Effective Asymmetric Hydroboration Catalysed by a Rhodium Complex of 1-(2-Diphenylphosphino-1-naphthyl)isoquinoline

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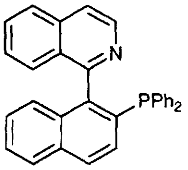
Hydroboration–oxidation of vinylarenes with the title catalyst gives the corresponding 1-arylethanols in up to 99% chemoselectivity and 94% enantiomeric excess.

Among recent advances in asymmetric organometallic catalysis, hydroboration of alkenes with catecholborane holds specific promise because of the wide applicability of the resulting boranes. Most reported examples[1] have involved moderate enantiomer excesses, typically 40–80%, which do not rival the best cases of stoichiometric asymmetric synthesis reported by Brown, Masamune and respective coworkers.[2] An exception is the application of binap† rhodium complexes for catalytic hydroboration of vinylarenes, which can be effected in up to 96% enantiomeric excess (e.e.), provided that the reaction is carried out at −78 °C.[3] Recently we presented the synthesis and resolution of 1-(2-diphenylphosphino-1-naphthyl)isoquinoline[4] **1**, and in view of the recent upsurge of interest in P–N chelates for asymmetric catalysis,[5] applications of its rhodium complex in hydroboration with catecholborane are reported here.

Reaction of (*S*)-**1**, $[\alpha]_D^{21}$ −157.3 (*c* = 1, $CHCl_3$) with 1 equiv. of $[Rh(cod)(acac)]–CF_3SO_3SiMe_3$†[6] gave the 1 : 1 complex **2** [*m/z* (Electrospray) = 650 (100% M^+), δ_P (101.3 MHz, tetrahydrofuran, thf) 31.5 (d, *J* 141 Hz)]. With 2 equiv. the 2 : 1 complex **3** [*m/z* (FAB+) = 981 (100%, M^+), δ_P (101.3 MHz, thf) 60.5 (d, *J* 178 Hz)] was produced. The 1 : 1 bicyclo[2.2.1]heptadiene complex was much less stable on storage and hence the former complex **2** was employed for catalysis. In preliminary experiments it was established that hydroboration of 4-methoxyphenylethene **4** with catecholborane was efficiently catalysed by complex **2** in thf *at ambient temperature*, with *ca.* 100 turnovers in 15 minutes, and that the main product (after H_2O_2 oxidation) was the secondary alcohol **5**, with *ca.* 2% each of the primary alcohol and alkane formed as by-products. It was found that the e.e. and chemoselectivity were both sensitive to the nature of the catalyst. If excess of the ligand was present, then the amount of primary alcohol decreased, but the reaction was slower and the e.e. was significantly reduced. The best results were obtained when the rhodium complex was reprecipitated before use (thf–light petroleum, b.p. 30–40 °C).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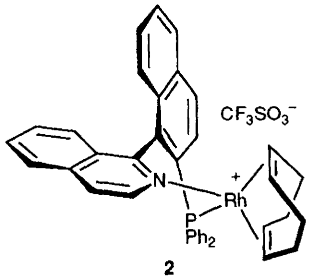

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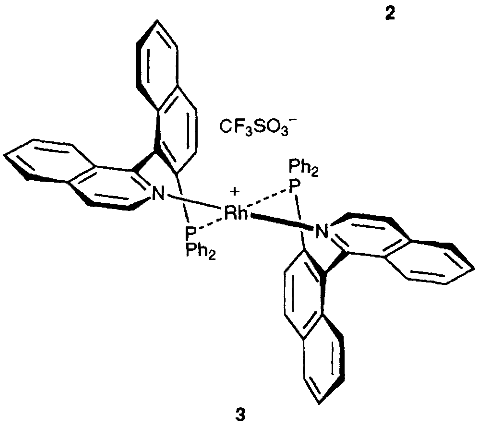

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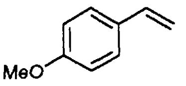
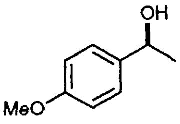
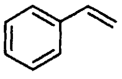
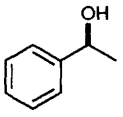
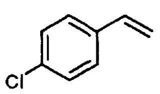
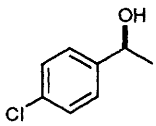
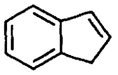
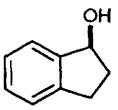
Several related alkenes were subjected to the hydroboration reaction. Since the observed e.e. for 2-chlorophenylethene **12** was rather lower than that for related alkenes (and therefore more responsive to reaction conditions) it was used in attempts to optimise the reaction. In the course of this it was found that (*a*) lowering the temperature did not enhance the e.e., but reduced the chemoselectivity; (*b*) higher concentrations of catecholborane in thf were deleterious, although slow addition of the reagent did not improve the result; (*c*) the e.e. was relatively insensitive to solvent change, and the initial results obtained in thf were not enhanced. It was also noted that a mixture of two different alkenes gave the same e.e.s as in separate experiments. The results for a series of arylalkenes are recorded in Table 1, and further examples, for which less

Table 1 Catalytic hydroborations proceeding in high enantiomer excess[a]

Reactant	Product	Yield[b], e.e. and data
 **4**	 **5**	57%, 94% e.e.[c] α 1.02 95% sec. alcohol, remainder prim. plus alkane
 **6**	 **7**	69%, 88% e.e.[c] α 1.05 3% prim., 2% alkane
 **8**	 **9**	56%, 78% e.e[c] α 1.04 2% prim., 2% alkane
 **10**	 **11**	58%, 91% e.e.[d] Indan-2-ol and indane not detected

[a] Standard conditions: 0.375 mmol of olefin, 0.375 mmol of catecholborane, 3.8 μmol of catalyst, thf, 20 °C; then H_2O_2, OH^-. [b] Isolated yield of pure product on 0.4 mmolar scale; material balance of crude product is always ≥90% sec. alcohol. [c] E.e. determined on a 20 m permethylated cyclodextrin column, at 110 °C (*p*-methoxystyrene), 100 °C (styrene), 120 °C (*p*-chlorostyrene), He flow 3 ml min^{-1} α values quoted represent baseline separation. [d] E.e.s determined *via* ^1H NMR using the oxazaborolidine method, ref. 9.

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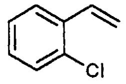
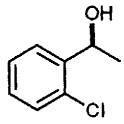
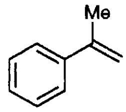
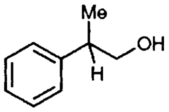
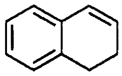
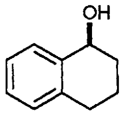
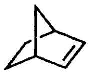
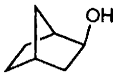
† binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; cod = cyclooctadiene; Hacac = pentane-2,4-dione.

Table 2 Other catalytic hydroborations[a]

Reactant	Product	E.e. and data
 **12**	 **13**	59%[b], 55% e.e.[c,e] α 1.11 4% prim., 1% alkane
 **14**	 **15**	42% prim. alcohol, low e.e. (*S*)? by rotation remainder tert. isomer
 **16**	 **17**	37% e.e.[d]
 **18**	 **19**	52% e.e.[d]

[a] Conditions and footnotes *b–d* as Table 1. [e] Same e.e when catalyst was prepared *in situ* from the ligand and $[(C_2H_4)_2RhCl]_2$.

satisfactory enantioselectivities were obtained and less effort applied to optimisation, are reported in Table 2. A high e.e. in the hydroboration of indene **10** is noteworthy since in previous work,[3,7] the result was much less promising. With simple styrenes **4**, **6**, **8** and **12** the relative configuration of ligand and product is the same as had been observed previously with (*S*)-binap, but for indene **10** the relative configuration is opposite to that claimed by Hayashi and coworkers,‡ who obtained 13% e.e. at 25 °C. For comparison,[3] the e.e. on hydroboration of alkene **6** is 57% at ambient temperature, and 76% at −30 °C. The difference in e.e. between indene **10** and its homologue dihydronaphthalene **16** is quite striking, and reflects the crucial effect of steric factors in the vicinity of the alkene double bond. The regiochemistry of reaction of 2-phenylpropene **14** varies with the ligands at rhodium,[7,8] and the result obtained here is similar to that observed with binap.

These results demonstrate the potential of chelating P–N ligands in asymmetric hydroboration, adding to their promise in Pd-catalysed allylic alkylation revealed earlier.[3,10] Future work will be concerned with the effects of varying the electronic and steric character of the 1-(phosphinoaryl)isoquinoline ligand and the ensuing effect on enantioselectivity.

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‡ But these authors stated[3] that (*S*)-indanol is (−) in $CHCl_3$, which is not the case.

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10 D. I. Hulmes, unpublished work.