inter- and intra-molecular exchange is fast and that all such processes happen at similar rates at room temperature. It is not possible, however, to comment in any detail on the relative rates of these various processes since at any one temperature no process is apparently frozen out preferentially. In the case of **1** and mpy the intermolecular exchange involving the bis adduct **4** is considerably slower than inter- and intra-molecular exchange involving **3** for reasons which are not clear at present. With **2** and PEt_3 the situation is more similar to that of **2** and mpy except that all rates are apparently considerably slower. The fact

Table 2 Crystallographic data for compounds **5–9**

	5	**6**	**7**	**8**	**9**
Formula	$C_{18}H_{15}B_2NS_4$	$C_{24}H_{22}B_2N_2S_4\cdot 2C_4H_8O$	$C_{20}H_{19}B_2PS_4$	$C_{28}H_{30}B_2P_2S_4$	$C_{18}H_{23}B_2PS_4$
M	395.2	632.5	440.2	578.3	420.2
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$Pna2_1$	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
a/Å	15.6471(13)	9.1824(10)	23.037(3)	15.249(2)	7.4848(7)
b/Å	10.2712(9)	20.337(2)	7.7451(9)	6.6329(9)	10.5491(10)
c/Å	11.3880(10)	9.1929(10)	11.7344(14)	27.556(4)	14.2250(14)
α/°					78.574(2)
β/°		112.613(2)	102.310(3)	94.925(3)	77.849(2)
γ/°					72.686(2)
U/Å^3	1830.2(3)	1584.7(3)	2045.6(4)	2777.0(6)	1037.2(2)
Z	4	2	4	4	2
D_c/g cm^{-3}	1.434	1.326	1.429	1.383	1.345
μ/mm^{-1}	0.52	0.33	0.55	0.48	0.54
F(000)	816	668	912	1208	440
Crystal size/mm	0.32 × 0.28 × 0.10	0.30 × 0.20 × 0.06	0.42 × 0.16 × 0.02	0.46 × 0.40 × 0.26	0.30 × 0.12 × 0.10
θ_{max}/°	26.4	25.3	25.9	25.5	25.5
Maximum hkl indices	18, 12, 14	10, 23, 10	28, 9, 14	18, 8, 32	8, 12, 16
Reflections measured	9405	6637	8713	5731	8918
Unique reflections	3498	2603	3523	2312	3423
R_{int}	0.0527	0.0493	0.0541	0.0345	0.0387
Weighting parameters a, b	0, 4.0687	0.0141, 5.2286	0.0182, 2.6895	0.0222, 4.7693	0.0251, 0.7595
No. refined parameters	228	190	247	165	230
$wR2$ (all data)	0.1050	0.1427	0.0961	0.0757	0.0753
$R1$ ('observed' data)	0.0408 (3448)	0.0630 (2310)	0.0464 (2828)	0.0320 (2209)	0.0291 (3103)
Goodness of fit	1.218	1.208	1.143	1.140	1.056
Maximum, minimum electron density/e Å^{-3}	0.276, −0.271	0.858, −0.342	0.314, −0.267	0.290, −0.295	0.346, −0.256



Scheme 2

that intermolecular exchange in this case is slow may reflect the fact that the B–P bonds are less labile than the B–N bonds, but with regard to intramolecular exchange in either **5** or **9** we note that the intermediate or transition state in the case of **5** (**A** in Scheme 2) is formally isoelectronic with the so-called phenonium ion **B** (Scheme 2).[12] The aromatic nature of mpy may therefore be important in stabilising the exchange transition state for **5**, a factor which is not possible in the case of PEt_3. A diagram illustrating the interaction between the filled σ- and π-type orbitals for the mpy group and the vacant π and π* orbitals of the diborane(4) unit is shown in **C** in Scheme 2.

Finally, we note that compound **1** shows no evidence of binding phosphines inasmuch as a ^{1}H NMR spectrum of a solution of it containing a large excess of PEt_3 resulted in no upfield shift of the catecholate resonances characteristic of coordination to the boron centre. Compound **1** does, however, appear to bind dmf (dimethylformamide) as evidenced by a 0.6 ppm upfield shift of the catecholate resonances in solutions where dmf is present, but the pinacolate compound $B_2(OCMe_2CMe_2O)_2$ **11** shows no evidence of binding dmf even when present as a 50 fold excess. On this basis we would rank the order of Lewis acidity of the diborane(4) compounds **2** > **1** > **11** which is undoubtedly important in understanding certain aspects of their reactivity.

Experimental

General procedures

All reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were distilled from appropriate drying agents immediately prior to use (sodium–benzophenone for Et_2O and thf, CaH_2 for CH_2Cl_2 and sodium for hexanes). Microanalytical data were obtained at the University of Newcastle. The NMR spectra were recorded on JEOL GX 270, GX 400 and Bruker AMX 500 spectrometers and referenced to $SiMe_4$, 85% H_3PO_4 and $BF_3\cdot Et_2O$ for ^{1}H, ^{31}P and ^{11}B respectively. Compounds **1** and **2** were prepared as described in ref. 4. All other reagents were obtained commercially and used as received although mpy was dried over sieves or distilled over KOH prior to use.

Preparations

Preparative details for compounds **3** and **4** are described in ref. 7.

$B_2(1,2\text{-}S_2C_6H_4)_2(mpy)$ 5. A sample of mpy (4.2×10^{-3} cm^3, 0.043 mmol) was added to a stirred, colourless solution of compound **2** (0.013 g, 0.043 mmol) in thf (1.0 cm^3) at room temperature. After stirring for a few minutes, hexanes (≈6 cm^3) were added as an overlayer and solvent diffusion over 24 h at −30 °C afforded colourless crystals comprising mostly **5** but containing some **6**. Satisfactory analytical data were not obtained since the solid product was a mixture of **5** and **6**. A precise yield is not quoted for the same reason.

$B_2(1,2\text{-}S_2C_6H_4)_2(mpy)_2$ 6. 2.0 Equivalents of mpy (6.4×10^{-3} cm^3, 0.066 mmol) were added to a stirred, colourless solution of compound **2** (0.010 g, 0.033 mmol) in thf (4.0 cm^3) resulting in a pale yellow solution. After stirring for a few minutes, hexanes (≈6 cm^3) were added as an overlayer and solvent

diffusion over 24 h at −30 °C afforded pale yellow crystals comprising mostly **6** but containing some **5**. Results for analysis and yield are not quoted for the reasons stated above.

$B_2(1,2\text{-}S_2C_6H_4)_2(PMe_2Ph)$ 7. A sample of PMe_2Ph (0.02 cm^3, 0.146 mmol) was added to a stirred solution of compound **2** (0.044 g, 0.146 mmol) in CH_2Cl_2 (10 cm^3) at room temperature. Cooling to −30 °C for 72 h afforded a crop of colourless crystals which analysed correctly for **7** (0.032 g, 50%) (Found: C, 54.35; H, 4.10. $C_{20}H_{19}B_2PS_4$ requires C, 54.55; H, 4.35%).

$B_2(1,2\text{-}S_2C_6H_4)_2(PMe_2Ph)_2$ 8. 2.0 Equivalents of PMe_2Ph (0.03 cm^3, 0.198 mmol) were added to a stirred solution of compound **2** (0.030 g, 0.099 mmol) in CH_2Cl_2 (4.0 cm^3) at room temperature which afforded a fine white precipitate. This was dissolved by adding thf (≈2 cm^3). On cooling to 5 °C for 24 h a small crop of colourless crystals was obtained which analysed correctly for **8** (Found: C, 58.65; H, 4.90. $C_{28}H_{30}B_2P_2S_4$ requires C, 58.15; H, 5.25%).

$B_2(1,2\text{-}S_2C_6H_4)_2(PEt_3)$ 9. Compound **2** (0.044 g, 0.146 mmol) was dissolved in CH_2Cl_2 (4.0 cm^3) at room temperature and the solution stirred. 1.0 Equivalent of PEt_3 (0.02 cm^3, 0.146 mmol) was then added and the reaction mixture was stirred for 0.5 h. After this time, hexanes (≈6 cm^3) were added as an overlayer and solvent diffusion over 24 h at −30 °C afforded colourless crystals of **9**. Some crystalline **2** was also present.

The NMR spectroscopic data for complexes **3**–**6** and **9** are given in the text.

X-Ray crystallography

Crystallographic data for all structures are presented in Table 2. Data were measured at 160 K on a Siemens SMART CCD area-detector diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 73$ Å). Cell parameters were refined in each case from the observed ω-scan angles for several thousand strong reflections selected from the complete data set. Intensities were integrated with three-dimensional profile fitting from series of 0.3° ω-scan frames. Intensity decay (assessed by repeating the initial 50 frames at the end of data collection and analysing the common reflections) and absorption effects were negligible. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 for all unique reflections; the weighting scheme was $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (2F_c + F_o)/3$. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included with a riding model for their coordinates and isotropic displacement parameters. Extinction effects were negligible for three of the structures, and small corrections were applied for the other two, such that F_c was multiplied by $(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)^{\frac{1}{4}}$, x being a refined isotropic parameter. Residuals were defined as $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all data, conventional $R = ||F_o| - |F_c||/\Sigma|F_o|$ for 'observed' reflections with $F_o^2 > 6\sigma(F_o^2)$; the goodness of fit S was calculated on F^2. Programs: Siemens SMART (control) and SAINT (integration) diffractometer software, SHELXTL[13] and local programs.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/366.

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