Selective Ir-catalysed borylation of polycyclic aromatic hydrocarbons: structures of naphthalene-2,6-bis(boronate), pyrene-2,7-bis(boronate) and perylene-2,5,8,11-tetra(boronate) esters

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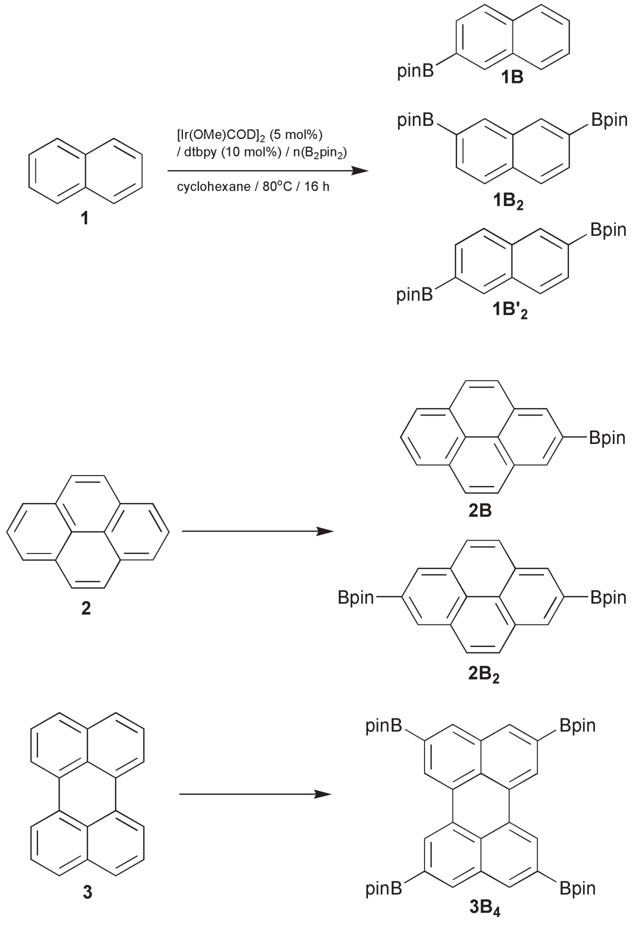
The selectivity of the iridium boryl complex-catalysed reaction of pyrene and perylene with $B_2(pin)_2$ (pin = $OCMe_2CMe_2O$) has been employed in the synthesis of D_{2h}-symmetry pyrene-2,7-$(Bpin)_2$ and D_{4h}-symmetry perylene-2,5,8,11-$(Bpin)_4$ providing direct borylation of positions which are otherwise difficult to derivatise.

A number of rhodium[1–4] and more active iridium[5–11] catalyst systems for the direct borylation of C–H bonds in aromatics have been developed in recent years following the observation of aryl boronates as sub-stoichiometric by-products during the synthesis of the first transition metal tris(boryl) [(η^6-Arene)Ir(Bcat)$_3$] complexes.[12]

The Ir-based catalyst, prepared *in situ via* reaction of $[Ir(OMe)COD]_2$ with 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy), has been shown to be particularly efficient and selective in the catalysed borylation of arenes.[9,10] This catalyst has also been used in the borylation of compounds such as azulene and ferrocene.[13,14] The selectivity observed is likely due to the very crowded nature of the five-coordinate *fac*-tris(boryl) species, $[Ir(bpy)(Bpin)_3]$, which is proposed as the key intermediate performing the rate-determining C–H activation step.[15] The avoidance of borylation of C–H bonds *ortho* to any substituent or ring junction when alternative sites are available led us to examine the catalysed reaction of naphthalene, pyrene and perylene with B_2pin_2, as the resulting aryl boronate esters are of considerable interest in the synthesis of conjugated systems and optical materials. We speculated that pyrene would be preferentially borylated at the 2 and then 7 positions, and that perylene would react at the 2,5,8 and 11 positions, just those which are normally most difficult to substitute.

Electrophilic substitution of naphthalene can be either kinetically or thermodynamically controlled to occur at the 1- or 2-positions respectively.[16] Electrophilic substitution of pyrene and perylene is possible, but some product isomers are not formed. It is possible to produce 2-substituted or 2,7-disubstituted pyrenes by the reduction of pyrene to 4,5,9,10-tetrahydropyrene followed by electrophilic substitution and subsequent rearomatisation;[17] however, this is a multi-step, low yielding process. This method has previously been used in the synthesis of 2,7-$(Bpin)_2$-4,5,9,10-tetrahydro-pyrene.[18] Of the relatively few 2-substituted pyrenes present in the Cambridge Structural Database (CSD, November 2004 release),[19] none contain boron.



Scheme 1 Borylation of polycyclic aromatic compounds.

Reaction of perylene with a variety of electrophiles leads to substitutions occurring at the 1,3,4,9 and 10 positions.[20] It requires partial hydrogenation of perylene to obtain reaction at the 2 position.[21] An indication of the rarity of 2-substitution is the fact that the only structurally characterised 2-substituted perylene derivative is 1,2:7,8-bis(tetrahydrofuro)perylene[22] (CSD ref. code WODJAA),[19] and there are no examples of 2,5,8,11-tetra-substituted perylenes in the CSD.

Reaction of naphthalene (3.9 mmol), B_2pin_2 (4.3 mmol), $[Ir(OMe)COD]_2$ (5 mol%) and dtbpy (10 mol%) in cyclohexane (15 mL) under N_2 at 80 °C for 16 h gave a dark red solution. Removal of the volatiles and subsequent column chromatography on silica gel, eluting with hexane:CH_2Cl_2, 1:1, resulted in four colourless compounds, **1**, **1B**, **$1B_2$** and **$1B'_2$** in 29%, 49%, 10% and 12% yields respectively (Table 1).

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The borylation of naphthalene giving **1B** was found, by ^{1}H COSY NMR spectroscopy, to occur exclusively at the 2-position, as expected, *i.e.* the position *not* adjacent to the ring junctions. However, the second borylation could take place at either of two chemically inequivalent positions, namely 6 or 7, both being *meta* with respect to the ring junctions. Indeed, the existence of the two isomeric, diborated species (**$1B_2$** and **$1B'_2$**), in almost equal proportions, was determined *via* ^{1}H NOESY NMR spectroscopy (Fig. 1). The peak at 8.58 ppm corresponds to the 2 protons of **$1B'_2$** situated at the 1 and 5 positions and *ortho* to a Bpin. This correlates with the signal at 7.68 ppm, assigned to the protons at the 4 and 8 positions, which shows a second correlation to the protons at positions 3 and 7. Whilst the signals relating to the protons at positions 3 and 6 of **$1B_2$** show correlation with those at positions 4 and 5, no correlation is observed to the protons situated at the 1 and 8 positions. The total yield of compounds **$1B_2$** and **$1B'_2$** can be increased to 93% by the use of 2.2 molar equivalents of B_2pin_2, and crystals of **$1B'_2$** which were suitable for X-ray diffraction studies† (Fig. 2) were obtained by evaporation of CH_2Cl_2 from a CH_2Cl_2/hexane mixture.

Reaction of pyrene with 1.1 molar equiv. of B_2pin_2 under the same catalytic conditions as for naphthalene produced **2B** and **$2B_2$**‡ in 68% and 6% yields respectively after purification by column chromatography (hexane:CH_2Cl_2, 1:1) with unreacted pyrene also being recovered. The exclusive synthesis of **$2B_2$** (97%) was achieved using excess boron (2.2 molar equiv. of B_2pin_2). To obtain analytically pure material, the reaction mixture was passed through a silica pad with CH_2Cl_2, the solvents were removed on a rotary evaporator and the volatiles were removed *in vacuo* (150 °C @ 5.4 × 10^{-5} torr). ^{1}H COSY NMR spectroscopy and a single crystal X-ray diffraction study† (Fig. 3) proved that the 2- and 7-positions of pyrene are the sites of borylation. It should also be noted that trace amounts of a tri-borylated pyrene were observed by EI/MS when 2.2 molar equivalents of B_2pin_2 were used after extended reaction times of 3–4 days.

Table 1 Borylation of polycyclic aromatic compounds

Entry	Polycyclic aromatic	Mol equiv of B_2pin_2	Product	% Yield[a]
1	1	1.1	1B + ($1B_2$/$1B'_2$)[b]	49:22[c]
2	1	2.2	$1B_2$/$1B'_2$[b]	93
3	2	1.1	2B + $2B_2$	68:6[d]
4	2	2.2	$2B_2$	97
5	3	4.4	$3B_4$	83

[a] Isolated yields based on polycyclic aromatic substrates. [b] See text. [c] 29% unreacted **1** recovered. [d] 26% unreacted **2** recovered.

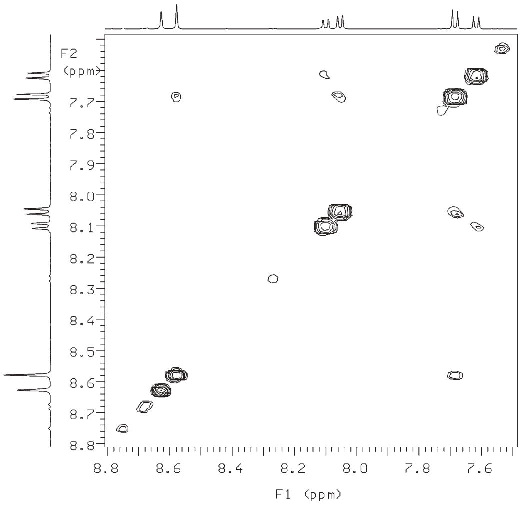

Fig. 1 ^{1}H NOESY spectrum of the mixture of **$1B_2$** and **$1B'_2$** produced by catalysed borylation of naphthalene.

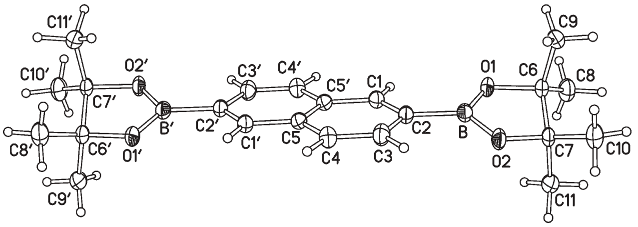

Fig. 2 Molecular structure of **$1B'_2$** with thermal ellipsoids shown at 50% probability level and the disorder omitted for clarity. Primed atoms are generated by the inversion centre. B–C(2) distance 1.560(2) Å, angle C(1)C(2)C(3) 118.6(1)°.

The reaction of perylene with 2.2 molar equiv. of B_2pin_2, $[Ir(OMe)COD]_2$ (5 mol %) and dtbpy (10 mol %) in cyclohexane for 16 h yields $C_{20}H_{11}(Bpin)$, three $C_{20}H_{10}(Bpin)_2$ isomers, one isomer of $C_{20}H_9(Bpin)_3$ and one isomer of $C_{20}H_8(Bpin)_4$ **$3B_4$**‡. The products with different degrees of borylation were easily separated by HPLC; however, as yet it has not been possible to separate the three isomers of $C_{20}H_{10}(Bpin)_2$ from one another.

To produce **$3B_4$** as the major product (83%), perylene (1.98 mmol) was reacted with 4.4 molar equivalents of B_2pin_2, $[Ir(OMe)COD]_2$ (5 mol %) and dtbpy (5 mol %) in cyclohexane for 16 h. Purification of the solid by Kugelrohr distillation (300 °C @ 4.2 × 10^{-5} torr) and recrystallisation by layering Et_2O over CH_2Cl_2 gave orange prismatic crystals suitable for X-ray diffraction† (Fig. 4).

As indicated, the positions of borylation in compounds **$1B'_2$**, **$2B_2$** and **$3B_4$** were confirmed by single-crystal X-ray diffraction (Figs. 2–4). Molecule **$1B'_2$** lies on a crystallographic inversion centre; the boryl group is disordered between two orientations, A and B, in an 85:15 ratio, except for the B, C(8) and C(10) atoms, whose positions coincide (Fig. 5). Molecule **$2B_2$** has no crystallographic symmetry, and the boryl substituent at C(20) has both O atoms and methyl groups $C(1)H_3$ and $C(3)H_3$ disordered equally between two positions, A and B (Fig. 5). The asymmetric unit of **$3B_4$** is comprised of half of the crystallographically centrosymmetric molecule and one CH_2Cl_2 molecule of crystallisation.

The borolane ring always adopts a somewhat asymmetric twist conformation, the carbon atoms being displaced to opposite sides of the BO_2 plane, with displacements varying from 0.14 to 0.32 Å.

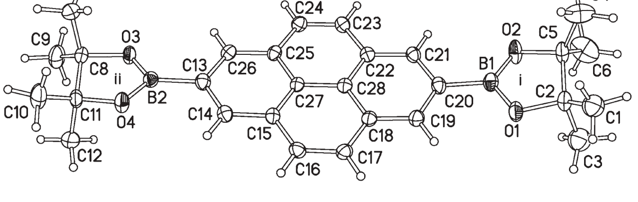

Fig. 3 Molecular structure of **$2B_2$** (not showing the disorder). Bond distances B(1)–C(20) and B(2)–C(13) 1.558(4) Å, angles C(14)C(13)C(26) 118.6(2), C(19)C(20)C(21) 118.8(2)°.

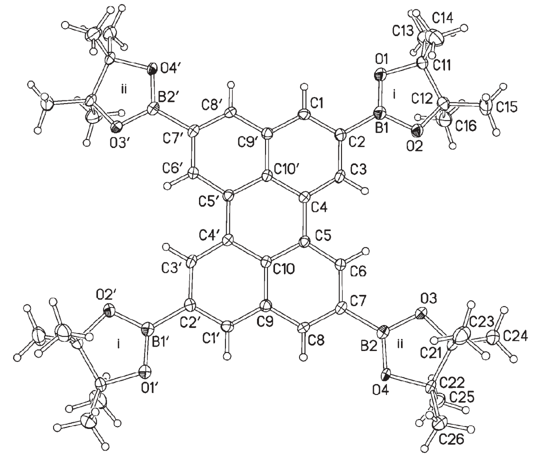

Fig. 4 Molecular structure of $\mathbf{3B_4}$. Primed atoms are generated by the inversion centre. The unit cell also contains two molecules of CH_2Cl_2 per perylene, which have been omitted for clarity. Selected bond distances (Å): B(1)–C(2) 1.555(3), B(2)–C(7) 1.558(3), angles C(1)C(2)C(3) and C(6)C(7)C(8) 118.1(2)°.

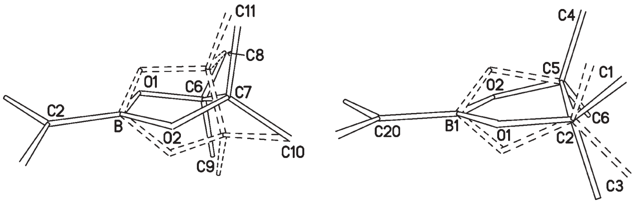

Fig. 5 View of the disorder present in the Bpin units of $\mathbf{1B'_2}$ (left) and ring *i* of $\mathbf{2B_2}$ (right). Positions A drawn solid, B dashed.

The dihedral angle between the BO_2 plane and the aromatic system planes is usually small: 14.7 (A) and 19.2° (B) in $\mathbf{1B'_2}$; 11.5 (i, A), 31.8 (i, B) and 12.5° (ii) in $\mathbf{2B_2}$; 3.5 (i) and 10.9° (ii) in $\mathbf{3B_4}$. Whilst the B atoms in $\mathbf{1B'_2}$, B(1) in $\mathbf{2B_2}$ and in $\mathbf{3B_4}$ lie close to the aromatic planes, B(2) in $\mathbf{2B_2}$ and $\mathbf{3B_4}$ deviate from these planes by 0.41 and 0.25 Å, respectively, with the adjacent C(19)C(20)C(21) and C(6)C(7)C(8) moieties tilting in the same direction by 4.2 and 2.4°.

In summary, we have utilised the selectivity of the Ir-catalysed aromatic borylation process to produce, exclusively, novel pyrene-bis(boronate) and perylene-tetra(boronate) esters which will be of considerable utility in Suzuki–Miyaura and other cross-coupling reactions to produce new conjugated systems and optical materials. Applications of this chemistry are underway in our laboratory.

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Notes and references

† X-ray diffraction experiments: Bruker SMART 6000 CCD area detector, Mo–K_α radiation (λ = 0.71073 Å). Computations: SHELXTL software v. 6.12 (Bruker AXS, Madison, WI, USA, 2001). *Crystal data:* for $\mathbf{1B'_2}$: $C_{22}H_{30}B_2O_4$, $M = 380.08$, $T = 120$ K, monoclinic, space group $P2_1/n$ (No. 14), $a = 6.501$ (1), $b = 16.249$ (2), $c = 10.146$ (2) Å, $\beta = 99.70$ (1)°, $U = 1056.4$ (3) Å^3, $Z = 2$, $\mu = 0.08$ mm^{-1}, 14776 reflections with $2\theta \leqslant 60°$, 3082 unique, $R_{int} = 0.061$, $R = 0.048$ [2138 data with $F^2 \geqslant 2\sigma(F^2)$], $wR(F^2) = 0.145$ (all data). CCDC-263078. For $\mathbf{2B_2}$: $C_{28}H_{32}B_2O_4$, $M = 454.16$, T =120 K, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 6.7931$ (5), $b = 17.790$ (2), $c = 20.368$ (2) Å, $U = 2461.5$ (4) Å^3, $Z = 4$, $\mu = 0.08$ mm^{-1}, 23207 reflections with $2\theta \leqslant 61°$, 4237 unique, $R_{int} = 0.091$, $R = 0.051$ [2697 data with $F^2 \geqslant 2\sigma(F^2)$], $wR(F^2) = 0.114$ (all data). CCDC-263079. For $\mathbf{3B_4}$: $C_{44}H_{56}B_4O_8{\cdot}2CH_2Cl_2$, $M = 925.98$, $T = 120$ K, triclinic, space group *P-1* (No. 2), $a = 6.6669$ (5), $b = 12.519$ (1), $c = 14.791$ (1) Å, $\alpha = 103.68$ (1), $\beta = 99.11$ (1), $\gamma = 96.50$ (1)°, $U = 1169.7$ (2) Å^3, $Z = 1$, $\mu = 0.31$ mm^{-1}, 11294 reflections with $2\theta \leqslant 55°$, 5352 unique, $R_{int} = 0.056$, $R = 0.048$ [3459 data with $F^2 \geqslant 2\sigma(F^2)$], $wR(F^2) = 0.125$ (all data). CCDC-263080. See http://www.rsc.org/suppdata/cc/b5/b501778e/ for crystallographic data in .cif or other electronic format.

‡ Selected characterisation data for $\mathbf{2B_2}$: ^{1}H NMR (400 MHz, C_6D_6) δ 8.93 (s, 4H), 7.84 (s, 4H), 1.21 (s, 24H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2) δ 130.3, 130.0, 126.8, 125.3, 83.4, 24.0, C attached to B not observed; $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6) δ 32.1; Anal. Found: C, 73.78; H, 7.22%. $C_{28}H_{32}BO_4$ requires: C, 74.05; H, 7.10; EI+ -MS [*m*/*z*]: 454 $[M]^+$, 354 $[M - C_6H_{12}O]^+$, 254 $[M - (C_6H_{12}O)_2]^+$, 228 $[M - C_{12}H_{21}BO_3]^+$. For $\mathbf{3B_4}$: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.56 (s, 4H), 8.23 (s, 4H), 1.47 (s, 24H). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2) δ 29.4; Anal. Found: C, 64.56; H, 7.09%. $C_{44}H_{56}B_4O_8.CH_2Cl_2$ requires: C, 64.26; H, 6.95; EI+ -MS [*m*/*z*]: 756 $[M]^+$, 656 $[M - C_6H_{12}O]^+$, 630 $[M - Bpin]^+$, 530 $[M - Bpin(C_6H_{12}O)]^+$, 504 $[M - (Bpin)_2]^+$, 378 $[M - (Bpin)_3]^+$.

1 H. Chen, S. Schlect, T. C. Semple and J. F. Hartwig, *Science*, 2000, **287**, 1995.
2 J.-Y. Cho, C. N. Iverson and M. R. Smith, III, *J. Am. Chem. Soc.*, 2000, **122**, 12868.
3 M. K. Tse, J.-Y. Cho and M. R. Smith, III, *Org. Lett.*, 2001, **3**, 2831.
4 S. Shimada, A. S. Batsanov, J. A. K. Howard and T. B. Marder, *Angew. Chem. Int. Ed.*, 2001, **40**, 2168; W. H. Lam, K. C. Lam, Z. Lin, S. Shimada, R. N. Perutz and T. B. Marder, *Dalton Trans.*, 2004, 1556.
5 For an early Ir system, see: C. N. Iverson and M. R. Smith, III, *J. Am. Chem. Soc.*, 1999, **121**, 7696.
6 J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, Jr. and M. R. Smith, III, *Science*, 2002, **295**, 305.
7 T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 390.
8 J. Takagi, K. Sato, J. F. Hartwig, T. Ishiyama and N. Miyaura, *Tetrahedron Lett.*, 2002, **43**, 5649.
9 T. Ishiyama, J. Takagi, J. F. Hartwig and N. Miyaura, *Angew. Chem. Int. Ed.*, 2002, **41**, 3056.
10 T. Ishiyama, Y. Nabuta, J. F. Hartwig and N. Miyaura, *Chem. Commun.*, 2003, 2924.
11 For a review on C–H borylation, see: T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2003, **680**, 3.
12 P. Nguyen, H. P. Blom, S. A. Westcott, N. J. Taylor and T. B. Marder, *J. Am. Chem. Soc.*, 1993, **115**, 9329.
13 K. Kurotobi, M. Miyauchi, K. Takakura, T. Murafuji and Y. Sugihara, *Eur. J. Org. Chem.*, 2003, 3663.
14 A. Datta, A. Köllhofer and H. Plenio, *Chem. Commun.*, 2004, 1508.
15 H. Tamura, H. Yamazaki, H. Sato and S. Sakaki, *J. Am. Chem. Soc.*, 2003, **125**, 16114.
16 L. D. Field, S. Sternhell and H. V. Wilton, *J. Chem. Ed.*, 1999, **76**, 1246.
17 H. Lee and R. G. Harvey, *J. Org. Chem.*, 1986, **51**, 2847; D. M. Connor, S. D. Allen, D. M. Collard, C. L. Liotta and D. A. Schiraldi, *J. Org. Chem.*, 1999, **64**, 6888; C. E. Godinez, G. Zepeda and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 2002, **124**, 4701.
18 X. Zheng, M. E. Mulcahy, D. Horinek, F. Galeotti, T. F. Magnera and J. Michl, *J. Am. Chem. Soc.*, 2004, **126**, 4540.
19 F. H. Allen and R. Taylor, *New J. Chem.*, 2004, **33**, 463.
20 H. Cerfontain, A. Koeberg-Telder and U. Lerch, *Recl. Trav. Chim. Pays-Bas.*, 1993, **112**, 584.
21 R. Lapouyade, J. Pereyre and P. Garrigues, *C. R. Acad. Sci., Ser. II*, 1986, **303**, 903.
22 Y. Yamaguchi, S. Kobayashi, T. Wakamiya, Y. Matsubara and Z.-I. Yoshida, *J. Am. Chem. Soc.*, 2000, **122**, 7404.