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FULL PAPER

Platinum-catalysed 1,4-diboration of 1,3-dienes

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The chiral diborane(4) compounds $B_2[R,R\text{-}O_2CH(CO_2Me)CH(CO_2Me)]_2$, $B_2(S\text{-}O_2CH_2CHPh)_2$, $B_2(R,R\text{-}O_2CHPhCHPh)_2$ and $B_2(O_2C_{20}H_{12})_2$ ($O_2C_{20}H_{12}$ = 1,7′-bi-2-naphtholate) have been synthesized. All four compounds have been characterised by X-ray crystallography, the latter as a racemate. The B–B bond oxidative-addition reactions of the first three compounds with $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ resulted in the platinum(II) bis(boryl) complexes *cis*-$[Pt(PPh_3)_2\{B[R,R\text{-}O_2CH(CO_2Me)CH(CO_2Me)]\}_2]$, *cis*-$[Pt(PPh_3)_2\{B(S\text{-}O_2CH_2CHPh)\}_2]$ and *cis*-$[Pt(PPh_3)_2\{B(R,R\text{-}O_2CHPhCHPh)\}_2]$; the former two were also characterised by X-ray crystallography. The platinum-catalysed diborations of a range of prochiral 1,3-dienes with the compounds $B_2[R,R\text{-}O_2CH(CO_2Me)CH(CO_2Me)]_2$, $B_2(S\text{-}O_2CH_2CHPh)_2$ and $B_2(R,R\text{-}O_2CHPhCHPh)_2$ were studied. Although these reactions were clean and quantitative, observed product d.e.s (measured by ^{1}H NMR spectroscopy) were low or non-existent indicating that chirality transfer from the diborane(4) diolate groups to the diene diboration product is not efficient in these cases.

The platinum-catalysed addition of diborane(4) compounds to the C–C/C–O multiple bonds present in alkenes,[1] alkynes,[2] 1,3-dienes[3] and α,β unsaturated ketones[4] (diboration) is now well established with key intermediates in these reactions thought to be platinum(II) bis(boryl) complexes formed by oxidative addition of the B–B bond of the diborane(4) compound to a platinum(0) centre;[1–5] many examples of complexes with the general formula *cis*-$[Pt(BR_2)_2(PR'_3)_2]$ have now been isolated and structurally characterised.[2b,c,e,6–8] As an extension to this work, we have recently sought to carry out asymmetric diboration reactions using enantiomerically pure diborane(4) compounds and have had limited success using alkene substrates.[9] Herein we report on our attempts to diborate prochiral 1,3-dienes asymmetrically using platinum phosphine catalyst precursors, and include full details of the synthesis and structural characterisation of a range of chiral diborane(4) compounds.

Results and Discussion

The chiral diborane(4) compounds $B_2[R,R\text{-}O_2CH(CO_2Me)CH(CO_2Me)]_2$ **1**, $B_2(S\text{-}O_2CH_2CHPh)_2$ **2**, $B_2(R,R\text{-}O_2CHPhCHPh)_2$ **3** and $B_2(O_2C_{20}H_{12})_2$ **4** ($O_2C_{20}H_{12}$ = binaphthalenolate or binolate) were prepared as described in the Experimental section from $B_2(NMe_2)_4$ and the corresponding diol according to established literature procedures;[10] **4** was prepared as a racemate.

Compounds **1**–**4** were characterised by normal spectroscopic and analytical methods as well as by X-ray crystallography. Their molecular structures are shown in Figs. 1–4 respectively with an additional view of **4** in Fig. 5. Selected bond lengths and angles are presented in Table 1 and crystallographic data in Table 3. The structures of **1**–**3** are largely unexceptional and similar to those of the many diborane(4) bis(diolates) which have previously been structurally characterised.[11–13] Compounds **1** and **2** crystallise with two molecules per asymmetric unit and **3** has crystallographic C_2 symmetry. Since all three were prepared from enantiomerically pure diol, they all crystallise in chiral space groups (Table 3). The B–B bond distances

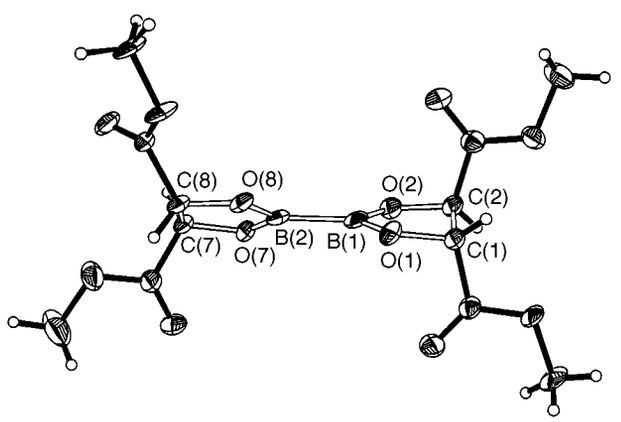
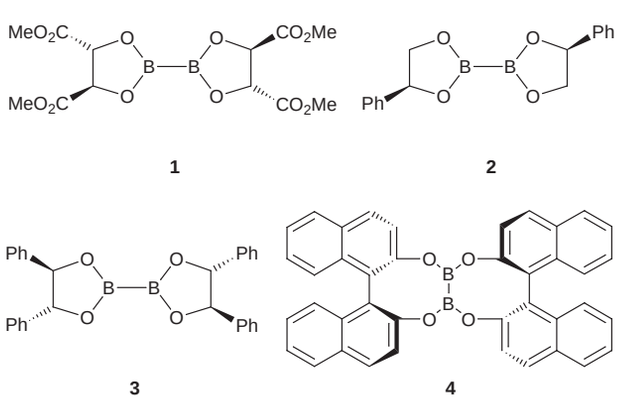


Fig. 1 Molecular structure of compound **1** (one of two independent molecules) with key atoms labelled. Non-hydrogen atoms are drawn as ellipsoids to enclose 50% probability density



(Table 1) are within the range previously established for this type of compound,[11,13] and we note that the torsion angles about the B–B bond, *i.e.* that defined by the interplanar angle between the two adjacent boron trigonal planes, are 28.1 and 26.8° for **1**, 4.5 and 5.0° for **2** and 34.7° for **3**, which, in the cases of **1** and **3**, are somewhat larger than the corresponding angles found in most other diborane(4) bis(diolate) structures.

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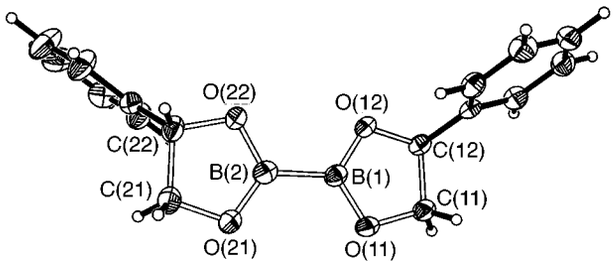


Fig. 2 Molecular structure of compound **2** (one of two independent molecules). Details as in Fig. 1

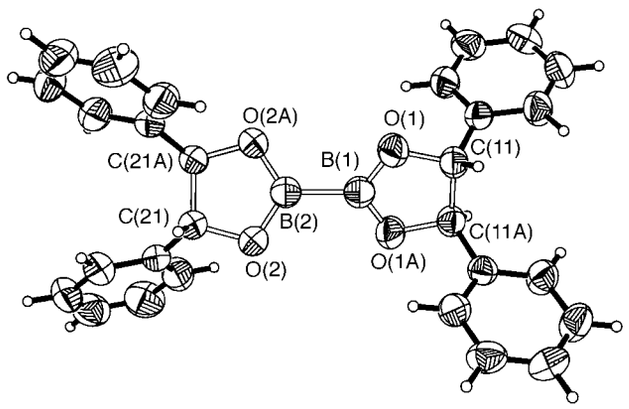


Fig. 3 Molecular structure of compound **3**. Details as in Fig. 1

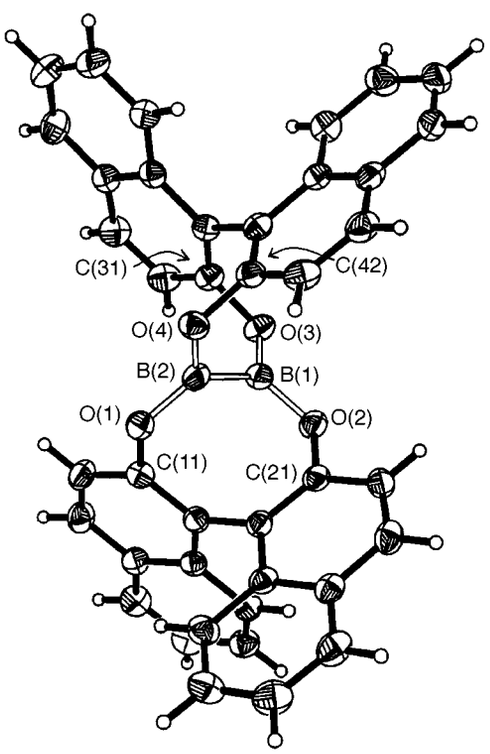


Fig. 4 Molecular structure of compound **4**. Details as in Fig. 1

However, the barrier to rotation about the B–B bond is likely to be very low such that these torsion angles would be expected to vary widely as a result of crystal packing forces especially when markedly non-planar diolate groups are present as is the case here.

The structure of compound **4** (Figs. 4 and 5), which crystallises as a toluene solvate, has a relatively long B–B bond [1.715(5) Å], although still within the range observed for diborane(4) compounds,[11] and an angle between the boron trigonal planes of 37.6° similar to the corresponding angle in **3**. However, the most notable feature is that the diolate groups are

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1**–**4**

1		**2**	
B(1)–B(2)	1.701(4)	B(1)–B(2)	1.695(3)
B(1)–O(1)	1.373(3)	B(1)–O(11)	1.370(2)
B(1)–O(2)	1.369(3)	B(1)–O(12)	1.358(2)
B(2)–O(7)	1.363(3)	B(2)–O(21)	1.362(2)
B(2)–O(8)	1.366(3)	B(2)–O(22)	1.368(2)
B(3)–B(4)	1.688(4)	B(3)–B(4)	1.694(3)
B(3)–O(13)	1.368(3)	B(3)–O(31)	1.360(2)
B(3)–O(14)	1.365(3)	B(3)–O(32)	1.373(2)
B(4)–O(19)	1.377(3)	B(4)–O(41)	1.366(2)
B(4)–O(20)	1.352(3)	B(4)–O(42)	1.371(2)
B(2)–B(1)–O(1)	122.6(2)	B(2)–B(1)–O(11)	124.4(2)
B(2)–B(1)–O(2)	124.9(2)	B(2)–B(1)–O(12)	122.4(2)
O(1)–B(1)–O(2)	112.5(2)	O(11)–B(1)–O(12)	113.3(2)
B(1)–B(2)–O(7)	124.8(2)	B(1)–B(2)–O(21)	125.2(2)
B(1)–B(2)–O(8)	121.3(2)	B(1)–B(2)–O(22)	121.5(2)
O(7)–B(2)–O(8)	113.9(2)	O(21)–B(2)–O(22)	113.3(2)
B(4)–B(3)–O(13)	124.1(2)	B(4)–B(3)–O(31)	123.8(2)
B(4)–B(3)–O(14)	123.0(2)	B(4)–B(3)–O(32)	123.2(2)
O(13)–B(3)–O(14)	112.9(2)	O(31)–B(3)–O(32)	113.0(2)
B(3)–B(4)–O(19)	122.3(2)	B(3)–B(4)–O(41)	123.4(2)
B(3)–B(4)–O(20)	124.8(2)	B(3)–B(4)–O(42)	123.5(2)
O(19)–B(4)–O(20)	112.8(2)	O(41)–B(4)–O(42)	113.1(2)
3		**4**	
B(1)–B(2)	1.700(5)	B(1)–B(2)	1.715(5)
B(1)–O(1)	1.359(2)	B(1)–O(2)	1.377(4)
B(2)–O(2)	1.361(2)	B(1)–O(3)	1.372(4)
		B(2)–O(1)	1.375(4)
		B(2)–O(4)	1.367(4)
B(2)–B(1)–O(1)	123.37(13)	B(2)–B(1)–O(2)	123.6(3)
O(1)–B(1)–O(1A)	113.3(3)	B(2)–B(1)–O(3)	122.5(2)
B(1)–B(2)–O(2)	123.21(13)	O(2)–B(1)–O(3)	113.8(3)
O(2)–B(2)–O(2A)	113.6(3)	B(1)–B(2)–O(1)	123.6(3)
		B(1)–B(2)–O(4)	122.5(2)
		O(1)–B(2)–O(4)	113.8(3)

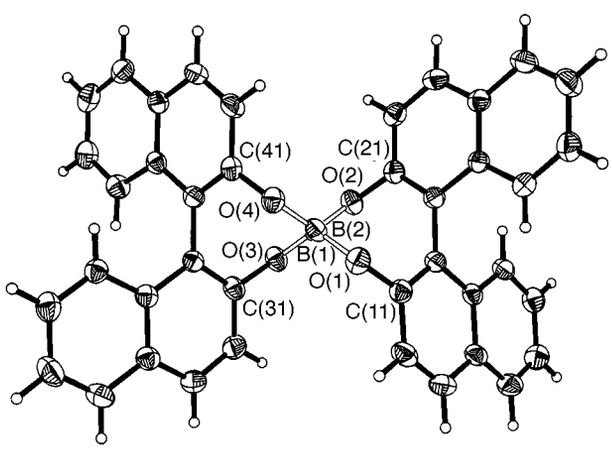


Fig. 5 Alternative view of the molecular structure of compound **4**

attached such that they bridge the B–B bond. Compound **4** is therefore an example of a 1,2 rather than the 1,1 isomer observed for all previous diborane(4) bis(diolates).[11,13] Such a structure presumably results from the eight-membered $B_2O_2C_4$ ring being more stable than the alternative seven-membered BO_2C_4 ring which would be present in the 1,1 isomer and the similarity of the B–O lengths and B–B–O and O–B–O angles in **4** as compared with **1**–**3** indicates that the 1,2-isomer form in **4** is essentially unstrained. Unlike compounds **1**–**3**, **4** was prepared from the racemic diol and both enantiomers of the particular conformational form adopted in the solid state, which have approximate (non-crystallographic) D_2 symmetry, are present in the crystal (centrosymmetric space group $P2_1/n$); the torsion angles between the naphthalene planes are 76.5 and

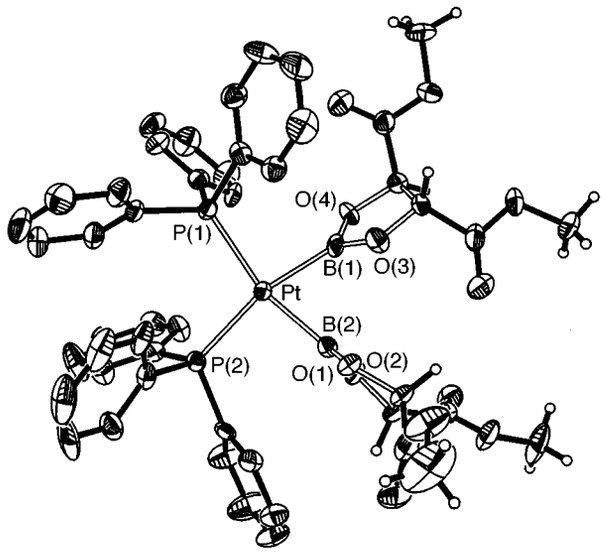
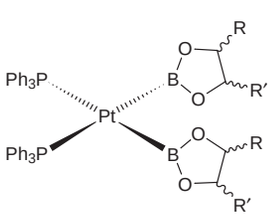


Fig. 6 Molecular structure of *cis*-[Pt(PPh_3)$_2${B[*R*,*R*-$O_2CH(CO_2Me)CH(CO_2Me)$]}$_2$] with key atoms labelled; PPh_3 hydrogen atoms are omitted for clarity. Non-hydrogen atoms are drawn as ellipsoids to enclose 50% probability density

86.2°. A more detailed look at the structure of **4** reveals that the two eight-membered $B_2O_2C_4$ rings have boat conformations and that, for a given enantiomer, the chirality of the two binol groups is the same. The use of models indicates that an alternative twist-boat conformation for the rings is also possible. For the twist-boat/twist-boat isomer, the binol groups must also both have the same chirality (for a given enantiomer) but for a boat/twist-boat isomer the binol group chiralities are opposite. There are, therefore, three possible diastereomeric conformational forms for **4**, although NMR studies indicate that only one of these (presumably the one found in the crystal structure) is present in solution.

Compounds **1**–**3**, but not **4**, reacted cleanly and quantitatively with [Pt(PPh_3)$_2$(η-C_2H_4)] affording the platinum(II) bis(boryls) *cis*-[Pt(PPh_3)$_2${B[*R*,*R*-$O_2CH(CO_2Me)CH(CO_2Me)$]}$_2$], *cis*-[Pt(PPh_3)$_2${B(*S*-O_2CH_2CHPh)}$_2$] and *cis*-[Pt(PPh_3)$_2${B(*R*,*R*-$O_2CHPhCHPh$)}$_2$], consistent with previously established routes to this class of compound,[2,6,7] and were characterised by normal spectroscopic and analytical methods. In addition, the first two were characterised by X-ray crystallography, the results of which are shown in Figs. 6 and 7; selected bond lengths and angles are given in Table 2 and crystallographic data in Table 3.



R = R′ = CO_2Me; R = Ph, R′ = H; or R = R′ = Ph

The compound *cis*-[Pt(PPh_3)$_2${B[*R*,*R*-$O_2CH(CO_2Me)CH(CO_2Me)$]}$_2$] crystallises as a toluene solvate and *cis*-[Pt(PPh_3)$_2${B(*S*-O_2CH_2CHPh)}$_2$] as a CH_2Cl_2 solvate. Both adopt structures now well established for this class of compound,[2b,c,e,6,7] a key feature being the *cis* arrangement of the boryl ligands about the square-planar platinum centre. Other features are also unexceptional with the Pt–B distances and P–Pt–P and B–Pt–B angles (Table 2) all falling within or close to observed ranges for these parameters, and the angles between the boryl boron trigonal planes and the platinum mean square plane [86.4 and 62.4° and 84.5 and 81.1° respectively] also being

Table 2 Selected bond lengths (Å) and angles (°) for the complexes

cis-[Pt(PPh_3)$_2${B[*R*,*R*-$O_2CH(CO_2Me)CH(CO_2Me)$]}$_2$]		*cis*-[Pt(PPh_3)$_2${B(*S*-O_2CH_2CHPh)}$_2$]	
Pt–B(1)	2.065(5)	Pt–B(1)	2.070(3)
Pt–B(2)	2.054(7)	Pt–B(2)	2.054(4)
Pt–P(1)	2.368(2)	Pt–P(1)	2.3456(9)
Pt–P(2)	2.341(2)	Pt–P(2)	2.3505(9)
B(1)–O(3)	1.385(8)	B(1)–O(1)	1.389(4)
B(1)–O(4)	1.417(9)	B(1)–O(2)	1.383(4)
B(2)–O(1)	1.398(9)	B(2)–O(3)	1.378(5)
B(2)–O(2)	1.387(9)	B(2)–O(4)	1.375(6)
B(1)–Pt–B(2)	73.3(4)	B(1)–Pt–B(2)	75.5(2)
B(1)–Pt–P(1)	91.5(3)	B(1)–Pt–P(1)	164.7(2)
B(1)–Pt–P(2)	165.0(3)	B(1)–Pt–P(2)	91.7(2)
B(2)–Pt–P(1)	163.7(2)	B(2)–Pt–P(1)	89.63(12)
B(2)–Pt–P(2)	92.4(2)	B(2)–Pt–P(2)	166.16(13)
P(1)–Pt–P(2)	103.14(6)	P(1)–Pt–P(2)	102.75(3)
Pt–B(1)–O(3)	127.3(5)	Pt–B(1)–O(1)	125.2(2)
Pt–B(1)–O(4)	123.3(5)	Pt–B(1)–O(2)	124.3(2)
O(3)–B(1)–O(4)	109.5(4)	O(1)–B(1)–O(2)	110.5(3)
Pt–B(2)–O(1)	119.6(5)	Pt–B(2)–O(3)	127.3(3)
Pt–B(2)–O(2)	130.5(6)	Pt–B(2)–O(4)	122.4(3)
O(1)–B(2)–O(2)	109.9(6)	O(3)–B(2)–O(4)	110.2(3)

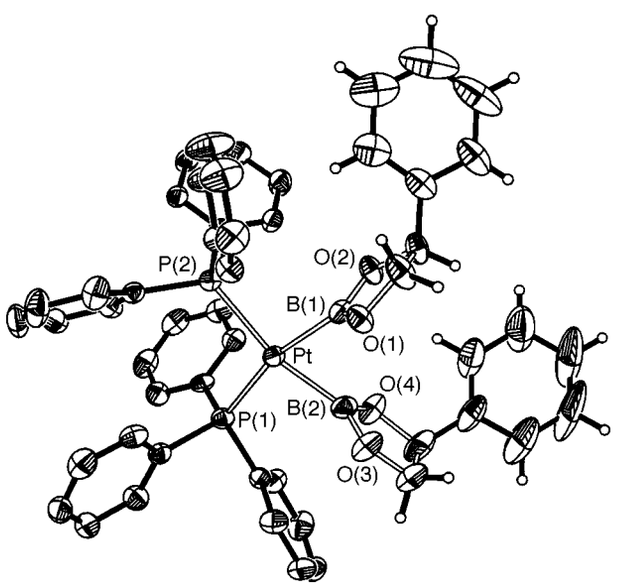
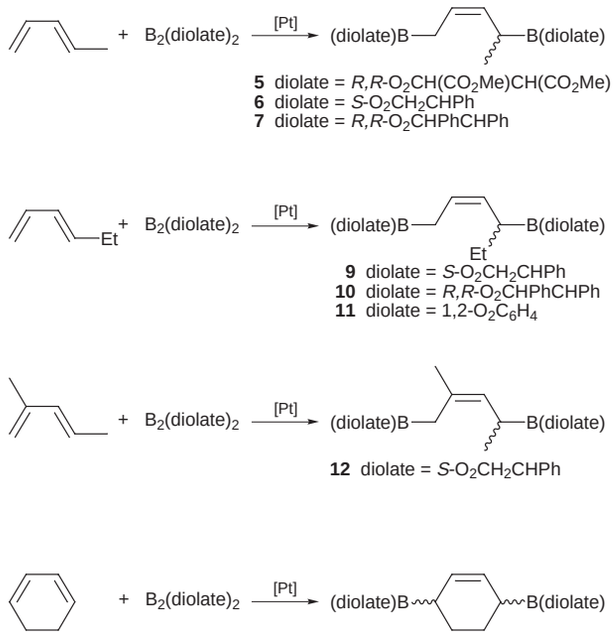


Fig. 7 Molecular structure of *cis*-[Pt(PPh_3)$_2${B(*S*-O_2CH_2CHPh)}$_2$]. Details as in Fig. 6

within previously observed limits.[2b,c,e,6,7] A discussion of these structural features is given in ref. 6 and will not be reiterated here.

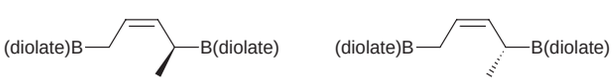
Having established routes to chiral diborane(4) compounds and shown that these compounds (in the case of **1**–**3**) reacted with [Pt(PPh_3)$_2$(η-C_2H_4)] to afford platinum(II) bis(boryls), we were interested to see whether or not we could effect a platinum-catalysed, asymmetric diboration of prochiral 1,3-dienes. Miyaura and co-workers[3] were the first to report platinum-catalysed diene diboration reactions. These workers had shown that [Pt(PPh_3)$_4$] would catalyse the addition of B_2($O_2CMe_2CMe_2$) to buta-1,3-diene, isoprene and 2,3-dimethylbuta-1,3-diene in either toluene or dmf (dmf = dimethylformamide) affording 1,4-diborated products in high yields (toluene giving the best product yields) as single, *Z* isomers. Interestingly, however, if the phosphine-free platinum species [Pt(dba)$_2$] (dba = dibenzylideneacetone) was used the diborated products were those resulting from diene dimerisation.[3]

As our first attempt we studied the reaction between compounds **1**–**3** and *trans*-penta-1,3-diene (Scheme 1), using 5 mol% [Pt(PPh_3)$_2$(η-C_2H_4)] as catalyst in toluene at 80 °C for 1 d. In all



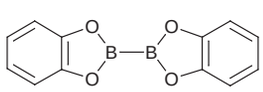
Scheme 1

cases, spectroscopic data were consistent with the formation of the expected 1,4-diboration products **5**–**7**, but it was clear, particularly from the ^{1}H NMR data, that the two possible diastereomers [**A**(*S*) and **B**(*R*) shown below] were formed in approximately equal amounts, the highest d.e. (20%) being seen for **5** (product d.e.s here and throughout this paper were estimated from ^{1}H NMR integrations).



A(*S*) **B**(*R*)

The analogous reactions between *trans*-hexa-1,3-diene and **2** or **3** were also examined, as was a reaction using the achiral diborane(4) compound $B_2(1,2\text{-}O_2C_6H_4)_2$ **8**, resulting in the products **9**–**11** (Scheme 1). Spectroscopic data revealed that these three reactions also afforded the expected products after similar reaction times and with similar yields, but as with **5**–**7** the observed d.e.s for **9** and **10** were poor.



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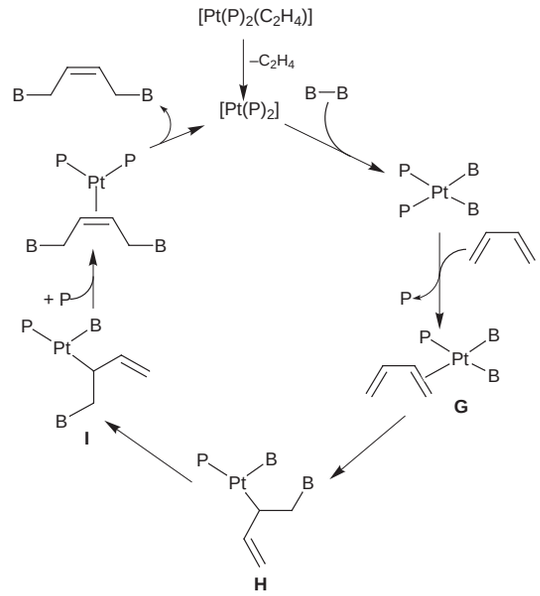
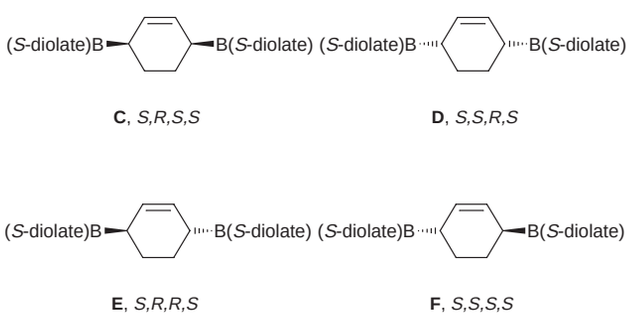
In the case of the reaction between compound **2** and *trans*-2-methylpenta-1,3-diene, spectroscopic data were consistent with the formation of the expected product **12** (Scheme 1) but, as well as a poor observed d.e., reaction times were considerably longer than for **5**–**7** and **9**–**11**.

In contrast, the reactions between **1**–**3** or **8** and cyclohexa-1,3-diene proceeded much more rapidly affording the diborated compounds **13**–**16** (Scheme 1), although the product stereochemistry was now more complicated since cyclohexa-1,3-diene contains two prochiral centres. In the case of **16**, for which the boron diolate group is achiral, the possible isomers are simply the expected diastereomerically related pairs of enantiomers *R*,*R*/*S*,*S* and the *meso* *R*,*S*/*S*,*R*. In the case of **13**–**15**, the same situation arises since, although the boron diolate group is now chiral, only one enantiomer is present. For a particular case



Scheme 2 P = PPh_3

where the boron diolate group contains a single chiral centre with an *S* configuration (as is the case in **14**), the possible isomers are **C**–**F** (**C** and **D** are a *meso* form and therefore the same in this case although they would differ for an unsymmetrically substituted cyclohexadiene), **C**/**D** (the *meso* form) having a *syn* configuration with respect to the boryl groups and **E**/**F** having an *anti* configuration.



The NMR data for compound **16** displayed a 2H singlet at δ 6.05 for the alkene hydrogens (=CH) of the cyclohexene ring indicating that only one diastereomer was present, although it was not possible to determine whether this was the *syn* or *anti* form. Such a determination was possible in principle, however, in the case of **13**–**15** since the *syn* diastereomer (**C**/**D**) would be expected to give rise to a mutually coupled pair of alkene =CH doublets whereas each *anti* diastereomer (**E** and **F**) should give rise to a singlet as a result of the C_2 symmetry axis present in these forms. For each of **13**–**15** what was observed was a pair of mutually coupled doublets of equal intensity consistent with the exclusive presence of the *meso* *syn* isomer in each case.

A possible mechanism for 1,3-diene diboration (in line with previously postulated alkyne and alkene mechanisms, and that proposed for diene diboration by Miyaura and co-workers[3]) is shown in Scheme 2. In the case of the acyclic dienes, initial co-ordination of the *s*-*cis*-diene conformer (intermediate **G**) and subsequent hindered rotation about the 2,3-C–C bond due to co-ordination of the remaining diene double bond to the platinum centre (not explicitly shown) in intermediates **H** and **I** (and **G**) would account for the fact that the resulting alkene product has a *Z* or *cis* configuration rather than the alternative *E* or *trans* configuration. For cyclohexadiene, the constraints of the ring require that the diboration product be the *Z* or *cis* isomer with respect to the C=C double bond, but the formation of *syn* diboration isomers (*i.e.* both borons added to one face of

the diene) would also follow from co-ordination of the second double bond in intermediates **H** and **I** (and **G**).

In conclusion, we have shown that chiral diborane(4) compounds can be readily prepared from easily available, enantiomerically pure diols and that these compounds, with the exception of **4**, react with $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ to afford platinum bis(boryls) in line with previous observations.[2,6,7] Moreover, 1,4-diboration of 1,3-dienes also occurs readily, consistent with the previous report from Miyaura and co-workers,[3] but in the systems studied here no significant asymmetric induction was observed although it is possible that other chiral diborane(4) compounds might afford better results in this regard. In any event, the stoichiometric use of the chiral reagent could be considered somewhat wasteful and an alternative approach might be to make the metal centre chiral by the use of suitable chiral phosphines. Most such systems in the literature, however, involve the use of a chiral chelating diphosphine,[14] but it is known from related studies dealing with alkyne diboration[2e] that chelating diphosphines cause a dramatic reduction in reaction rates presumably because the active catalytic species contains only one phosphine. This problem might be alleviated by using enantiomerically pure chiral monodentate phosphines. In situations where phosphine catalyst precursors are ineffective however, such as in platinum-catalysed alkene diboration, the use of chiral diborane(4) compounds provides the only means of controlling the product chirality, an area in which we have had modest success.[9]

Experimental

General procedures

All reactions were performed using standard Schlenk or glovebox techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were distilled from appropriate drying agents immediately prior to use (sodium for toluene and hexanes and sodium–benzophenone for Et_2O and thf). Microanalytical data were obtained at The University of Bristol. Proton, ^{13}C, ^{31}P and ^{11}B NMR spectra were recorded on a JEOL GX 400 spectrometer and referenced to $SiMe_4$, $SiMe_4$, 85% H_3PO_4 and $BF_3{\cdot}Et_2O$ respectively. Mass spectra (high and low resolution) were obtained in EI mode (unless otherwise stated) on a VG Micromass Autospec spectrometer. Optical rotation measurements were obtained on a Perkin-Elmer 141 polarimeter.

All starting materials were procured commercially and used without further purification unless otherwise stated; $B_2(NMe_2)_4$,[15] $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$[16] and *R*,*R*-1,2-diphenylethane-1,2-diol[17] were prepared by literature methods.

Preparations

(*a*) Diborane(4) compounds. $B_2[R,R\text{-}O_2CH(CO_2Me)CH(CO_2Me)]_2$ **1**. A solution of dimethyl L-tartrate (0.600 g, 3.4 mmol) in thf–Et_2O (1:1, 15 cm^3) was added to a solution of $B_2(NMe_2)_4$ (0.303 g, 1.53 mmol) in Et_2O (10 cm^3) and the reaction mixture stirred for 12 h resulting in a white precipitate. A solution of HCl (7.6 cm^3 of a 1.0 M solution in Et_2O) was then added and the suspension stirred for 12 h during which time most of the solid product dissolved. After this time the reaction solution was filtered any residual solid being washed with Et_2O (2 × 5 cm^3). Removal of all volatiles from the filtrate by vacuum afforded crude compound **1** as a colourless oil. Pure samples of **1** as a white crystalline solid were obtained after recrystallisation from toluene (yield 0.305 g, 53%). NMR ($CDCl_3$): ^1H, δ 4.95 (s, 4 H, C*H*CO_2Me) and 3.80 (s, 12 H, CO_2Me); $^{13}C\text{-}\{^1H\}$, δ 170.3 (*C*O_2Me), 78.6 (*C*HCO_2Me) and 53.8 (CO_2*Me*); $^{11}B\text{-}\{^1H\}$, δ 29.0 (br s). Mass spectrum: *m*/*z* 374 (M^+, 30%); high resolution, $C_{12}H_{16}B_2O_{12}$ requires 374.083, found 374.083 (Found: C, 39.0; H, 4.6. $C_6H_8BO_6$ requires C, 38.5; H, 4.3%). $[\alpha]_D^{20} = -0.25$ (*c* = 0.0032, CH_2Cl_2).

$B_2(S\text{-}O_2CH_2CHPh)_2$ **2**. A solution of $B_2(NMe_2)_4$ (0.305 g, 1.54 mmol) in Et_2O (5 cm^3) was added to a solution of *S*-1-phenylethane-1,2-diol (0.430 g, 3.12 mmol) in Et_2O (10 cm^3) and the reaction mixture stirred for 18 h. After this time a solution of HCl (7.6 cm^3 of a 1.0 M solution in Et_2O) was added and the reaction mixture stirred for 2 h. Subsequent filtration followed by removal of all volatiles from the filtrate by vacuum afforded crude compound **2** as a white solid. Recrystallisation from hexane afforded pure **2** as a white crystalline solid (yield 0.270 g, 60%). NMR ($CDCl_3$): ^1H, δ 7.35 (m, 10 H, Ph), 5.50 (dd, 2 H, CH, $^3J_{HH} = 8.6$), 4.60 (dd, 2 H, CH_2, $^2J_{HH} = 8.6$, $^3J_{HH} = 8.6$) and 4.10 (dd, 2 H, CH_2, $^2J_{HH} = 8.6$, $^3J_{HH} = 8.6$ Hz); $^{13}C\text{-}\{^1H\}$, δ 141.7 (*ipso*-C of Ph), 128.8 (*o*-C of Ph), 128.9 (*m*-C of Ph), 126.0 (*p*-C of Ph), 78.9 (CH) and 72.9 (CH_2); $^{11}B\text{-}\{^1H\}$, δ 28.9 (br s). Mass spectrum: *m*/*z* 294 (M^+, 100%); high resolution, $C_{16}H_{16}B_2O_4$ requires 294.123, found 294.124 (Found: C, 64.4; H, 6.0. $C_8H_8BO_2$ requires C, 65.4; H, 5.5%). $[\alpha]_D^{20} = 6.81$ (*c* = 0.0048, CH_2Cl_2).

$B_2(R,R\text{-}O_2CHPhCHPh)_2$ **3**. A solution of $B_2(NMe_2)_4$ (0.280 g, 1.4 mmol) in Et_2O (10 cm^3) was added to a suspension of *R*,*R*-1,2-diphenylethane-1,2-diol (0.606 g, 12.8 mmol) in Et_2O (10 cm^3) and the reaction mixture stirred for 18 h. After this time a solution of HCl (7.5 cm^3 of a 1.0 M solution in Et_2O) was added and the reaction mixture stirred for 6 h resulting in the formation of a white precipitate. The reaction mixture was then filtered, the residual solid being washed with Et_2O (2 × 5 cm^3) affording a colourless filtrate from which all volatiles were removed by vacuum affording crude compound **3** as a white solid. Washing with acetonitrile (3 × 3 cm^3) and recrystallisation from CH_2Cl_2–hexane mixtures afforded **3** as large colourless crystals (yield = 0.311 g, 50%). NMR ($CDCl_3$): ^1H, δ 7.35 (m, 20 H, Ph) and 5.30 (s, 4 H, CH); $^{13}C\text{-}\{^1H\}$, δ 139.8 (*ipso*-C of Ph), 128.8 (*m*-C of Ph), 128.4 (*o*-C of Ph), 126.1 (*p*-C of Ph) and 86.8 (CH); $^{11}B\text{-}\{^1H\}$, δ 29.4 (br s). Mass spectrum: *m*/*z* 446 (M^+, 60%); high resolution, $C_{28}H_{24}B_2O_4$ requires 446.186, found 446.187 (Found: C, 74.9; H, 5.6. $C_{14}H_{12}BO_2$ requires C, 75.4; H, 5.4%). $[\alpha]_D^{20} = 2.21$ (*c* = 0.0022, CH_2Cl_2).

$B_2(O_2C_{20}H_{12})_2$ **4**. A solution of $B_2(NMe_2)_4$ (0.210 g, 1.0 mmol) in Et_2O (10 cm^3) was added to a suspension of (±)-1,1′-bi-2-naphthol (0.600 g, 2.1 mmol) in Et_2O (10 cm^3) and the reaction mixture stirred for 18 h. After this time HCl (7.5 cm^3 of a 1.0 M solution in Et_2O) was added and the reaction mixture stirred for 6 h. All volatiles were then removed from the reaction mixture by vacuum and the resulting white solid extracted with warm toluene (3 × 5 cm^3). Evaporation and recrystallisation from toluene afforded compound **4** as colourless crystals, one of which was used for X-ray diffraction which showed the presence of toluene of crystallisation (yield 0.410 g, 65%). NMR ($CDCl_3$): ^1H, δ 7.94 (dd, 8 H, $C_{10}H_6$, $^3J_{HH} = 8.5$), 7.43 (dd, 4 H, $C_{10}H_6$, $^3J_{HH} = 8.5$), 7.23 (dd, 4 H, $C_{10}H_6$, $^3J_{HH} = 8.5$), 7.05 (d, 4 H, $C_{10}H_6$, $^3J_{HH} = 8.5$) and 6.93 (d, 4 H, $C_{10}H_6$, $^3J_{HH} = 8.5$ Hz); $^{13}C\text{-}\{^1H\}$, δ 152.4, 134.1, 131.0, 130.8, 128.0, 127.0, 126.4, 125.2, 120.5 and 120.4 ($C_{10}H_6$); $^{11}B\text{-}\{^1H\}$, δ 30.9 (br s). Mass spectrum: *m*/*z* 591 (M^+, 100%); high resolution, $C_{40}H_{24}B_2O_4$ requires 590.186, found 590.187 (Found: C, 82.1; H, 4.4. $C_{40}H_{24}B_2O_4{\cdot}C_7H_8$ requires C, 82.7; H, 4.7%).

(*b*) Platinum bis(boryls). *cis*-$[Pt(PPh_3)_2\{B[R,R\text{-}O_2CH(CO_2Me)CH(CO_2Me)]\}_2]$. A solution of $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ (0.100 g, 0.10 mmol) in toluene (5 cm^3) was added to a solution of compound **1** (0.050 g, 0.10 mmol) in toluene (5 cm^3) and the resulting reaction mixture stirred for 2 h. After this time the solvent volume was reduced to about 5 cm^3 and an overlayer of hexane (10 cm^3) was added. Cooling to −30 °C for 2–3 d afforded **5** as a colourless crystalline solid which was filtered off and washed with hexane (2 × 5 cm^3) (yield 0.060 g, 40%). One of the crystals present was used for X-ray diffraction. NMR ($[^2H_8]$toluene): ^1H, δ 7.36 (m, 12 H, PPh_3), 7.08 (m, 18 H, PPh_3), 4.95 (s, 4 H, C*H*CO_2Me) and 3.45 (s, 12 H, CHCO_2*Me*); $^{13}C\text{-}\{^1H\}$, δ 171.3 (*C*O_2Me), 135.9 (t, *o*-C of PPh_3), 135.2 (t, *ipso*-C of PPh_3), 129.4 (s, *p*-C of PPh_3), 128.5 (t, *m*-C of PPh_3), 78.0

(*C*HCO$_2$Me) and 51.9 (CHCO$_2$*Me*); ^{11}B-{^{1}H}, δ 48.1 (br s); ^{31}P-{^{1}H}, δ 29.7 (t, 2P, $^1J_{PtP}$ = 1634 Hz) (Found: C, 51.2; H, 3.6. $C_{48}H_{46}B_2O_{12}P_2Pt$ requires C, 52.7; H, 4.2%). Crystals were shown by X-ray diffraction to be a toluene solvate but this solvent was readily lost on vacuum pumping, the calculated analytical data being quoted for the unsolvated material.

cis-[Pt(PPh$_3$)$_2${B(*S*-O$_2$CH$_2$CHPh)}$_2$]. A solution of [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)] (0.130 g, 0.17 mmol) in toluene (5 cm^3) was added to a solution of compound **2** (0.050 g, 0.17 mmol) in toluene (5 cm^3) and the resulting reaction mixture stirred for 2 h. After this time the solvent volume was reduced to about 5 cm^3 and an overlayer of hexane (10 cm^3) was added. Cooling to −30 °C for 2–3 d afforded the complex as a colourless crystalline solid which was filtered off and washed with hexane (2 × 5 cm^3) (yield 0.088 g, 40%). X-Ray-quality crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution. NMR ([$^2H_8$]toluene): ^{1}H, δ 7.25 (m, 40 H, PPh$_3$), 4.95 (dd, 2 H, CH, $^3J_{HH}$ = 8.1), 4.07 (dd, 2 H, CH$_2$, $^2J_{HH}$ = 8.1, $^3J_{HH}$ = 8.1) and 3.70 (dd, 2 H, CH$_2$, $^2J_{HH}$ = 8.1, $^3J_{HH}$ = 8.1 Hz); ^{13}C-{^{1}H}, δ 142.7 (*ipso*-C of Ph), 134.8 (t, *o*-C of PPh$_3$), 134.8 (t, *ipso*-C of PPh$_3$), 127.6 (*p*-C of PPh$_3$), 127.5 (*o*-C of Ph), 126.4 (*m*-C of PPh$_3$), 125.2 (*m*-C of Ph), 124.4 (*p*-C of Ph), 75.9 (CH) and 70.6 (CH$_2$); ^{11}B-{^{1}H}, δ 48.2 (br s); ^{31}P-{^{1}H}, δ 30.8 (t, 2P, $^1J_{PtP}$ = 1578 Hz) (Found: C, 62.1; H, 4.8. $C_{52}H_{46}B_2O_4P_2Pt$ requires C, 61.6; H, 4.6%). Crystals were shown by X-ray diffraction to be a CH_2Cl_2 solvate but this solvate was readily lost on vacuum pumping, the calculated analytical data being quoted for the unsolvated material.

cis-[Pt(PPh$_3$)$_2${B(*R*,*R*-O$_2$CHPhCHPh)}$_2$]. This complex was prepared in a manner analogous to that described above, although it was not isolated and was characterised in solution *in situ* by ^{11}B and ^{31}P NMR spectroscopy. NMR (C_6D_6): ^{11}B-{^{1}H}, δ 47.3 (br s); ^{31}P-{^{1}H}, δ 29.7 (t, 2P, $^1J_{PtP}$ = 1584 Hz).

(*c*) Diene diboration. A representative procedure for the platinum-catalysed diene diboration reactions is given below. For each reaction discussed in the text full spectroscopic data are given together with details on reaction time, yield and d.e. (calculated on the basis of ^{1}H NMR integrations).

To a Young's tap tube charged with compound **3** (0.050 g, 0.11 mmol) and [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)] (5 mol %), toluene (5 cm^3) was added and the reaction allowed to stand for 15 min. After this time cyclohexadiene (16 μl, 0.17 mmol) was added by syringe and the reaction was then placed in an oil-bath at 80 °C for 2 d. All volatiles were then removed by vacuum affording a crude product as a pale red oil. Extraction into hexane and subsequent removal of the solvent by vacuum gave the product as a colourless oil (yield = 0.049 g, 75%).

Compound **5**: reaction time 12 h, yield 70%, d.e. 20%. NMR (C_6D_6): (major isomer), ^{1}H, δ 5.88 (m, 1 H, HC=), 5.75 (m, 1 H, =CH), 5.02 (s, 2 H, C*H*CO$_2$Me), 4.98 (s, 2 H, C*H*CO$_2$Me), 3.31 (s, 12 H, CO$_2$*Me*), 2.60 (m, 1 H, C*H*Me), 2.15 (m, 2 H, CH$_2$) and 1.45 (d, 3 H, Me); (minor isomer), ^{1}H, δ 5.88 (m, 1 H, HC=), 5.75 (m, 1 H, =CH), 5.01 (s, 2 H, C*H*CO$_2$Me), 4.98 (s, 2 H, C*H*CO$_2$Me), 3.31 (s, 12 H, CO$_2$Me), 2.60 (m, 1 H, C*H*Me), 2.15 (m, 2 H, CH$_2$) and 1.42 (d, 3 H, Me). Mass spectrum (CI, NH$_3$): *m*/*z* 460 (M^+ + NH$_4$); high resolution, $C_{17}H_{25}B_2O_{12}$ requires 442.145, found 442.144.

Compound **6**: reaction time 48 h, yield 60%, d.e. 0%. NMR (C_6D_6): (isomer a), ^{1}H, δ 7.40 (m, 10 H, Ph), 6.15 (ddt, 1 H, CH$_2$C*H*=, $^3J_{HH}$ = 10.5, 4.1, $^4J_{HH}$ = 4.0), 5.94 (dd, 1 H, =C*H*CHMe, $^3J_{HH}$ = 10.5, 9.0), 5.20 (m, 2 H, PhC*H*O), 4.31 (m, 2 H, CH$_2$O), 4.00 (m, 2 H, CH$_2$O), 2.81 (ddq, 1 H, C*H*Me, $^3J_{HH}$ = 9.0, 7.1, $^4J_{HH}$ = 4.0), 2.35 (d, 2 H, =CHCH_2, $^3J_{HH}$ = 4.1 Hz) and 1.55 (d, 3 H, Me, $^3J_{HH}$ = 7.1 Hz); ^{13}C-{^{1}H}, δ 142.2, 142.0 (*ipso*-C of Ph), 132.7 (CH$_2$*C*H=), 128.8, 128.7 (*o*-C of Ph), 125.6, 125.5 (*m*-C of Ph), 123.5 (*p*-C of Ph), 123.4 (=*C*HCHMe), 78.4, 78.3 (Ph*C*HO), 73.0, 72.9 (CH$_2$O) and 16.4 (Me); ^{11}B-{^{1}H}, δ 32.4 (br s); (isomer b), ^{1}H, δ 7.40 (m, 10 H, Ph), 6.14 (ddt, 1 H, CH$_2$C*H*=, $^3J_{HH}$ = 10.5, 4.1, $^4J_{HH}$ = 4.0), 5.95 (dd, 1 H =C*H*CHMe, $^3J_{HH}$ = 10.5, 9.0 Hz), 5.20 (m, 2 H, PhC*H*O), 4.31 (m, 2 H, CH$_2$O), 4.00 (m, 2 H, CH$_2$O), 2.81 (ddq, 1 H, C*H*Me, $^3J_{HH}$ = 9.0, 7.1, $^4J_{HH}$ = 4.0), 2.35 (d, 2 H, =CHCH_2, $^3J_{HH}$ = 4.1) and 1.55 (d, 3 H, Me, $^3J_{HH}$ = 7.1 Hz); ^{13}C-{^{1}H}, δ 142.1, 142.0 (*ipso*-C of Ph), 132.6 (CH$_2$*C*H=), 128.8, 128.7 (*o*-C of Ph), 125.7, 125.6 (*m*-C of Ph), 123.5 (*p*-C of Ph), 123.4 (=*C*HCHMe), 78.5, 78.4 (Ph*C*HO), 73.0, 72.9 (CH$_2$O) and 16.4 (Me); ^{11}B-{^{1}H}, δ 32.4 (br s). Mass spectrum (EI): *m*/*z* 347 (M^+ − CH$_3$, 70%).

Compound **7**: reaction time 12 h, yield 80%, d.e. 10%. NMR (C_6D_6): (major isomer), ^{1}H, δ 7.30 (m, 20 H, Ph), 5.71 (m, 1 H, =CH), 5.60 (m, 1 H, =CH), 5.14 (s, 2 H, PhC*H*O), 5.12 (s, 2 H, PhC*H*O), 2.55 (m, 1 H, C*H*Me), 2.07 (m, 2 H, CH$_2$) and 1.29 (d, 3 H, CH*Me*, $^3J_{HH}$ = 7.2 Hz); ^{13}C-{^{1}H}, δ 140.6, 140.3 (*ipso*-C of Ph), 132.5 (=CH), 128.7 (*o*-C of Ph), 128.2 (*m*-C of Ph), 125.8, 125.7 (*p*-C of Ph), 123.0 (=CH), 86.6 (Ph*C*HO), 86.5 (Ph*C*HO) and 16.2 (Me); ^{11}B-{^{1}H}, δ 32.3 (br s); (minor isomer), ^{1}H, δ 7.30 (m, 20 H, Ph), 5.71 (m, 1 H, =CH), 5.60 (m, 1 H, =CH), 5.14 (s, 2 H, PhC*H*O), 5.13 (s, 2 H, PhC*H*O), 2.55 (m, 1 H, C*H*Me), 2.07 (m, 2 H, CH$_2$), 1.28 (d, 3 H, CH*Me*, $^3J_{HH}$ = 7.3 Hz); ^{13}C-{^{1}H}, δ 140.6, 140.3 (*ipso*-C of Ph), 132.3 (=CH), 128.7 (*o*-C of Ph), 128.2 (*m*-C of Ph), 125.7, 125.6 (*p*-C of Ph), 122.7 (=CH), 86.4 (Ph*C*HO), 86.3 (Ph*C*HO) and 16.1 (Me); ^{11}B-{^{1}H}, δ 32.3 (br s). Mass spectrum (CI, CH$_4$): *m*/*z* 352 (M^+ + H, 40%); high resolution, $C_{33}H_{32}B_2O_4$ requires 514.249, found 514.248.

Compound **9**: reaction time 4 d, yield 55%, d.e. 10%. NMR ($CDCl_3$): (major isomer), ^{1}H, δ 7.36 (m, 10 H, Ph), 5.65 (m, 1 H, CH$_2$C*H*=), 5.45 (m, 1 H, =C*H*CHEt), 5.40 (m, 2 H, PhC*H*O), 4.50 (m, 2 H, CH$_2$O), 4.00 (m, 2 H, CH$_2$O), 2.21 (m, 1 H, C*H*Et), 1.89 (d, 2 H, =CHCH_2, $^3J_{HH}$ = 7.4 Hz), 1.71 (m, 1 H, CH_2Me), 1.55 (m, 1 H, CH_2Me) and 0.95 (t, 3 H, Me, $^3J_{HH}$ = 7.2 Hz); ^{13}C-{^{1}H}, δ 141.3, 141.1 (*ipso*-C of Ph), 130.6 (CH$_2$*C*H=), 128.6 (*o*-C of Ph), 128.1 (*m*-C of Ph), 125.4, 125.3 (*p*-C of Ph), 123.6 (=*C*HCHEt), 78.3, 78.2 (Ph*C*HO), 72.8, 72.7 (CH$_2$O), 24.3 (*C*H$_2$CH$_3$) and 13.8 (CH$_2$*C*H$_3$); ^{11}B-{^{1}H}, δ 32.3 (br s); (minor isomer), ^{1}H, δ 7.36 (m, 10 H, Ph), 5.65 (m, 1 H, CH$_2$C*H*=), 5.45 (m, 1 H, =C*H*CHEt), 5.40 (m, 2 H, PhC*H*O), 4.50 (m, 2 H, CH$_2$O), 4.00 (m, 2 H, CH$_2$O), 2.21 (m, 1 H, C*H*Et), 1.89 (d, 2 H, =CHCH_2, $^3J_{HH}$ = 7.4), 1.71 (m, 1 H, CH_2Me), 1.55 (m, 1 H, CH_2Me) and 0.95 (t, 3 H, Me, $^3J_{HH}$ = 7.2 Hz); ^{13}C-{^{1}H}, δ 141.3, 141.1 (*ipso*-C of Ph), 130.6 (CH$_2$*C*H=), 128.6 (*o*-C of Ph), 128.1 (*m*-C of Ph), 125.4, 125.3 (*p*-C of Ph), 123.6 (=*C*HCHEt), 78.3, 78.2 (Ph*C*HO), 72.9, 72.6 (CH$_2$O), 24.3 (*C*H$_2$CH$_3$) and 13.8 (CH$_2$*C*H$_3$); ^{11}B-{^{1}H}, δ 32.3 (br s). Mass spectrum (EI): *m*/*z* 375 (M^+ − H, 20%); high resolution, $C_{22}H_{25}B_2O_4$ requires 375.194, found 375.194.

Compound **10**: reaction time 48 h, yield 90%, d.e. 0%. NMR ($CDCl_3$): (major isomer), ^{1}H, δ 7.30 (m, 20 H, Ph), 5.77 (ddd, 1 H, CH$_2$C*H*=, $^3J_{HH}$ = 10.5, 7.2, 6.2), 5.56 (dd, 1 H, =C*H*CHEt, $^3J_{HH}$ = 10.5, 7.6), 5.13 (s, 2 H, PhC*H*O), 5.12 (s, 2 H, PhC*H*O), 2.42 (ddd, 1 H, C*H*Et, $^3J_{HH}$ = 7.6, 6.8, 3.4), 2.12 (dd, 1 H, CH_2CH=, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 7.2), 2.05 (dd, 1 H, CH_2CH=, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 6.2), 1.83 (ddq, 1 H, CH_2CH$_3$, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 7.3, 6.8), 1.63 (ddq, 1 H, CH_2CH$_3$, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 7.3, 3.4) and 1.07 (t, 3 H, CH$_2$CH_3, $^3J_{HH}$ = 7.3 Hz); ^{13}C-{^{1}H}, δ 140.6, 140.3 (*ipso*-C of Ph), 130.8 (CH$_2$*C*H=), 128.8, 128.7 (*o*-C of Ph), 128.2, 128.2 (*m*-C of Ph), 125.7, 125.6 (*p*-C of Ph) 123.8 (=*C*HCHEt), 86.5, 86.4 (Ph*C*HO), 24.6 (*C*H$_2$CH$_3$) and 13.9 (CH$_2$*C*H$_3$); ^{11}B-{^{1}H}, δ 32.1 (br s); (minor isomer), ^{1}H, δ 7.30 (m, 20 H, Ph), 5.76 (ddd, 1 H, CH$_2$C*H*=, $^3J_{HH}$ = 10.5, 7.2, 6.2), 5.56 (dd, 1 H, =C*H*CHEt, $^3J_{HH}$ = 10.5, 7.6), 5.13 (s, 2 H, PhC*H*O), 5.11 (s, 2 H, PhC*H*O), 2.42 (m, 1 H, C*H*Et), 2.12 (dd, 1 H, CH_2CH=, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 7.2), 2.05 (dd, 1 H, CH_2CH=, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 6.2), 1.83 (m, 1 H, CH_2CH$_3$), 1.63 (m, 1 H, CH_2CH$_3$) and 1.07 (t, 3 H, CH$_2$CH_3, $^3J_{HH}$ = 7.3 Hz); ^{13}C-{^{1}H}, δ 140.6, 140.3 (*ipso*-C of Ph), 130.6 (CH$_2$*C*H=), 128.7, 128.6 (*o*-C of Ph), 128.2, 128.1 (*m*-C of Ph), 125.7, 125.6 (*p*-C of Ph), 123.6 (=*C*HCHEt), 86.5, 86.4 (Ph*C*HO), 24.5 (*C*H$_2$CH$_3$) and 14.0 (CH$_2$*C*H$_3$); ^{11}B-{^{1}H}, δ 32.1 (br s). Mass spectrum (EI):

Table 3 Crystallographic data for the structure determinations of compounds **1**–**3**, **4**·1.0C_6H_5Me, *cis*-[Pt(PPh_3)$_2${B[*R*,*R*-$O_2CH(CO_2Me)$-$CH(CO_2Me)$]}$_2$]·1.5 C_6H_5Me and *cis*-[Pt(PPh_3)$_2${B(*S*-O_2CH_2CHPh)}$_2$]·2.0CH_2Cl_2

	1	**2**	**3**	**4**·1.0C_6H_5Me	*cis*-[Pt(PPh_3)$_2$-{B[*R*,*R*-$O_2CH(CO_2$-Me)$CH(CO_2Me)$]}$_2$]·1.5C_6H_5Me	*cis*-[Pt(PPh_3)$_2$-{B(*S*-O_2CH_2-CHPh)}$_2$]·2.0CH_2Cl_2
Crystal data						
Empirical formula	$C_{12}H_{16}B_2O_{12}$	$C_{16}H_{16}B_2O_4$	$C_{28}H_{24}B_2O_4$	$C_{47}H_{32}B_2O_4$	$C_{58.5}H_{58}B_2O_{12}P_2Pt$	$C_{54}H_{50}B_2Cl_4O_4P_2Pt$
M	373.87	587.82	446.09	682.35	1231.70	1183.39
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P4_12_12$ (no. 92)	$P2_1/n$ (no. 14)	$P2_12_12$ (no. 18)	$C2$ (no. 5)
a/Å	9.0355(8)	9.6718(12)	12.731(2)	14.063(2)	15.668(2)	38.311(3)
b/Å	16.9385(15)	11.8885(12)	12.731(2)	10.8214(11)	28.485(3)	12.1983(13)
c/Å	22.3820(19)	26.482(5)	14.653(4)	24.853(5)	12.696(2)	11.1210(7)
β/°				105.194(10)		94.350(7)
U/Å^{-3}	3425.5(5)	3045.0(8)	2374.8(7)	3649.9(10)	5666.0(12)	5180.9(8)
Z	8	8	4	4	4	4
μ/mm^{-1}	0.129	0.089	0.081	0.077	2.593	3.021
Data collection and reduction						
T/K	160(2)	173(2)	292(2)	173(2)	173(2)	173(2)
Reflections collected	21 864	19 284	3020	18 479	35 886	16 962
Unique reflections with $I > -3\sigma(I)$	8031	6936	2083	6411	12 895	11 487
R_{int}	0.0400	0.0348	0.0350	0.0365	0.0631	0.0148
Solution and refinement						
Absolute structure parameter	−0.26(74)	−0.79(71)	0(2)	—	−0.010(7)	−0.021(3)
Final *R*	0.0512	0.0382	0.0384	0.0546	0.0442	0.0219

m/*z* 528 (M^+, 1%); high resolution, $C_{34}H_{34}B_2O_4$ requires 528.264, found 528.265.

Compound **11**: reaction time 12 h, yield 70%, d.e. n/a. NMR ($CDCl_3$): ^{1}H, δ 7.05 (m, 8 H, 1,2-$O_2C_6H_4$), 5.80 (dddd, 1 H, CH_2CH=, $^3J_{HH}$ = 10.3, 16.0, 16.3, $^4J_{HH}$ = 5.7), 5.59 (dd, 1 H, =C*H*CHEt, $^3J_{HH}$ = 10.3, 9.8), 2.57 (dddd, 1 H, C*H*Et, $^3J_{HH}$ = 8.9, 9.8, 13.9, $^4J_{HH}$ = 5.7), 2.34 (dd, 1 H, =CHCH_2, $^2J_{HH}$ = 8.0, $^3J_{HH}$ = 16.3), 2.23 (dd, 1 H, =CHCH_2, $^2J_{HH}$ = 8.0, $^3J_{HH}$ = 16.0), 1.87 (ddq, 1 H, CH_2CH$_3$, $^2J_{HH}$ = 6.5, $^3J_{HH}$ = 13.9, 6.1), 1.67 (ddq, 1 H, CH_2CH$_3$, $^2J_{HH}$ = 6.5, $^3J_{HH}$ = 8.9, 6.1) and 1.01 (t, 3 H, CH$_2$CH_3, $^3J_{HH}$ = 6.1 Hz); ^{13}C-{^{1}H}, δ 148.2, 148.1 (C^{1,2} of 1,2-$O_2C_6H_4$), 134.5 (=*C*HCHEt), 128.1 (CH$_2$*C*H=), 122.5, 122.4 (C^{4,5} of 1,2-$O_2C_6H_4$), 122.3, 122.2 (C^{3,6} of 1,2-$O_2C_6H_4$), 24.1 (*C*H$_2$CH$_3$) and 13.7 (CH$_2$*C*H$_3$); ^{11}B-{^{1}H}, δ 32.4 (br s). Mass spectrum (EI): *m*/*z* 320 (M^+, 10%); high resolution, $C_{18}H_{18}B_2O_4$ requires 320.139, found 320.139.

Compound **12**: reaction time 10 d, yield 50%, d.e. 0%. NMR (C_6D_6): (major isomer), ^{1}H, δ 7.35 (m, 10 H, Ph), 5.34 (m, 2 H, PhC*H*O), 5.19 (dq, 1 H, =CH, $^3J_{HH}$ = 10.0, 1.5), 4.47 (m, 2 H, CH$_2$O), 3.95 (m, 2 H, CH$_2$O), 2.19 (dq, 1 H, C*H*Me, $^3J_{HH}$ = 10.0, 7.3), 2.00 (d, 1 H, =CMeCH_2, $^2J_{HH}$ = 15.5), 1.80 (d, 1 H, =CMeCH_2, $^2J_{HH}$ = 15.5), 1.85 (d, 3 H, MeC=, $^3J_{HH}$ = 1.5) and 1.15 (d, 3 H, CHMe, $^3J_{HH}$ = 7.3 Hz); ^{13}C-{^{1}H}, δ 142.2, 142.1 (*ipso*-C of Ph), 130.8 (Me*C*=), 128.3 (*o*-C of Ph), 128.3 (*m*-C of Ph), 126.8 (=CH), 125.7, 125.6 (*p*-C of Ph), 78.5, 78.4, (Ph*C*HO), 73.0, 72.9 (CH$_2$O), 26.2 (*Me*C=) and 16.7 (CH*Me*); ^{11}B-{^{1}H}, δ 32.5 (br s); (minor isomer), ^{1}H, δ 7.35 (m, 10 H, Ph), 5.34 (m, 2 H, PhC*H*O), 5.21 (dq, 1 H, =CH, $^3J_{HH}$ = 10.0, 1.5), 4.47 (m, 2 H, CH$_2$O), 3.95 (m, 2 H, CH$_2$O), 2.23 (dq, 1 H, C*H*Me, $^3J_{HH}$ = 10.0, 7.3), 2.00 (d, 1 H, =CMeCH_2, $^2J_{HH}$ = 15.5), 1.89 (d, 1 H, =CMeCH_2, $^2J_{HH}$ = 15.5), 1.85 (d, 3 H, =CMe, $^3J_{HH}$ = 1.5) and 1.16 (d, 3 H, CHMe, $^3J_{HH}$ = 7.3 Hz); ^{13}C-{^{1}H}, δ 142.2, 142.1 (*ipso*-C of Ph), 131.0 (Me*C*=), 128.3 (*o*-C of Ph), 128.3 (*m*-C of Ph), 126.7 (=CH), 125.7, 125.5 (*p*-C of Ph), 78.5, 78.3, (Ph*C*HO), 72.8, 72.7 (CH$_2$O), 26.1 (*Me*C=) and 16.6 (CH*Me*); ^{11}B-{^{1}H}, δ 32.5 (br s). Mass spectrum (EI): *m*/*z* 375 (M^+ − H, 20%); high resolution, $C_{22}H_{25}B_2O_4$ requires 375.194, found 375.194.

Compound **13**: reaction time 4 h, yield 60%, d.e. n/a. NMR ($CDCl_3$): ^{1}H, δ 5.82 (d, 1 H, =CH, $^3J_{HH}$ = 10.0), 5.77 (d, 1 H, =CH, $^3J_{HH}$ = 10.0 Hz), 4.90 (s, 4 H, C*H*CO$_2$Me), 3.83 (s, 12 H, OMe), 2.05 (m, 2 H, =CHC*H*) and 1.85 (m, 4 H, CH$_2$); ^{13}C-{^{1}H}, δ 169.9 (C=O), 169.8 (C=O), 125.9 (=CH), 125.7 (=CH), 77.5 (*C*HCO$_2$Me), 77.4 (*C*HCO$_2$Me), 53.1 (OMe), 53.0 (OMe) and 23.4 (CH$_2$); ^{11}B-{^{1}H}, δ 33.5 (br s). Mass spectrum (EI): *m*/*z* 454 (M^+, 20%); high resolution, $C_{18}H_{24}B_2O_{12}$ requires 454.145, found 454.146.

Compound **14**: reaction time 12 h, yield 80%, d.e. n/a. NMR (C_6D_6): ^{1}H, δ 7.20 (s, 10 H, Ph), 6.47 (d, 1 H, =CH, $^3J_{HH}$ = 10.5), 6.45 (d, 1 H, =CH, $^3J_{HH}$ = 10.5), 5.08 (dd, 1 H, PhC*H*O, $^3J_{HH}$ = 7.8, 4.2), 5.06 (dd, 1 H, PhC*H*O, $^3J_{HH}$ = 7.8, 4.2), 4.14 (dd, 2 H, OCH$_2$, $^2J_{HH}$ = 7.8, $^3J_{HH}$ = 7.8), 3.81 (dd, 1 H, OCH$_2$, $^2J_{HH}$ = 7.8, $^3J_{HH}$ = 4.2), 3.79 (dd, 1 H, OCH$_2$, $^2J_{HH}$ = 7.8, $^3J_{HH}$ = 4.2 Hz), 2.45 (m, 2 H, CH$_2$), 2.35 (m, 2 H, =CHC*H*) and 2.18 (m, 2 H, CH$_2$); ^{13}C-{^{1}H}, δ 142.1 (*ipso*-C of Ph), 128.7 (*o*-C of Ph), 126.9 (=CH), 126.8 (=CH), 125.6 (*m*-C of Ph), 125.5 (*p*-C of Ph), 78.5 (Ph*C*HO), 73.1 (OCH$_2$), 73.0 (OCH$_2$) and 24.5 (CH$_2$); ^{11}B-{^{1}H}, δ 32.2 (br s). Mass spectrum (EI): *m*/*z* 374 (M^+, 5%); high resolution, $C_{22}H_{24}B_2O_4$ requires 374.186, found 374.185.

Compound **15**: reaction time 12 h, yield 75%, d.e. n/a. NMR ($CDCl_3$): ^{1}H, δ 7.30 (m, 20 H, Ph), 6.00 (d, 1 H, =CH, $^3J_{HH}$ = 10.5), 5.96 (d, 1 H, =CH, $^3J_{HH}$ = 10.5 Hz), 5.18 (s, 2 H, PhC*H*O), 5.17 (s, 2 H, PhC*H*O), 2.21 (m, 2 H, =CHC*H*) and 2.04 (m, 4 H, CH$_2$); ^{13}C-{^{1}H}, δ 140.5 (*ipso*-C of Ph), 128.8 (*o*-C of Ph), 128.2 (*m*-C of Ph), 126.6 (=CH), 126.4 (=CH), 125.7 (*p*-C of Ph), 86.6 (Ph*C*HO), 86.5 (Ph*C*HO), 24.1 (CH$_2$) and 24.0 (CH$_2$); ^{11}B-{^{1}H}, δ 31.8 (br s). Mass spectrum (EI): *m*/*z* 526 (M^+, 5%); high resolution, $C_{34}H_{32}B_2O_4$ requires 524.256, found 524.256.

Compound **16**: reaction time 12 h, yield 90%, d.e. n/a. NMR ($CDCl_3$): ^{1}H, δ 7.20 (dd, 4 H, H^{3,6} of 1,2-$O_2C_6H_4$, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 3.4), 7.05 (dd, 4 H, H^{4,5} of 1,2-$O_2C_6H_4$, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 3.4 Hz), 6.05 (s, 2 H, =CH), 2.45 (m, 2 H, =CHC*H*) and 2.05 (m, 4 H, CH$_2$); ^{13}C-{^{1}H}, δ 148.1 (C^{1,2} of 1,2-$O_2C_6H_4$), 126.1 (=CH), 122.6 (C^{4,5} of 1,2-$O_2C_6H_4$), 112.4 (C^{3,6} of 1,2-

$O_2C_6H_4$) and 23.6 (CH_2); ^{11}B-{^1H}, δ 32.3 (br s). Mass spectrum (EI): *m*/*z* 318 (M^+, 100%); high resolution, $C_{18}H_{16}B_2O_4$ requires 318.123, found 318.124.

X-Ray crystallography

Details of the structure determination of compounds **1**–**3**, **4**·C_6H_5Me, *cis*-[Pt(PPh_3)$_2${B[*R*,*R*-$O_2CH(CO_2Me)CH(CO_2Me)$]}$_2$]·1.5C_6H_5Me and *cis*-[Pt(PPh_3)$_2${B(*S*-O_2CH_2CHPh)}$_2$]·2.0CH_2Cl_2 are given in Table 3. All hydrogen atoms were assigned isotropic thermal parameters and were constrained to idealised geometries. Absorption effects were corrected for the latter two structures on the basis of multiple equivalent reflections. An extinction parameter, *x*, of the form $k[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-0.25}$ was refined to 0.0042(6) and 0.0032(6) for **1** and **4**·C_6H_5Me, respectively. In **4**·C_6H_5Me the bond lengths of the toluene solvate were restrained to idealised geometry. In *cis*-[Pt(PPh_3)$_2${B[*R*,*R*-$O_2CH(CO_2Me)CH(CO_2Me)$]}$_2$]·1.5C_6H_5Me one toluene was disordered over a two-fold axis and this was refined isotropically without any restraints. The second toluene molecule was constrained to idealised geometry. Unresolved disorder is probably present in one of the boryl ligands where O(11) and C(66) of the terminal OMe group have large U_{ij} values. In *cis*-[Pt(PPh_3)$_2${B(*S*-O_2CH_2CHPh)}$_2$]·2.0CH_2Cl_2 the solvent molecules were disordered and each chlorine was refined over two atomic positions. The first molecule, C(96)Cl(1)Cl(2), lay on a general position and the chlorine positions were refined in the occupancy ratio 73:27, whereas two CH_2Cl_2 molecules which lay on two-fold axes were refined in the occupancy ratio 50:50. Unresolved disorder is also apparent as shown by large U_{ij} values in both of the phenyl groups of the boryl ligands. The absolute structure[18] was confirmed by refinement for all compounds except **4**. Refinements converged to residuals given in Table 3.

CCDC reference number 186/915.

See http://www.rsc.org/suppdata/dt/1998/1431/ for crystallographic files in .cif format.

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References

1 T. Ishiyama, M. Yamamoto and N. Miyaura, *Chem. Commun.*, 1997, 689; C. N. Iverson and M. R. Smith, *Organometallics*, 1997, **16**, 2757.
2 (*a*) T. Ishiyama, N. Matsuda, N. Miyaura and A. Suzuki, *J. Am. Chem. Soc.*, 1993, **115**, 11 018; (*b*) T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki and N. Miyaura, *Organometallics*, 1996, **15**, 713; (*c*) C. N. Iverson and M. R. Smith, *J. Am. Chem. Soc.*, 1995, **117**, 4403; (*d*) C. N. Iverson and M. R. Smith, *Organometallics*, 1996, **15**, 5155; (*e*) G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg and N. C. Norman, *Organometallics*, 1996, **15**, 5137; (*f*) A. Maderna, H. Pritzkow and W. Siebert, *Angew. Chem., Int. Ed. Engl.*, 1995, **35**, 1501.
3 T. Ishiyama, M. Yamamoto and N. Miyaura, *Chem. Commun.*, 1996, 2073.
4 Y. G. Lawson, M. J. G. Lesley, T. B. Marder, N. C. Norman and C. R. Rice, *Chem. Commun.*, 1997, 2051.
5 S. Sakaki and T. Kikuno, *Inorg. Chem.*, 1997, **36**, 226; Q. Cui, D. G. Musaev and K. Morokuma, *Organometallics*, 1997, **16**, 1355.
6 W. Clegg, F. J. Lawlor, G. Lesley, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, A. J. Scott and F. E. S. Souza, *J. Organomet. Chem.*, in the press.
7 A. Kerr, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, P. L. Timms and G. R. Whittell, *Chem. Commun.*, 1998, 319.
8 H. Wadepohl, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2441; T. B. Marder and N. C. Norman, *Top. Catalysis*, eds. W. Leitner and D. G. Blackmond, Baltzer Science Publishers, Amsterdam, 1998, in the press; G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper and G. R. Whittell, *Chem. Rev.*, submitted.
9 T. B. Marder, N. C. Norman and C. R. Rice, *Tetrahedron Lett.*, 1998, **39**, 155.
10 F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, P. Nguyen, G. Lesley, T. B. Marder, J. A. Ashmore and J. C. Green, *Inorg. Chem.*, in the press.
11 W. Clegg, M. R. J. Elsegood, F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, A. J. Scott, P. Nguyen, N. J. Taylor and T. B. Marder, *Inorg. Chem.*, in the press.
12 H. Nöth, *Z. Naturforsch., Teil B*, 1984, **39**, 1463.
13 G. Lesley, T. B. Marder, N. C. Norman and C. R. Rice, *Main Group Chem. News*, 1997, **5**, 4.
14 K. Burgess and M. J. Ohlmeyer, *Chem. Rev.*, 1991, **91**, 1179; K. Burgess and W. A. van der Donk, *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, Wiley, Chichester, 1994, vol. 3, p. 1420; G. C. Fu, D. A. Evans and A. R. Muci, *Advances in Catalytic Processes*, ed. M. P. Doyle, JAI Press, Greenwich, CT, 1995, pp. 95–121; I. Beletskaya and A. Pelter, *Tetrahedron*, 1997, **53**, 4957.
15 R. J. Brotherton, J. L. McCloskey, L. L. Petterson and H. Steinberg, *J. Am. Chem. Soc.*, 1960, **82**, 6242.
16 M. Camalli, F. Caruso, S. Chaloupka, E. M. Leber, H. Rimml and L. M. Venanzi, *Helv. Chim. Acta*, 1990, **73**, 2263.
17 B. H. McKee, D. G. Gilheany and K. B. Sharpless, *Org. Synth.*, 1992, **70**, 47.
18 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

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