



Platinum Catalysed Diboration of Terminal Alkenes with Chiral Diborane(4) Compounds

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Abstract: Chiral diborane(4) compounds, synthesised from $B_2(NMe_2)_4$ and the relevant chiral diols, react with terminal alkenes in the presence of $Pt(dba)_2$ (dba = dibenzylidene acetone) affording 1,2-diboryl compounds which have diastereoselectivities up to 60% d.e.
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Asymmetric hydroboration of prochiral alkenes is now well established, the chiral induction being achieved by using either a chiral borane or a chiral catalyst. For example, the chiral borane *diisopinocampheylborane* (IPC_2BH) reacts with *Z*-alkenes to give, after oxidation, enantiomerically enriched alcohols,¹ whilst styrene has been shown to react with catecholborane ($HBcat$; $cat = 1,2-O_2C_6H_4$), in the presence of a rhodium/(*R*)-BINAP catalyst affording, after oxidation, the corresponding alcohol with an e.e. of 96% (*R*).² Large enantioselectivities were also observed in the rhodium catalysed reaction of catecholborane with *E*- $PhCH=CH(Bcat)$ in the presence of the chiral diphosphine (*S,S*)-chiraphos, the corresponding 1,2-*bis*-boronate ester being formed with an e.e. in excess of 70 %.³ *Bis*-boronate esters can, however, be prepared directly from unsaturated precursors and diborane(4) compounds as has been demonstrated for 1,3-dienes,⁴ alkynes⁵ and terminal alkenes⁶ which react, in the presence of a source of $Pt(0)$ (or $Rh(I)$ and $Au(I)$ sources in the case of alkenes^{6a}), to give either 1,4- (dienes) or 1,2- (alkynes and alkenes) *bis*-boronate esters. By analogy with the hydroboration studies outlined above, the potential clearly exists to carry out such diboration reactions asymmetrically using either chiral diborane(4) compounds or chiral metal catalysts. Herein we describe the results of studies of the former type.

The reaction of the chiral diols dimethyl-*L*-tartrate, (*S*)-1-phenylethane-1,2-diol or (*R,R*)-1,2-diphenylethane-1,2-diol with $B_2(NMe_2)_4$ afforded the corresponding chiral diborane(4) compounds $B_2\{R,R-OCH(CO_2Me)CH(CO_2Me)O\}_2$ **1**, $B_2(S-OCH_2CHPhO)_2$ **2** and $B_2(R,R-OCHPhCHPhO)_2$ **3** in excellent yields, full details of which will be reported elsewhere.⁷ Compounds **1** - **3** react with the alkenes 4-vinylanisole (**4**), 4'-vinylbiphenyl (**5**) and 2-vinylnaphthalene (**6**) in the presence of the phosphine-free platinum catalyst $[Pt(dba)_2]$ (dba = dibenzylidene acetone), recently employed by Miyaura and coworkers,^{6b} according to Scheme 1, the results of which are tabulated in Table 1.^{8,9}

The yields and diastereomeric excesses (d.e.) of the reactions shown in Scheme 1 and Table 1 were determined by 1H nmr spectroscopy. For example, the 1H nmr spectrum of **9** in C_6D_6 in the region of 1.95 -

2.20 ppm revealed two sets of doublets of doublets (Fig. 1), one major, δ 2.02, and one minor, δ 2.11, corresponding to one of the diastereotopic methylene protons of the central CHCH₂ group in each of the two product diastereomers, present in a ratio of about 4:1 for which the diastereomeric excess is therefore 60 %. The presence of two diastereomers in a 4:1 ratio was also evident from that part of the spectrum corresponding to the OCHPh protons. In general, it is apparent from Table 1 that the highest diastereoselectivities are found when the diborane(4) compound **3** is employed and whilst none of the d.e.'s is exceptional, the principle of asymmetric alkene diboration using chiral diborane(4) compounds has been demonstrated.

Related studies dealing with the asymmetric diboration of prochiral dienes will be reported elsewhere.⁷

Scheme 1

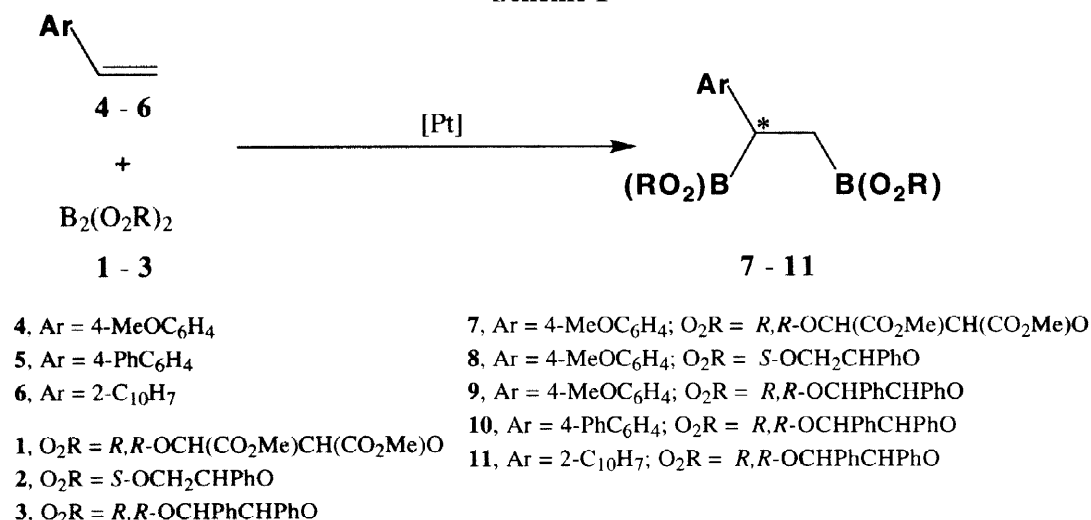


Table 1. Yield and % d.e. data for reactions between the terminal alkenes **4 - 6** and the chiral diborane(4) compounds **1 - 3**.

Alkene	B ₂ (O ₂ R) ₂	% Yield ^a	% d.e. ^a	Product
4	1	20	N/A ^b	7
4	2	60	5	8
4	3	80	60	9
5	3	40	50	10
6	3	60	10	11

^a Measured by ¹H nmr. ^b In this case, coincidence of the signals due to the two diastereomers in the ¹H nmr spectrum of the reaction prevented any accurate determination of the reaction d.e.

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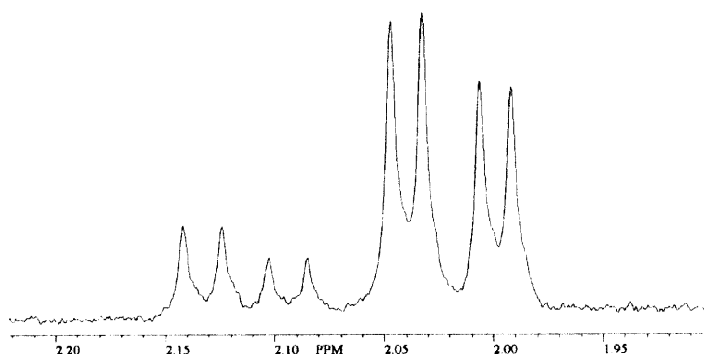


Figure 1. The ^1H nmr spectrum of **9** in C_6D_6 in the region of 1.95 - 2.20 ppm showing two sets of doublets of doublets (one major and one minor) corresponding to one of the diastereotopic methylene protons of the central CHCH_2 group in each of the two product diastereomers. The peak height asymmetry in each set is due to second order effects involving nearby coupled resonances not shown.

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8. In a typical preparation, a Youngs tap tube was charged with **3** (0.05 g, 0.11 mmol), $[\text{Pt}(\text{dba})_2]$ (5 mol%) and toluene (5 cm^3) and cooled to 0°C , to which a sample of 4-vinylanisole (0.020 cm^3 , 0.15 mmol) was then added. After 3 days at 4°C , the toluene was removed by vacuum leaving a dark brown solid from which the product was extracted with hexane (2 x 5 cm^3). After evaporation, **9** was obtained as a white solid (0.05 g, 80%) along with small amounts of the hydrolysis product $\{\text{B}(\text{OCHPhCHPhO})\}_2(\mu\text{-O})$.
Spectroscopic data: Compound **7**. ^1H nmr (400 MHz, CDCl_3): δ 7.20 (m, 4H, Ar); 5.49 (s, 4H, $\text{OCH}(\text{CO}_2\text{Me})\text{CH}(\text{CO}_2\text{Me})\text{O}^*$); 3.80 (s, 12H, CO_2CH_3)*; 3.70 (s, 3H, CH_3O); 2.80 (dd, 1H, $\text{ArCH}(\text{B})\text{CH}_2(\text{B})$, $^3J_{\text{HH}} = 9.3$ and 9.3 Hz)*; 1.60 (dd, 1H, $\text{ArCH}(\text{B})\text{CH}_2(\text{B})$, $^3J_{\text{HH}} = 9.3$ and 16.4 Hz)*;

1.40 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 9.3 and 16.4 Hz)*. ¹¹B-{¹H} nmr (128.15 MHz, CDCl₃): δ 33.5. Hrms calculated for C₂₁H₂₆B₂O₁₃ 508.157, found 508.156.

Compound **8**. ¹H nmr (400 MHz, CDCl₃): δ (Major diastereomer) 7.20 (m, 14H, Ar); 5.24 (m, 2H, OCHPhCH₂O)*; 4.52 (m, 2H, OCHPhCH₂O)*; 4.00 (m, 2H, OCHPhCH₂O)*; 3.83 (s, 3H, CH₃O); 2.79 (m, 1H, ArCH(B)CH₂(B))*; 1.59 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 5.1 and 10.3 Hz); 1.41 (m, 1H, ArCH(B)CH₂(B))* (Minor diastereomer) 7.20 (m, 14H, Ar); 5.24 (m, 2H, OCHPhCH₂O)*; 4.52 (m, 2H, OCHPhCH₂O)*; 4.00 (m, 2H, OCHPhCH₂O)*; 3.81 (s, 3H, CH₃O); 2.79 (m, 1H, ArCH(B)CH₂(B))*; 1.63 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 5.1 and 10.3 Hz); 1.41 (m, 1H, ArCH(B)CH₂(B))* ¹¹B-{¹H} nmr (128.15 MHz, CDCl₃): δ 33.2. Hrms calculated for C₂₅H₂₆B₂O₅ 428.197, found 428.197.

Compound **9** (Nmr data are reported here in CDCl₃ although the spectrum shown in Fig. 1 and discussed in the text was obtained in C₆D₆ since this solvent provided better chemical shift dispersion of the relevant signals). ¹H nmr (400 MHz, CDCl₃): δ (Major diastereomer) 6.80 (m, 24H, Ar); 5.13 (s, 2H, OCHPhCHPhO); 5.08 (s, 2H, OCHPhCHPhO); 3.81 (s, 3H, CH₃O)*; 3.20 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 11.5 and 5.9 Hz)*; 1.83 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 11.5 and 16.4 Hz); 1.60 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 5.9 and 16.4 Hz). (Minor diastereomer) 6.80 (m, 24H, Ar); 5.11 (s, 2H, OCHPhCHPhO); 5.06 (s, 2H, OCHPhCHPhO); 3.81 (s, 3H, CH₃O)*; 3.20 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 8.8 and 7.6 Hz)*; 1.80 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 8.8 and 14.2 Hz); 1.64 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 7.6 and 14.2 Hz). ¹¹B-{¹H} nmr (128.15 MHz, CDCl₃): δ 33.4. Hrms calculated for C₃₇H₃₄B₂O₅ 580.260, found 508.260.

Compound **10**. ¹H nmr (400 MHz, CDCl₃): δ (Major diastereomer) 7.40 (m, 29H, Ar); 5.16 (s, 2H, OCHPhCHPhO)*; 5.15 (s, 2H, OCHPhCHPhO); 3.12 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 11.6 and 5.8 Hz); 1.93 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 11.6 and 16.0 Hz); 1.67 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 5.8 and 16.0 Hz). (Minor diastereomer) 7.40 (m, 29H, Ar); 5.16 (s, 2H, OCHPhCHPhO)*; 5.13 (s, 2H, OCHPhCHPhO); 3.06 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 8.9 and 7.9 Hz); 1.87 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 8.9 and 15.1 Hz); 1.79 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 7.9 and 15.1 Hz). ¹¹B-{¹H} nmr (128.15 MHz, CDCl₃): δ 32.2. Hrms calculated for C₄₂H₃₆B₂O₃ 626.281, found 626.280.

Compound **11**. ¹H nmr (400 MHz, CDCl₃): δ (Major diastereomer) 7.30 (m, 27H, Ar); 5.16 (s, 2H, OCHPhCHPhO); 5.10 (s, 2H, OCHPhCHPhO); 3.20 (m, 1H, ArCH(B)CH₂(B))*; 1.93 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 8.3 and 15.8 Hz); 1.80 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 8.1 and 15.8 Hz). (Minor diastereomer) 7.30 (m, 27H, Ar); 5.14 (s, 2H, OCHPhCHPhO); 5.05 (s, 2H, OCHPhCHPhO); 3.20 (m, 1H, ArCH(B)CH₂(B))*; 1.99 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 11.1 and 16.2 Hz); 1.75 (dd, 1H, ArCH(B)CH₂(B), ³J_{HH} = 6.2 and 16.2 Hz). ¹¹B-{¹H} nmr (128.15 MHz, CDCl₃): δ 31.9. Hrms calculated for C₄₀H₃₄B₂O₄ 600.267, found 600.265.

Signals marked * are coincidental with those of the other diastereomer.

9. In systems where sources of ligand-free Pt(0) are the catalyst precursors (such as [Pt(dba)₂]), the only means of controlling the chirality of the diborated products is by employing enantiomerically pure chiral diborane(4) compounds.