HYDROBORATION OF 1,1′-BI(CYCLOPENT-1-ENE) AND 3,3′-BIINDENE: EXPERIMENTAL AND THEORETICAL STUDY

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Hydroboration of bi(cyclopent-1-ene) (**1**) or 3,3′-biindene (**2**) with borane, thexylborane or (–)-isopinocampheylborane afforded, regardless of reaction conditions, *meso*-isomers of polycyclic 1,4-diols **3a**, **4a** as the main products. No reaction was observed with 9-BBN. The structure of the major product **4a**, as well as of the minor racemic product **4b** was assigned based on ¹H NMR spectra of the corresponding Mosher's diesters **5a–5c**. Finally, the stereochemistry of the product **4a** was confirmed by a single-crystal X-ray analysis of the corresponding dimesylate **6**. To elucidate preferential formation of the *meso*-isomers, complexes of monohydroborated intermediate with borane were studied theoretically by DFT methods.

Keywords: Dienes; Asymmetric hydroboration; Boranes; Chiral diols; Mosher's esters; Absolute configuration; DFT calculations; X-ray diffraction.

Chiral diols rank among the main groups of compounds forming a chiral pool in organic synthesis. Although they can be used directly as ligands in many catalytic reactions[1], their key application area consists in transformations to other classes of chiral substances. Among them, chiral diphosphines are employed extensively as chiral ligands in enantioselective catalytic reactions and attract thus the attention of both academic and industrial chemists[2,3]. The aims to achieve still higher yields and enantioselectivities of catalytic processes result in continuous search for new ligands.

Quite recently, bi(cyclopentane) based ligands were synthesized[4] and employed in various catalytic reactions, e.g. asymmetric hydrogenation[4–9], cyclocarbonylation[10], or cycloisomerization[11]. The key precursor, chiral 1,1′-bi(cyclopentane)-2,2′-diol (**3**) was synthesized[4] by enantioselective hydroboration of bi(cyclopent-1-ene) (**1**) with isopinocampheylborane

(pinan-3-ylborane)[12]. Unfortunately, neither experimental details nor yields were published. In the corresponding patent[13], which includes the detailed description of the hydroboration experiment, only 18% yield of chiral diol **3b** is claimed, the *meso*-diol **3a** being the main reaction product. The recently published improved procedure included the preparation of *rac*-diol **3b** followed by enzymatic resolution[14]. Again, no experimental details of the preparation of *rac*-diol **3b** were included. The original achiral version of hydroboration of diene **1** with the borane–THF complex was probably employed[15], which afforded the target diol **3b** in a 15% yield together with the major product, *meso*-diol **3a**.

In contrast to the hydroboration of diene **1**, enantioselective hydroboration of 3,3′-biindene (**2**) with isopinocampheylborane was reported to give the corresponding chiral 1,1′-biindane-2,2′-diol (**4**) in a good yield[16]. Chiral diol **4** was employed in enantioselective alkylation of aldehydes[16] and enantioselective reduction of ketones[17].

In the course of our search for novel chiral boranes and silanes, we envisaged chiral diols **3** and **4** as useful precursors for their syntheses. Due to the absence of full experimental details in the case of diene **1** and an unknown composition of the crude reaction mixture in the case of diene **2** we decided to start a short experimental and theoretical study of hydroboration of this class of dienes.

EXPERIMENTAL

Temperature data were uncorrected. NMR spectra were recorded with a Varian MercuryPlus spectrometer, ^{1}H NMR spectra at 299.97 MHz and ^{13}C NMR spectra at 75.43 MHz using residual deuterated solvent signals as the internal standards, ^{19}F NMR spectra at 282.23 MHz using CCl_3F as the internal standard. Chemical shifts are given in ppm, coupling constants in Hz. In some cases, gCOSY and gHSQC experiments were accomplished to allow full assignment of signals. FTIR spectra were recorded with an FT-IR Nicolet 740 instrument in $CHCl_3$. Elemental analyses were performed with an Elementar Vario EI III instrument. Mass spectra were measured with an Autospec Ultima (Micromass) instrument.

All reactions were performed in dry inert atmosphere in oven-dried apparatuses. Cyclopentanone (99%), indene (technical grade, 90%), Cu(II) chloride (97%), butyllithium (2.5 M solution in hexanes), borane–THF complex (1 M in THF), 2,3-dimethylbut-2-ene (1 M in THF), bis[(–)-isopinocampheylborane]–TMEDA complex ((*R*)-Alpine–Boramine™), 9-BBN (9-borabicyclo[3.3.1]nonane; 0.5 M in THF), mesyl chloride and (+)-(*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride (**7**; chloride of Mosher's acid, 99%, 99.5% ee) were purchased from Aldrich. Diethyl ether and THF were dried over sodium benzophenone ketyl and distilled prior to use. Cupric chloride was dried at 80 °C in vacuo for 12 h, followed by cooling in dry inert atmosphere.

1,1′-Bicyclopentane-1,1′-diol was prepared by reductive coupling of cyclopentanone with aluminium, catalyzed with mercuric chloride according to ref.[18] in a 66% yield. Its dehydra-

tion with acetic anhydride according to ref.[19] afforded bi(cyclopent-1-ene) (**1**) in a 70% yield. 1,1′-Biindene was prepared by oxidative coupling with butyllithium and Cu(II) chloride in an 85% yield as a 60:40 mixture of *meso-* and *rac-*diastereoisomers[20]. Thexylborane [(1,1,2-trimethylpropyl)borane] was prepared[21] prior to use by mixing equivalent amounts of BH₃–THF complex solution and 2,3-dimethylbut-2-ene solution at 0 °C. (–)-Isopinocampheylborane was prepared prior to use by mixing bis[(–)-isopinocampheylborane]–TMEDA complex, dissolved in THF, with boron trifluoride etherate, followed by removal of insoluble salts by filtration under inert gas[12].

3,3′-Biindene (**2**)

A 250-ml flask equipped with a magnetic stirbar was charged with 1,1′-biindene (7.00 g, 30.4 mmol, 60:40 mixture of *meso-* and *rac-*diastereoisomers) and dichloromethane (30 ml). To the stirred mixture was dropwise added triethylamine (12.3 g, 16.9 ml, 121 mmol) at room temperature and the mixture was stirred for 4 h. The solvent and triethylamine were removed on vacuum rotary evaporator. The target diene **2** (6.4 g, 91%, light yellow crystals, m.p. 126–128 °C, ref.[20] 131 °C) was obtained by recrystallization from methanol. The product gave NMR spectra identical with the published data[20].

Hydroboration of Dienes **1**, **2**. General Procedure

A hydroboration reagent was dissolved in THF, cooled to the desired temperature and diene **1** or **2**, dissolved in THF, was added dropwise while stirring. The stirring was continued at the same temperature. The mixture was quenched by a dropwise addition of methanol (2 ml/mmol of diene) and allowed to warm to room temperature. Aqueous H_2O_2 (30%, 4 ml/mmol of diene) and 3 M NaOH solution (4 ml/mmol of diene) were added dropwise while stirred and the mixture was heated to 55 °C for 1 h. After cooling, the organic layer was separated, the aqueous layer was extracted 3 times with ethyl acetate (diene **1**) or diethyl ether (diene **2**). Combined organic layers were evaporated on vacuum rotary evaporator, redissolved in the above solvent and extracted with water. The separated organic layer was dried with anhydrous $MgSO_4$. Final evaporation afforded crude product mixture, which was purified by column chromatography (silica, eluent dichloromethane/methanol 12:1 for diene **1**, dichloromethane/methanol 24:1 for diene **2**). As a rule, product of the oxidation of the hydroboration reagent (2,3-dimethylbutan-2-ol or pinan-3-ol) was eluted first, followed by minor *rac-*diastereoisomer (if obtained) **3b** or **4b**. The last compound eluted was major *meso-*diastereoisomer **3a** or **4a**.

Hydroboration of Bi(cyclopent-1-ene) (**1**) with Borane–THF Complex[15] (Run 1)

7.13 g (53.1 mmol) of diene **1** and 127.5 ml (127.5 mmol) of BH₃·THF solution afforded after 20-h reaction at room temperature and isolation *meso-*diastereoisomer (1R^*,1′S^*,2S^*,2′R^*)-1,1′-bi(cyclopentane)-2,2′-diol (**3a**; 3.71 g, 41.0%, white crystals, m.p. 142–145 °C, ref.[15] 145 °C) and *rac-*diastereoisomer (1R^*,1′R^*,2S^*,2′S^*)-1,1′-bi(cyclopentane)-2,2′-diol (**3b**; 0.79 g, 8.7%, white crystals, m.p. 90–105 °C, ref.[15] 109 °C). Diol **3a**: ¹H NMR[15]: 1.20–1.40 m, 2 H (CH**H**); 1.48–1.94 m, 12 H (CH₂, CH); 4.00 dt, 2 H, $^3J_{HH}$ = 6.9 (d), 4.8 (t) (C**H**OH); 4.96 bs, 2 H (OH). ¹³C NMR: 22.4 (CH₂**C**H₂CH₂); 28.8 (CH**C**H₂); 35.1 (CH(OH)**C**H₂); 50.9 (CH); 75.7 (**C**HOH). Diol **3b**: ¹H NMR[15,21]: 1.07–1.21 m, 2 H (CH**H**); 1.37–1.80 m, 10 H (CH₂, CH); 1.90–2.02 m (C**H**H); 3.79 q, $^3J_{HH}$ = 8.0 (C**H**OH); 4.96 bs, 2 H

(OH). HSQC 1.13, 2 H (CH**H**); 1.41, 2 H (C**H**); 1.50, 2 H (CH**H**); 1.57, 2 H (CH**H**); 1.68, 2 H (CH**H**); 1.75, 2 H (CH**H**); 1.97, 2 H (CH**H**); 3.79 (C**H**OH). ^{13}C NMR[21]: 20.5 (CH$_2$**C**H$_2$CH$_2$); 29.3 (CH**C**H$_2$); 33.6 (CH(OH)**C**H$_2$); 52.2 (**C**H); 78.6 (**C**HOH).

Hydroboration of Bi(cyclopent-1-ene) (**1**) with Thexylborane (Run 2)

1.10 g (8.20 mmol) of diene **1**, 25 ml (25.0 mmol) of BH$_3$·THF and 25 ml (25.0 mmol) of 2,3-dimethylbut-2-ene afforded, after 14-h reaction at 0 °C and isolation, 558 mg (40.0%) of mixture of *meso*-diastereoisomer **3a** and *rac*-diastereoisomer **3b** in a 93:7 ratio (^{1}H NMR).

Hydroboration of Bi(cyclopent-1-ene) (**1**) with (–)-Isopinocampheylborane (Run 4)

448 mg (3.34 mmol) of diene **1**, 2.50 g (6.00 mmol) of bis[(–)-isopinocampheylborane]–TMEDA complex and 1.70 g (12.0 mmol) of BF$_3$·Et$_2$O afforded, after 24-h reaction at –25 °C and isolation, 337 mg (59.3%) of *meso*-diastereoisomer **3a**. No *rac*-diastereoisomer **3b** was isolated.

Hydroboration of Bi(cyclopent-1-ene) (**1**) with Equivalent of (–)-Isopinocampheylborane (Run 8)

268 mg (2.00 mmol) of diene **1**, 416 mg (1.00 mmol) of bis[(–)-isopinocampheylborane]–TMEDA complex and 284 mg (2.00 mmol) of BF$_3$·Et$_2$O afforded, after 18-h reaction at room temperature and isolation, 112 mg (32.9%) of the mixture of *meso*-diastereoisomer **3a** and *rac*-diastereoisomer **3b** in a 74:26 ratio (^{1}H NMR).

Hydroboration of Bi(cyclopent-1-ene) (**1**) with 9-BBN (Run 9)

After 20-h reaction of diene **1** (300 mg, 2.24 mmol) with 9-BBN (11.0 ml, 5.5 mmol) at room temperature, only starting compound **1** was isolated.

Hydroboration of 3,3′-Biindene (**2**) with Borane–THF Complex (Run 10)

1.15 g (5.00 mmol) of diene **2** and 12.0 ml (12.0 mmol) of BH$_3$·THF afforded after 20-h reaction at room temperature and isolation 1.221 g (91.8%) of a mixture of *meso*-diastereoisomer ($1R^*,1'S^*,2R^*,2'S^*$)-1,1′-biindane-2,2′-diol (**4a**) and *rac*-diastereoisomer ($1R^*,1'R^*,2R^*,2'R^*$)-1,1′-biindane-2,2′-diol (**4b**) in a 73:27 ratio. By repeated column chromatography, *meso*-diol **4a** (500 mg, 37.6%, R_F 0.24 in CH$_2$Cl$_2$/MeOH 16:1, light yellow crystals, m.p. 115–116 °C, ref.[16] 116 °C) and *rac*-diol **4b** (199 mg, 15.0%, R_F 0.28 in CH$_2$Cl$_2$/MeOH 16:1, light yellow crystals, m.p. 64–66 °C). Diol **4a**: ^{1}H NMR [16] (in ref.[16], the spectrum was erroneously assigned to *rac*-diastereoisomer **4b**): 1.92 bs, 2 H (OH); 2.83 dd, 2 H, $^2J_{HH}$ = 16.1, $^3J_{HH}$ = 5.3 (CH**H**); 3.19 dd, 2 H, $^2J_{HH}$ = 16.1, $^3J_{HH}$ = 7.0 (C**H**H); 3.61 d, 2 H, $^3J_{HH}$ = 4.4 (CH); 4.54 dt, 2 H, $^3J_{HH}$ = 7.0 (d), $^3J_{HH}$ = 5.3 (t) (CHOH); 6.88 d, 2 H, $^3J_{HH}$ = 7.7 (C$_{Ar}$H); 7.07–7.28 m, 6 H (C$_{Ar}$H). ^{13}C NMR: 41.3 (CH$_2$); 54.9 (CH); 75.9 (CHOH); 124.5 (C$_{Ar}$H); 124.9 (C$_{Ar}$H); 126.8 (C$_{Ar}$H); 127.2 (C$_{Ar}$H); 140.9 (C$_{Ar}$); 142.1 (C$_{Ar}$). Diol **4b**: ^{1}H NMR: 2.35 bs, 2 H (OH); 2.88 dd, 2 H, $^2J_{HH}$ = 16.5, $^3J_{HH}$ = 4.4 (CH**H**); 3.29 dd, 2 H, $^2J_{HH}$ = 16.5, $^3J_{HH}$ = 6.6 (C**H**H); 3.60 d, 2 H, $^3J_{HH}$ = 2.8 (CH); 4.32 ddd, 2 H, $^3J_{HH}$ = 6.6, $^3J_{HH}$ = 4.4, $^3J_{HH}$ = 2.8 (CHOH); 7.12 d, 2 H, $^3J_{HH}$ = 7.2 (C$_{Ar}$H); 7.20–7.34 m, 6 H (C$_{Ar}$H). ^{13}C NMR: 41.0 (CH$_2$); 55.5 (CH); 75.7 (CHOH); 125.0 (C$_{Ar}$H); 125.0 (C$_{Ar}$H); 126.5 (C$_{Ar}$H); 127.2 (C$_{Ar}$H); 140.6 (C$_{Ar}$); 142.0 (C$_{Ar}$). MS (EI), *m/z* (%): 266 [M, 3], 248 [(M – H$_2$O),

78], 230 [(M – 2 H$_2$O), 27], 134 [(M/2 + H), 89], 116 [(M/2 + H – H$_2$O), 100]. For C$_{18}$H$_{18}$O$_2$ (266.3) calculated: 81.17% C, 6.81% H; found: 80.54% C, 7.05% H.

Hydroboration of 3,3′-Biindene (2) with Thexylborane (Run 11)

2.31 g (10.0 mmol) of diene **2**, 30 ml (30.0 mmol) of BH$_3$·THF and 30 ml (30.0 mmol) of 2,3-dimethylbut-2-ene afforded, after 20-h reaction at room temperature and isolation, 2.96 g of crude product containing 2,3-dimethylbutan-2-ol, *meso*-diastereoisomer **4a** and *rac*-diastereoisomer **4b** (82:18 ratio, ^{1}H NMR). By second column chromatography and recrystallization, 1.36 g (50.9%) of pure crystalline diol **4a** was obtained.

Hydroboration of 3,3′-Biindene (2) with (–)-Isopinocampheylborane (Run 12)

1.15 g (5.00 mmol) of diene **2**, 3.12 g (7.5 mmol) of bis[(–)-isopinocampheylborane]–TMEDA complex and 1.90 ml (2.13 g, 15.0 mmol) of BF$_3$·Et$_2$O afforded, after 24-h reaction at room temperature and isolation, 3.107 g of crude product containing (^{1}H NMR) 68% of pinan-3-ol[23] and 32% of diols **4** (estimated yield 74%, **4a**:**4b** = 85:15). Separation of diols **4** from pinan-3-ol was tedious, required repeated column chromatography and furnished finally 242 mg (18.2%) of *meso*-diol **4a** and 73 mg (5.5%) of *rac*-diol **4b**. Diol **4b** showed no optical rotation and also its transformation to Mosher's diesters **5** confirmed its racemic structure (see below).

Hydroboration of 3,3′-Biindene (2) with 9-BBN (Run 13)

After 20-h reaction of diene **2** (200 mg, 0.87 mmol) with 9-BBN (4.5 ml, 2.3 mmol) at room temperature, only starting compound **2** was isolated.

Preparation of Esters of Mosher's Acid 5 from Diols 4. General Procedure[24]

To a stirred solution of diol **4** (13 mg, 50 µmol) in dry dichloromethane (1 ml), (+)-(*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride (**7**; 37 µl, 51 mg, 200 µmol) was syringed at room temperature. The mixture was cooled to 0 °C and pyridine (8 µl, 8 mg, 100 µmol) was added. The mixture was allowed to warm to room temperature and stirred for 5 h. To the crude mixture, diethyl ether (15 ml) and brine (15 ml) were added, organic layer was separated and washed successively with hydrochloric acid (5%, 15 ml), brine (15 ml), saturated solution of NaHCO$_3$ (15 ml) and brine (15 ml). Drying with anhydrous MgSO$_4$ and removal of solvents on vacuum rotary evaporator afforded the crude reaction mixture, which was analyzed by ^{1}H NMR and separated to individual diesters **5** and monoesters **8** by column chromatography (silica, eluent CHCl$_3$/MeOH 99:1).

Reaction of Acyl Chloride 7 with *meso*-(1*R*[*],1′*S*[*],2*R*[*],2′*S*[*])-1,1′-Biindane-2,2′-diol (4a)

Reaction of diol **4a** with acyl chloride **7** afforded 50 mg of crude reaction mixture containing (^{1}H NMR) 20% (1*R*,1′*S*,2*R*,2′*S*)-1,1′-biindane-2,2′-diyl bis[(*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate] (**5a**), 25% (1*R*,1′*S*,2*R*,2′*S*)-2′-hydroxy-1,1′-biindan-2-yl (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**8a**), 43% (1*S*,1′*R*,2*S*,2′*R*)-2′-hydroxy-1,1′-biindan-2-yl (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**8b**) and 12% of starting diol **4a** together with some unreacted Mosher's acid. Chromatographic separation afforded 5 mg (15%) of diester **5a** and 6 mg (25%) of a 37:63 mixture of monoesters **8a**, **8b**. Diester **5a**: ^{1}H NMR:

2.81 dd, 1 H, $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 3.0 (*cis*-3-CHH); 2.94 dd, 1 H, $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 3.3 (*cis*-3'-CHH); 3.19 dd, 1 H, $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 7.1 (*trans*-3-CHH); 3.26 dd, 1 H, $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 7.1 (*trans*-3'-CHH); 3.50 q, 3 H, $^5J_{HF}$ = 1.1 (OCH$_3$); 3.52 q, 3 H, $^5J_{HF}$ = 1.1 (OCH$_3$); 3.81 t, 1 H, $^3J_{HH}$ = 3.0 (1'-CH); 3.84 t, 1 H, $^3J_{HH}$ = 3.0 (1-CH); 5.40 dt, 1 H, $^3J_{HH}$ = 7.1 (d), $^3J_{HH}$ = 3.0 (t) (2-CHO-); 5.46 dt, 1 H, $^3J_{HH}$ = 6.9 (d), $^3J_{HH}$ = 3.3 (t) (2'-CHO-); 6.66 d, 2 H, $^3J_{HH}$ = 7.2 (C$_{Ar}$H); 7.08 t, 2 H, $^3J_{HH}$ = 7.2 (C$_{Ar}$H); 7.13–7.26 m, 4 H (C$_{Ar}$H); 7.36–7.43 m, 6 H (C$_{Ph}$H); 7.48–7.51 m, 4 H (C$_{Ph}$H). ^{13}C NMR: 38.5 (CH$_2$); 38.7 (CH$_2$); 54.2 (CH); 54.3 (CH); 55.4, 2 C (OCH$_3$); 80.1 (CHO-); 80.4 (CHO-); 123.2 q, 2 C (CF$_3$), $^1J_{CF}$ = 288; 124.3 (C$_{Ar}$H); 124.3 (C$_{Ar}$H); 124.7 (C$_{Ar}$H); 124.8 (C$_{Ar}$H); 127.1 (C$_{Ar}$H); 127.2, 5 C (C$_{Ar}$H + 4 C$_{Ph}$H); 127.9, 2 C (C$_{Ph}$H); 128.5, 4 C (C$_{Ph}$H); 129.6 (C$_{Ar}$H); 129.7 (C$_{Ar}$H); 132.0, 2 C (C$_{Ph}$); 140.3 (C$_{Ar}$); 140.3 (C$_{Ar}$); 140.4, 2 C (C$_{Ar}$); 166.5, 2 C (C=O); the quaternary C$_2$ of propanoyl was not found due to low intensity and splitting by CF$_3$ group. ^{19}F NMR: –71.9, s. Monoester **8a**: ^{1}H NMR: 2.84 dd, 1 H, $^2J_{HH}$ = 17.2, $^3J_{HH}$ = 4.3 (*cis*-3'-CHH); 2.85 dd, 1 H, $^2J_{HH}$ = 17.2, $^3J_{HH}$ = 4.3 (*cis*-3-CHH); 3.29 dd, 1 H, $^2J_{HH}$ = 17.2, $^3J_{HH}$ = 6.9 (*trans*-3'-CHH); 3.25 dd, 1 H, $^2J_{HH}$ = 17.2, $^3J_{HH}$ = 7.1 (*trans*-3-CHH); 3.51 q, 3 H, $^5J_{HF}$ = 1.1 (OCH$_3$); 3.63 dd, 1 H, $^3J_{HH}$ = 4.7, $^3J_{HH}$ = 4.3 (1'-CH); 3.91 t, 1 H, $^3J_{HH}$ = 4.3 (1-CH); 4.47 dt, 1 H, $^3J_{HH}$ = 6.9 (d), $^3J_{HH}$ = 5.4 (t) (2'-CHOH); 5.57 dt, 1 H, $^3J_{HH}$ = 7.1 (d), $^3J_{HH}$ = 3.6 (t) (2-CHO-); 6.67 d, 1 H, $^3J_{HH}$ = 7.2 (C$_{Ar}$H); 6.89 d, 2 H, $^3J_{HH}$ = 7.2 (C$_{Ar}$H); 7.01–7.24 m, 6 H (C$_{Ar}$H); 7.36–7.43 m, 3 H (C$_{Ph}$H); 7.48–7.51 m, 2 H (C$_{Ph}$H). ^{13}C NMR could not be assigned from the mixture due to high complexity of signals. ^{19}F NMR: –71.8, s. Monoester **8b**: ^{1}H NMR: 2.80 dd, 1 H, $^2J_{HH}$ = 16.4, $^3J_{HH}$ = 5.1 (*cis*-3'-CHH); 2.97 dd, 1 H, $^2J_{HH}$ = 16.4, $^3J_{HH}$ = 4.3 (*cis*-3-CHH); 3.11 dd, 1 H, $^2J_{HH}$ = 16.4, $^3J_{HH}$ = 6.9 (*trans*-3'-CHH); 3.34 dd, 1 H, $^2J_{HH}$ = 16.4, $^3J_{HH}$ = 7.1 (*trans*-3-CHH); 3.52 q, 3 H, $^5J_{HF}$ = 1.4 (OCH$_3$); 3.60 dd, 1 H, $^3J_{HH}$ = 5.1, $^3J_{HH}$ = 4.3 (1'-CH); 3.84 t, 1 H, $^3J_{HH}$ = 4.3 (1-CH); 4.32 dt, 1 H, $^3J_{HH}$ = 6.9 (d), $^3J_{HH}$ = 5.6 (t) (2'-CHOH); 5.53 dt, 1 H, $^3J_{HH}$ = 7.1 (d), $^3J_{HH}$ = 4.4 (t) (2-CHO-); 6.59 d, 1 H, $^3J_{HH}$ = 7.2 (C$_{Ar}$H); 6.89 d, 2 H, $^3J_{HH}$ = 7.2 (C$_{Ar}$H); 7.01–7.24 m, 6 H (C$_{Ar}$H); 7.36–7.43 m, 3 H (C$_{Ph}$-H); 7.48–7.51 m, 2 H (C$_{Ph}$-H). ^{13}C NMR could not be assigned from the mixture due to high complexity of signals. ^{19}F NMR: –72.0, s.

Reaction of Acyl Chloride **7** with *rac*-(1R^*,1'R^*,2R^*,2'R^*)-1,1'-Biindane-2,2'-diol (**4b**)

Reaction of diol **4b** with acyl chloride **7** afforded 47 mg of crude reaction mixture containing (^{1}H NMR) 15% (1R,1'R,2R,2'R)-1,1'-biindane-2,2'-diyl bis[(*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate] (**5b**), 16% (1S,1'S,2S,2'S)-1,1'-biindane-2,2'-diyl bis[(*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate] (**5c**), 19% (1R,1'R,2R,2'R)-2'-hydroxy-1,1'-biindan-2-yl (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**8c**), 38% (1S,1'S,2S,2'S)-2'-hydroxy-1,1'-biindan-2-yl (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**8d**) and 12% starting diol **4b** together with some unreacted Mosher's acid. Chromatographic separation afforded 1 mg (3%) of diester **5b**, 1 mg (3%) of a 1:1 mixture of diesters **5b**, **5c**, 4 mg (12%) of a 39:61 mixture of diesters **5b**, **5c** and 9 mg (38%) of a 28:72 mixture of monoesters **8c**, **8d**. Diester **5b**: ^{1}H NMR: 2.97 dd, 2 H, $^2J_{HH}$ = 17.7, $^3J_{HH}$ = 2.1 (*cis*-3,3'-CHH); 3.32 q, 6 H, $^5J_{HF}$ = 1.1 (OCH$_3$); 3.41 s, 2 H (1,1'-CH); 3.60 dd, 2 H, $^2J_{HH}$ = 17.7, $^3J_{HH}$ = 6.0 (*trans*-3,3'-CHH); 5.90 d, 2 H, $^3J_{HH}$ = 6.0 (2,2'-CHO-); 6.70 d, 2 H, $^3J_{HH}$ = 7.1 (C$_{Ar}$H); 7.04–7.12 m, 2 H (C$_{Ar}$H); 7.19–7.29 m, 4 H (C$_{Ar}$H); 7.32–7.42 m, 10 H (C$_{Ph}$H). ^{13}C NMR: 37.7 (CH$_2$); 53.2 (CH); 55.3 (OCH$_3$); 81.5 (CHO-); 123.2 q, 2 C (CF$_3$), $^1J_{CF}$ = 288; 125.0 (C$_{Ar}$H); 126.3 (C$_{Ar}$H); 127.2 (C$_{Ar}$H); 127.9 (C$_{Ar}$H + C$_{Ph}$H); 128.3 (C$_{Ph}$H); 129.5 (C$_{Ph}$H); 132.0 (C$_{Ph}$); 140.2 (C$_{Ar}$); 140.4 (C$_{Ar}$); 166.6, 2 C (C=O); quaternary C$_2$ atom of propanoyl was not found due to low intensity and splitting by CF$_3$ group. ^{19}F NMR: –72.2, s. Diester **5c**: ^{1}H NMR: 3.03 dd, 2 H, $^2J_{HH}$ =

17.8, $^3J_{HH}$ = 1.9 (*cis*-3,3′-CH**H**); 3.35 q, 6 H, $^5J_{HF}$ = 1.1 (OCH$_3$); 3.49 s, 2 H (1,1′-CH); 3.59 dd, 2 H, $^2J_{HH}$ = 17.8, $^3J_{HH}$ = 6.2 (*trans*-3,3′-CH**H**); 5.62 d, 2 H, $^3J_{HH}$ = 6.2 (2,2′-CHO-); 6.78 d, 2 H, $^3J_{HH}$ = 7.7 (C$_{Ar}$H); 7.04–7.12 m, 2 H (C$_{Ar}$H); 7.19–7.29 m, 4 H (C$_{Ar}$H); 7.32–7.42 m, 10 H (C$_{Ph}$H). ^{13}C NMR: 38.4 (CH$_2$); 53.3 (CH); 55.3 (OCH$_3$); 80.5 (CHO-); 123.2 q, 2 C (CF$_3$), $^1J_{CF}$ = 288; 124.8 (C$_{Ar}$H); 125.8 (C$_{Ar}$H); 126.6 (C$_{Ar}$H); 127.3 (C$_{Ar}$H); 127.8 (C$_{Ph}$H); 128.3 (C$_{Ph}$H); 129.5 (C$_{Ph}$H); 131.8 (C$_{Ph}$); 140.0 (C$_{Ar}$); 140.4 (C$_{Ar}$); 166.6, 2 C (C=O); quarterny C$_2$ atom of propanoic acid residue was not found due to low intensity and splitting by CF$_3$ group. ^{19}F NMR: –72.3, s. Monoester **8c**: ^{1}H NMR: 2.86 dd, 1 H, $^2J_{HH}$ = 15.5, $^3J_{HH}$ = 4.3 (*cis*-3′-CH**H**); 2.94 dd, 1 H, $^2J_{HH}$ = 17.2, $^3J_{HH}$ = 1.9 (*cis*-3-CH**H**); 3.32 dd, 1 H, $^2J_{HH}$ = 17.2, $^3J_{HH}$ = 6.0 (*trans*-3′-CH**H**); 3.40 q, 3 H, $^5J_{HF}$ = 1.1 (OCH$_3$); 3.43–3.51 m, 1 H (1′-CH); 3.58 dd, 1 H, $^2J_{HH}$ = 16.7, $^3J_{HH}$ = 6.2 (*trans*-3-CH**H**); 3.79 dd, 1 H, $^3J_{HH}$ = 6.3, $^3J_{HH}$ = 2.2 (1-CH); 4.44 dt, 1 H, $^3J_{HH}$ = 6.6 (d), $^3J_{HH}$ = 4.3 (t) (2′-C**H**OH-); 5.42 dt, 1 H, $^3J_{HH}$ = 6.2 (d), $^3J_{HH}$ = 2.3 (t) (2-CHO-); 6.98 d, 1 H, $^3J_{HH}$ = 7.7 (C$_{Ar}$H); 7.08–7.48 m, 12 H (C$_{Ar}$H + C$_{Ph}$H). ^{13}C NMR could not be assigned from the mixture due to high complexity of signals. ^{19}F NMR: –72.0, s. Monoester **8d**: ^{1}H NMR: 2.83 dd, 1 H, $^2J_{HH}$ = 15.5, $^3J_{HH}$ = 4.8 (*cis*-3′-CH**H**); 3.04 dd, 1 H, $^2J_{HH}$ = 16.7, $^3J_{HH}$ = 1.9 (*cis*-3-CH**H**); 3.25 dd, 1 H, $^2J_{HH}$ = 15.5, $^3J_{HH}$ = 6.4 (*trans*-3′-CH**H**); 3.37 q, 3 H, $^5J_{HF}$ = 1.1 (OCH$_3$); 3.43–3.51 m, 1 H (1′-CH); 3.58 dd, 1 H, $^2J_{HH}$ = 16.7, $^3J_{HH}$ = 6.2 (*trans*-3-CH**H**); 3.79 dd, 1 H, $^3J_{HH}$ = 6.3, $^3J_{HH}$ = 2.2 (1-CH); 4.31 q, 1 H, $^3J_{HH}$ = 6.6 (2′-C**H**OH-); 5.39 dt, 1 H, $^3J_{HH}$ = 6.2 (d), $^3J_{HH}$ = 1.9 (t) (2-CHO-); 6.92 d, 1 H, $^3J_{HH}$ = 7.2 (C$_{Ar}$H); 7.08–7.48 m, 12 H (C$_{Ar}$H + C$_{Ph}$H). ^{13}C NMR could not be assigned from the mixture due to high complexity of signals. ^{19}F NMR: –72.0, s.

(1R^*,1′S^*,2R^*,2′S^*)-1,1′-Biindane-2,2′-diyl Dimesylate (**6**)

To (1R^*,1′S^*,2R^*,2′S^*)-1,1′-biindane-2,2′-diol (**4a**; 1.00 g, 3.76 mmol) and anhydrous dichloromethane (15 ml), triethylamine (1.36 ml, 9.76 mmol) was added dropwise while stirring and cooling the mixture to 0 °C. After 15-min stirring, mesyl chloride was added dropwise and the mixture was stirred at 0 °C for 2.5 h. The reaction mixture was then quenched by addition of saturated NH$_4$Cl (15 ml). CH$_2$Cl$_2$ (15 ml) was added, organic layer was separated and aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 20 ml). Combined extracts were dried over anhydrous Na$_2$SO$_4$ and the solvent was removed on a vacuum rotary evaporator. Pure dimesylate **6** (1.462 g, 79.7%, white crystals, m.p. 167–168 °C) was obtained by column chromatography (silica, eluent hexane/CH$_2$Cl$_2$/methanol 24:24:1, R_F 0.20). ^{1}H NMR: 3.05 s, 6 H (CH$_3$SO$_2$); 3.13 dd, 2 H, $^2J_{HH}$ = 17.7, $^3J_{HH}$ = 4.7 (*cis*-CH**H**); 3.28 dd, 2 H, $^2J_{HH}$ = 17.7, $^3J_{HH}$ = 6.9 (*trans*-CH**H**); 4.06 d, 2 H, $^3J_{HH}$ = 2.2 (CH); 5.28 ddd, 2 H, $^3J_{HH}$ = 6.9, $^3J_{HH}$ = 4.7, $^3J_{HH}$ = 2.2 (CHO-); 6.75 d, 2 H, $^3J_{HH}$ = 7.4; 7.12 t, 2 H, $^3J_{HH}$ = 7.4; 7.19–7.28 m, 4 H. ^{13}C NMR: 38.5 (CH$_2$); 39.5 (CH$_3$); 54.0 (CH); 83.1 (CHO-); 124.3 (C$_{Ar}$H); 124.8 (C$_{Ar}$H); 127.5 (C$_{Ar}$H); 128.1 (C$_{Ar}$H); 139.8 (C$_{Ar}$); 149.8 (C$_{Ar}$). IR (CHCl$_3$): 903, 937, 960, 991, 1175, 1334, 1360. For C$_{20}$H$_{22}$O$_6$S$_2$ (422.5) calculated: 56.85% C, 5.25% H, 15.18% S; found: 56.84% C, 5.27% H, 15.31% S.

RESULTS AND DISCUSSION

Diene **1** was prepared[18] by reductive coupling of cyclopentanone with amalgamated Mg and TiCl$_4$ followed by dehydration with acetic anhydride[19]. 1,1′-Biindene was obtained[20] by oxidative coupling of indene with

anhydrous $CuCl_2$. However, we found that subsequent isomerization of 1,1′-biindene to 3,3′-biindene (**2**) with triethylamine in pyridine resulted in formation of polymeric products. Moreover, in removing last traces of pyridine, substantial isomerization to the side product, indanylideneindane[25], took place. Hence, we substituted pyridine with dichloromethane and obtained diene **2** of much higher quality.

To study the scope and limitations of hydroboration of cyclic dienes **1**, **2** we chose three standard achiral hydroboration reagents with different level of steric hindrance, i.e. borane, thexylborane and 9-BBN. To study enantioselectivity of hydroboration, we also included (–)-isopinocampheylborane. In the case of this reagent and diene **1**, we also varied the reagent ratio and reaction temperature. Before using the above reagents, we performed hydroborations of a model compound, 2-methylbut-1-ene, to verify their reactivity and, in the case of (–)-isopinocampheylborane, stereoselectivity.

In the course of hydroboration of dienes **1** or **2**, four new stereogenic centres are formed. Hydroboration is well known to proceed both regioselectively and stereoselectively. The regioselectivity depends on steric hindrance of the reagent; for sterically well-accesible alkenes, bulky reagents such as 9-BBN are generally recommended[26]. Indeed, with the exception of diene **1** and borane as the reagent, all hydroborations proceeded exclusively in a regioselective way. Moreover, all hydroborations are known to proceed with a *syn*-stereoselectivity. Hence, only two diastereomeric products are formed in hydroboration and, consequently, due to the stereoselectivity of the oxidative treatment of boranes formed, only two diastereoisomeric diols, *meso*-isomers **3a**, **4a** and *rac*-isomers **3b**, **4b**, were formed (Scheme 1).

Quite surprisingly, we found that in all cases the corresponding *meso*-isomers were formed preferentially (Table I). No products were obtained from both dienes **1** and **2** if 9-BBN was used, probably due to excessive steric hindrance (runs 9, 13). In general, the excess of the undesired *meso*-isomer was higher when monosubstituted boranes (thexylborane, (–)-isopinocampheylborane) were employed compared with unsubstituted borane (runs 1–3, 10–12). Reaction temperature did not seem to influence significantly the ratio of products formed (runs 3–6). On the other hand, we found that at least some racemic diol **3b** was formed if the amount of reagent was minimized; however, this was accompanied by a significant drop of the yield (run 8).

The structure of diols **3a**, **3b** was assigned according to the published NMR spectra. In the case of *meso*-diol **3a**, the upgraded information is in-
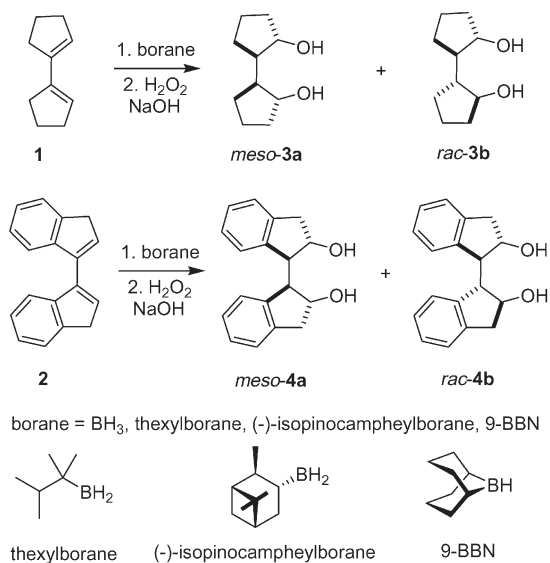
Scheme 1

Table I
**Hydroboration of dienes 1 and 2**

Run	Diene	Borane[a]	Temp., °C	Time, h	Yield[b], %	meso/rac[c]
1	1	BH$_3$	25	20	49.7	82:18
2	1	thexylborane	0	14	40.0	93:7
3	1	(–)-isopinocampheylborane	–70	136	50.4	>95:5
4	1	(–)-isopinocampheylborane	–25	24	59.3	>95:5
5	1	(–)-isopinocampheylborane	0	18	50.6	>95:5
6	1	(–)-isopinocampheylborane	25	2	53.6	>95:5
7[d]	1	(–)-isopinocampheylborane	25	2	50.9	>95:5
8[e]	1	(–)-isopinocampheylborane	25	18	32.9	74:26
9	1	9-BBN	25	20	0	
10	2	BH$_3$	25	20	91.8	73:27
11	2	thexylborane	25	20	62.1	82:18
12	2	(–)-isopinocampheylborane	25	24	74	85:15
13	2	9-BBN	25	20	0	

[a] 1 mol of borane per mol of substrate used; [b] isolated yield of the diol mixture; [c] determined by ^{1}H NMR; [d] 2 mol/mol used; [e] 0.5 mol/mol used.

cluded. For the *rac*-diol, the overlapped signals of CH_2 and CH groups were assigned using the gHSQC method.

In ref.[16], only one diastereoisomer of biindanediol **4** was described (the major one) and assigned arbitrarily the (1*S*,1′*S*,2*S*,2′*S*) configuration (incorrectly described as 1*R*,1′*R*,2*S*,2′*S* in ref.[16]). We isolated both diastereoisomers **4a**, **4b** and to confirm the original assigment unequivocally, we transformed them into the corresponding Mosher's esters **5** using the methodology described in ref.[24]

To our surprise, we found that the major stereoisomer **4a** forms only one diester **5a**, which lacks the original C_2-symmetry (Scheme 2). In the ¹H NMR spectra of diester **5a**, two sets of indane ring signals could be observed. In contrast to the diastereoisomeric mixture **5b**, **5c**, the two CH groups connecting both indane units of diester **5a** are coupled (as was confirmed by gCOSY experiment) connecting the whole biindane spin system.
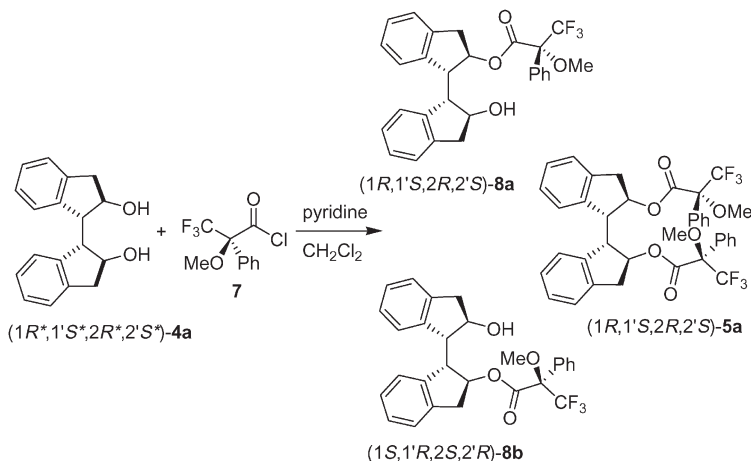
SCHEME 2

In agreement with the previous finding, the minor, so far unknown stereoisomer **4b** afforded, on the reaction with chloride **7**, two C_2-symmetric diastereoisomeric diesters **5b**, **5c**. Whereas we were able to isolate pure diester **5b** in a minute amount, diester **5c** was identified in its enriched mixture with diester **5b** (Scheme 3). Thus, the original assignment[16] is erroneous, the structure **4a** corresponds to the *meso*-stereoisomer and the much more valuable *rac*-stereoisomer is the minor product **4b**. Hydroboration of biindene **2** hence proceeds with similar stereochemical outcome as the hydroboration of diene **1**. Along with diesters **5a**–**5c**, mixtures of the corresponding monoesters **8a**, **8b** (from *meso*-diol **4a**) and **8c**, **8d** (from *rac*-diol **4b**) were obtained as by-products.
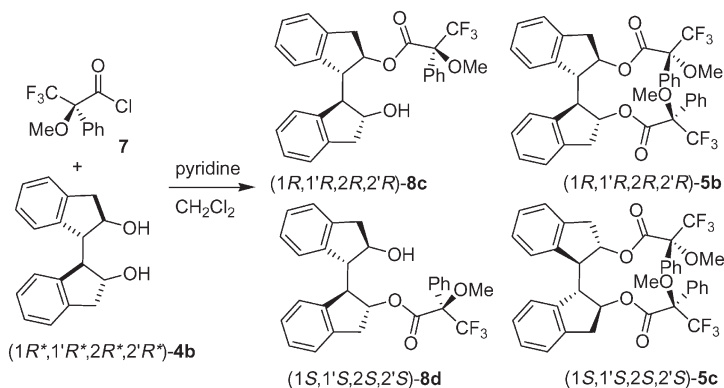
SCHEME 3

The absolute configuration of diesters **5** and monoesters **8** was estimated based on careful analysis of ^{1}H NMR spectra. The published[24,27] empirical observations for various esters of Mosher's acid showed that an idealized picture can be constructed in which the trifluoromethyl groups eclipses the carbonyl group of Mosher's ester and hydrogen of the chiral centre studied. Phenyl group of the ester moiety then shields hydrogens of one vicinal CH or CH_2 group more than the other (Fig. 1).

We used chloride of Mosher's acid **7** with the (*S*)-configuration and, consequently, esters with (*R*)-configuration were formed (due to a change in the priority of substituents on chiral carbon of the esters). Hence, biindanediol moieties with the probable (1*R*,2*R*)-configuration could be found in the ^{1}H NMR spectra on the basis of more shielded (upfield, lower ppm values) CH_2 group signals of the cyclopentane ring, whereas those with (1*S*,2*S*)-configuration were characterized by the more shielded CH group (connecting the two cyclopentane rings) signals. For illustration, the differences in shifts between the 1*R*,2*R* and 1*S*,2*S* centres of the three corresponding hydrogens are listed in Table II.
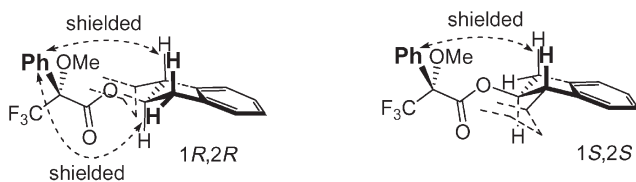

FIG. 1
Estimation of absolute configuration of esters **5**, **8** from ^{1}H NMR spectra

In the case of non-symmetrical diester **5a** and in the case of monoesters **8a**–**8d** the estimation of configuration was rather straightforward in agreement with ref.[27] However, in ^{1}H NMR spectra of C_2-symmetric diesters, the shielding of both CH_2 and CH groups was higher for one diastereoisomer. We decided to estimate the probable absolute configuration of diesters **5b**, **5c** based on the shift of the *cis*-hydrogen of the CH_2 group, as this should be less influenced by conformational changes of the molecule than the inner hydrogen of the C–H group linking both biindane units.

Surprisingly, diol **4b** prepared by hydroboration of diene **2** with the chiral reagent, (–)-isopinocampheylborane (Table I, run 12), afforded nearly equimolar amounts of diesters **5b**, **5c** and only small excess of monoester **8d** over **8c**, which is far from the published enantioselectivity for chiral hydroboration of analogous diene **1**. Indeed, measurements of optical rotation of diol **4b** confirmed that nearly a racemic mixture of enantiomers was formed by chiral hydroboration as no rotation was observed.

To allow further transformations of diols **4**, we reacted *meso*-diol **4a** with mesyl chloride and prepared the corresponding dimesylate **6** in a good yield (Scheme 4).

TABLE II
^{1}H NMR shifts of CH_2 and CH groups in diesters **5** and monoesters **8**

Esters	*cis*-CH**H**			*trans*-CH**H**			CH		
	1*R*,2*R*	1*S*,2*S*	*RR* – *SS*	1*R*,2*R*	1*S*,2*S*	*RR* – *SS*	1*R*,2*R*	1*S*,2*S*	*RR* – *SS*
5a	2.81	2.94	–0.13	3.19	3.26	–0.07	3.84	3.81	0.03
5b/5c	2.97	3.03	–0.06	3.60	3.59	0.01	3.41	3.49	–0.08
8a/8b	2.85	2.97	–0.12	3.25	3.34	–0.09	3.91	3.84	0.07
8c/8d	2.94	3.04	–0.10	3.58	3.58	0	3.79	3.79	0

(1*R**,1'*S**,2*R**,2'*S**)-**4a**   (1*R**,1'*S**,2*R**,2'*S**)-**6**
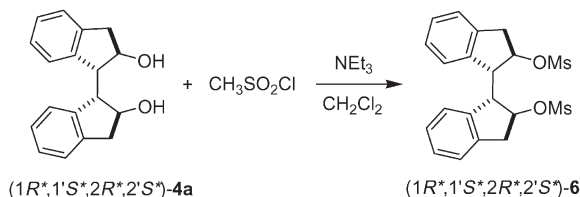
SCHEME 4

Single-crystal X-ray analysis of dimesylate **6** served as further confirmation of *meso*-structure of the starting diol **4a** (Fig. 2). CCDC 619802 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Highly preferential formation of the *meso*-isomers of diols **3a**, **4a** regardless of the reagent, its excess and reaction temperature is rather surprising. Negative experiments with 9-BBN and analogous reactivity of thexylborane and borane hint that the observed stereoselectivity is not caused by preferential formation of intermediate borolanes. To understand more the reasons we decided to perform a short theoretical study on dienes **1**, **2**. We logically envisioned the second hydroboration step as the key step for the stereoselectivity and thus the complexes **9a**, **9b**, **10a**, **10b** of monohydroborated dienes with second borane molecule as the key objects of study. As ethereal solvent was used in experiments, we microsolvated the borane molecule with one molecule of simulated solvent, dimethyl ether (DME). Due to efficiency reasons, we employed the DFT method using second-generation hybrid functional PBE1PBE (also named PBE0; this empirical-parameter-free functional has improved description of van der Waals complexes compared with traditional B3LYP functional[28]; another advantage is its implementation in both commercial Gaussian03W[29] and free of charge PCGAMESS[30,31] program packages) together with 6-31G(d) Gaussian basis set, a minimal set appropriate for DFT calculations. In this case, all calculations were performed with Gaussian03W[29] program package. We first care-
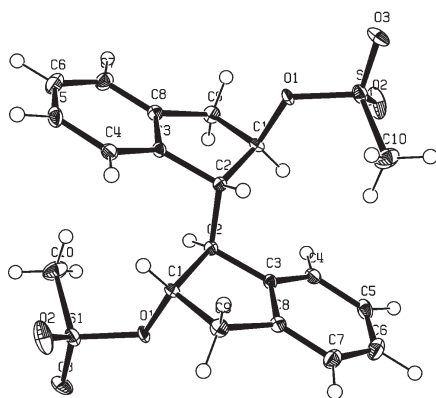

Fig. 2
ORTEP plot of ($1R^*,1'S^*,2R^*,2'S^*$)-1,1′-biindane-2,2′-diyl dimesylate (**6**, CCDC 619802)

fully investigated the conformational space of all four complexes to find global minima. In some cases, very flat inflexions were observed for the studied complexes instead of true minima. Nevertheless, the corresponding products of hydroboration (true minima in all cases) show analogous stability patterns. The geometries and relative energies of these complexes, **9a** (precursor of *meso*-diol **3a**), **9b** (precursor of *rac*-diol **3b**), **10a** (precursor of *meso*-diol **4a**) and **10b** (precursor of *rac*-diol **4b**), are depicted in Fig. 3.

Complex: **9a**
Precursor of:
meso-**3a**
Relative energy:
0.0 kJ/mol

Complex: **9b**
Precursor of:
rac-**3b**
Relative energy:
10.2 kJ/mol

Complex: **10a**; Precursor of: *meso*-**4a**
Relative energy: 0.0 kJ/mol

Complex: **10b**; Precursor of: *rac*-**4b**
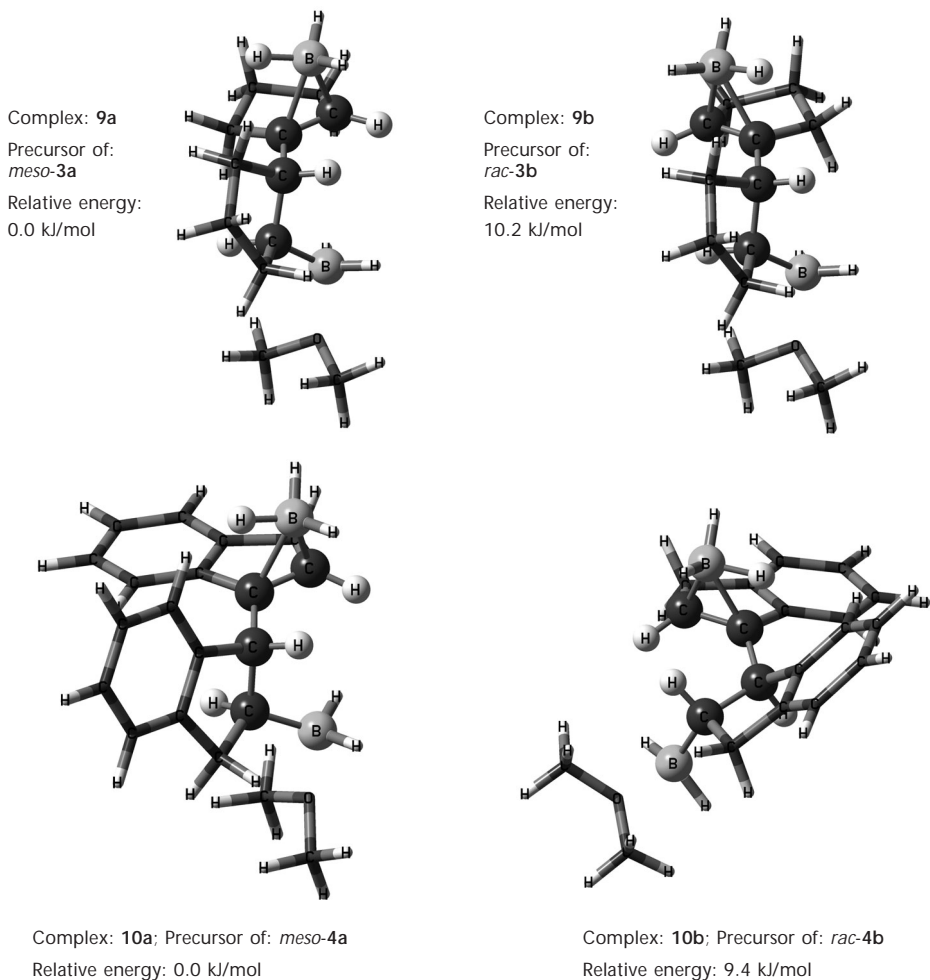Relative energy: 9.4 kJ/mol

FIG. 3
Calculated equilibrium geometries and relative energies of hydroboration intermediates **9a**, **9b**, **10a**, **10b**

In agreement with the experimental results, we found in both cases that complex precursors **9a**, **10a** of *meso*-diols **3a**, **4a** are more favorable by ca. 10 kJ/mol compared with precursors **9b**, **10b** of *rac*-diols **3b**, **4b**. This can be explained by the fact that the cyclopentane and cyclopentene rings of the monohydroborated intermediates are approximately perpendicular. The conformers with the cyclopentene ring double bond less shielded by the ring then lead to more stable complexes **9a**, **10a** with second molecule of borane which in turn afford *meso*-diols **3a**, **4a** after the standard oxidative work-up.

Thus, we confirmed both experimentally and theoretically that the major products of hydroboration/oxidation of cyclic dienes **1**, **2** are the undesired *meso*-diols **3a**, **4a** regardless of the reagent, its excess, reaction temperature and time. *rac*-Diols **3b**, **4b** are formed as minor products. Borane–THF complex is the hydroboration reagent of choice for the preparation of diols **3b**, **4b** as it is cheaper than other reagents and affords a little more advantageous ratio of stereoisomers. Moreover, the isolation of the desired diols **3b**, **4b** is more straightforward as the reaction mixture is not contaminated with organic oxidation products of the hydroboration reagent.

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