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Hydroborations Catalysed by Transition Metal Complexes

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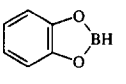
1. INTRODUCTION

The insertion of an unsaturated moiety into a B-H bond[1] (hydroboration) is one of the most studied of reactions in organic synthesis. It is the initial step in the introduction of a very wide variety of functional groups and it can also be used in the construction of carbon frameworks.[2-5] Perhaps the reaction is most used for the anti-Markovnikov hydration of alkenes, which involves hydroboration in a *syn*-fashion followed by stereospecific oxidation. Addition in a *syn*-manner also occurs with alkynes leading to a powerful method for the production of Z-disubstituted alkenes.

Usually the reaction needs no catalyst. However when the boron of the hydroborating agent is attached to heteroatoms that lower the electron deficiency at boron, then uncatalysed hydroboration requires elevated temperatures.[6,7a] (but see reference 7b). Examples of such boranes are **1** and **2**.[8] Some ten years ago it was shown that hydroborations by catecholborane, **1** (catBH) could be catalysed by some transition metal complexes so that reactions could be carried out at room temperature.[9] In addition the chemo-, regio- and stereoselectivity of hydroboration could all be affected, and this opened up a completely new field of chemistry that rapidly underwent intensive investigation.[10] It was clear from the beginning[9] that the differences in products between the catalysed and uncatalysed reactions reflected different mechanisms of hydroboration. It was also clear that there was the possibility of chiral hydroboration by the use of catalysts containing chiral ligands, which would allow for the 'multiplication' of chirality, depending on the turnover number.[11] This contrasts with the usual method of chiral hydroboration which requires one or two equivalents of a chiral auxiliary attached to boron.[12]



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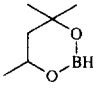

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2. THE CATALYSED HYDROBORATION OF ALKENES AND ALKYNES

2.1 Introduction

The transition metal complex catalysed hydroboration of alkenes has been intensively studied, particularly from the viewpoint of mechanism. Formally the reaction is one of a family of additions to alkenes, which includes hydrogenation (H-H), hydrosilation, hydrostannylation *etc* (H-E), hydrocyanation (H-CN) and, hydroformylation ($HCo(CO)_4$). Some of these reactions, such as hydrostannylation, can also be performed under either catalytic or non-catalytic conditions and change their regioselectivity as between the two sets of conditions.[13]

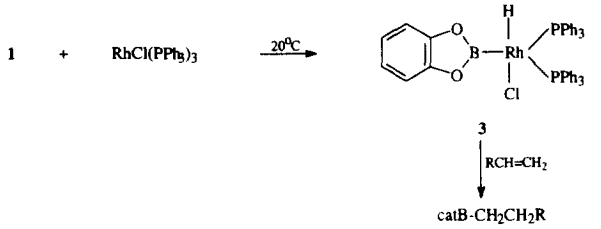
Although catalysed hydrogenations are the best studied of these reactions they may have much in common, and in particular all could go *via* an 'alkene' or 'hydride' pathway.[14] In the first case, the initial step is complexation of the alkene to the metal complex. In the second, addition of the H-E to the metal complex leads to a metal hydride. By analogy with hydrogenation one can also consider the participation of HME (H_2M for hydrogenation) or 'monohydride' complexes such as M-H (hydrogenation) or M-E. Thus the participation of Cp_2Ln-H or Cp_2Ln-SiR_3 in hydrosilation catalysed by lanthanide complexes is a matter of current discussion.[15]

There is also the possibility of radical mechanisms, particularly for substrates capable of stabilising radicals formed by hydrogen atom addition. Styrene and other alkenylarenes fall into this group and a radical mechanism was proposed for the reaction of styrene with $HCo(CO)_4$.[16] It is possible that the mechanism of catalysed hydroboration can change with the nature of the metallocomplex, as in hydrogenation when

changing from neutral rhodium to cationic rhodium complexes.[14]

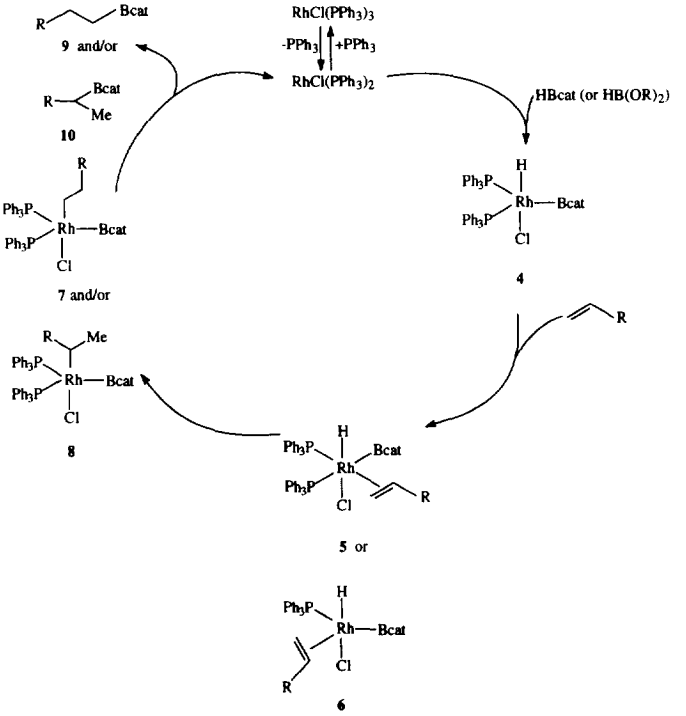
In this review we shall consider only the most general mechanistic features as any particular mechanism will in each case be dependent on the nature of the substrate, the catalyst, the reagent and the conditions used.

The most efficient catalysts for hydroboration appear to be rhodium complexes of the Wilkinson type.[9] These form H-Rh(III)-Bcat, the most probable intermediates in the catalytic cycle, by addition of H-B. In some cases the postulated intermediates such as **3** for the interaction of catecholborane, **1**, and various rhodium and iridium complexes have been isolated and characterised[16-20] from reactions in the absence of alkene. Compounds **3** can hydroborate alkenes (Scheme 1).



Scheme 1

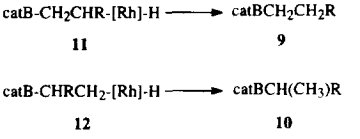
The catalytic cycle shown in Scheme 2 has been proposed.[9,32,126]



Scheme 2

The first step is insertion between the B-H bond to give **4** which adds alkene to yield **5** or **6**. Hydride migration then leads to either **7** or **8** which in turn undergo reductive elimination to give respectively the *anti*-Markovnikov product **9** and/or the Markovnikov product **10** together with $RhCl(PPh_3)_2$ to complete the catalytic cycle.

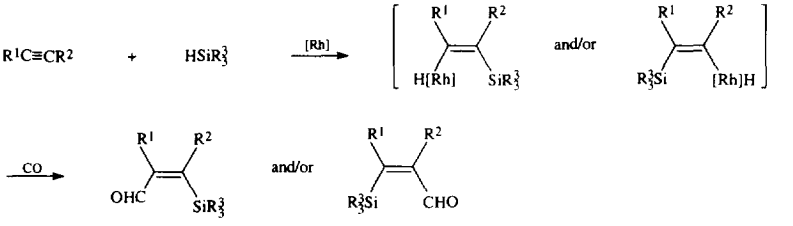
Another possibility is the insertion of the alkene into the Rh-B bond (boryl migration) to give **11** and/or **12** which undergo reductive elimination to give **9** and **10** (Scheme 3).



Scheme 3

The insertion into a Rh-B bond has been proven by the diborylation of alkenes (see section 4.1.).

Silylformylation provides an example of a similar process[21] (Scheme 4).



Scheme 4

In the case of hydrogenation and related processes both the oxidative addition and the migratory insertion are reversible. Hence if reductive elimination is slow, side products associated with isomerisation of the double bond may occur[22] as may exchange of label between B-D compounds and alkenes. The existence of complexation between the metallocomplex and alkene prior to migratory insertion may lead to the poisoning of the catalyst by competing ligands.

The catalytic effects of the metallocomplexes depend strongly on their nature. In the pioneering paper by Männig and Nöth,[9] it was shown that Wilkinson's complex was more active than $RhCl(CO)(PPh_3)_2$, $RhCl(CO)(AsPh_3)_2$ or $[RhCl(COD)]_2$, whilst the ruthenium complex $RuCl(CO)(PPh_3)_2$ is even less active. Complexes of Pt, Pd, Ir and Co were inactive under the conditions used. Later it was reported that complexes of Ce, Fe, Ni, Ti, Zr were inactive (but see sections 2.5.2., 2.6.2., 2.6.4., 2.6.5.).[23] However cationic complexes of rhodium and iridium were equally active for hydrogenation and hydroboration.

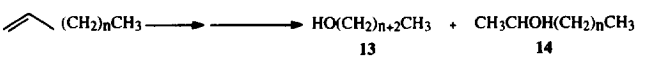
2.2 The regioselectivity of catalytic hydroborations of alkenes

2.2.1 Monoalkylethenes

The regioselectivity of hydroboration of simple terminal alkenes is almost the same for non-catalytic and catalytic hydroboration.[9,10,23] In both cases the anti-Markovnikov product is the major product (Table 1). The

largest difference between the two processes is that catalytic hydroboration with catBH takes less than 5 min. at 20°C as compared with extended heating at 90°C for the non-catalytic reaction.[23]

Table 1 Regiochemistry of hydroboration[a] with catBH at 20°C

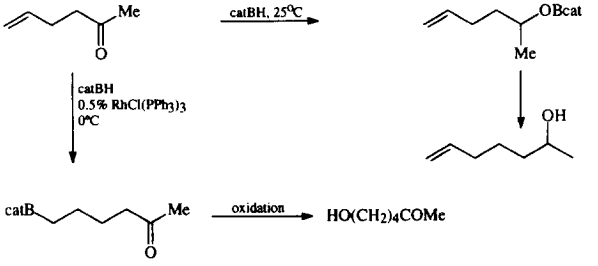


n	catalyst	13	:	14
7	none	98		2
3	$Rh(PPh_3)_3Cl$	99		1
3	$Rh(nbd)(diphos)BF_4$	90[b]		10
3	$Ir(COD)(PCy_3)Py)PF_6$	98		2

[a]THF used as solvent, [b]Ratio becomes 97:3 at -40°C.

The nature of the solvent is unimportant as regards Wilkinson and iridium complexes, but regioselectivity using a cationic rhodium complex was enhanced on changing solvent from THF to ether and then to 1,2-dichloroethane.[23]

The catalytic reaction can be *chemoselective* in a different fashion from the uncatalysed reaction[9] (Scheme 5), thus enhancing its value.



Scheme 5

2.2.2 Polyalkylethenes

In Figure 1 are shown the approximate times for complete hydroboration at 20°C of a variety of alkenes with two equivalents of catecholborane and $RhCl(PPh_3)_3$ in THF[23] (but see section 2.2.4).

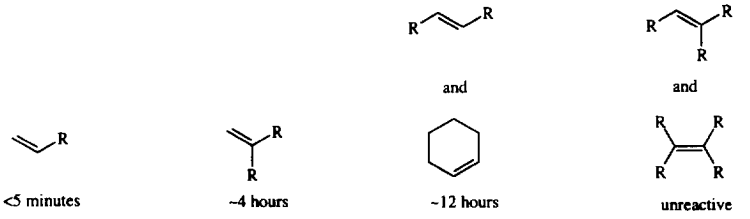
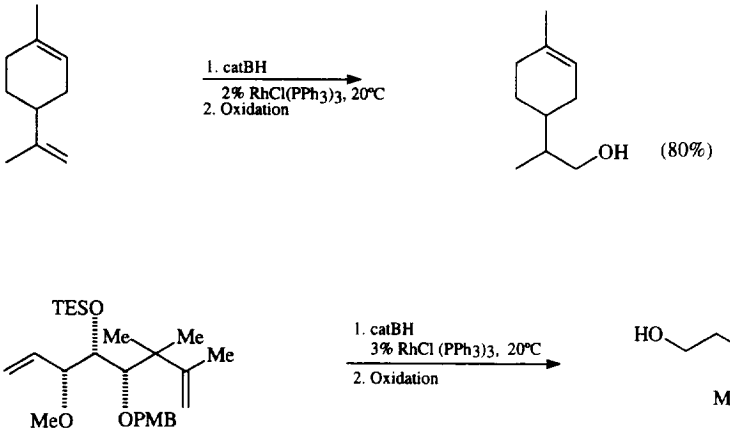


Figure 1

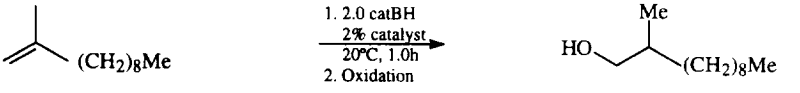
Clearly there are large rate variations, and this can be used in synthesis, as in the hydroboration of limonene[23] and in the synthesis of calyculin A (Scheme 6).[24]



Scheme 6

The nature of the complex and the solvent can also influence the rates of reaction of a particular hydroboration (Table 2).

Table 2 Effect of solvent and catalyst on the hydroboration of 2-methyl-2-nonylethene. % Conversion after 1h



Solvent	$Rh(nbd)(dppb)BF_4$	$RhCl(PPh_3)_3$	$Ir(cod)(PCy_3)(py)PF_6$
THF	59	46	2
ether[a]	44	5	2
toluene[a]	46	15	10
$ClCH_2CH_2Cl$	59	9	4

[a]Catalyst only partly soluble.

The nature of the hydroborating agent is important and whilst (**1**) and (**2**) react relatively easily, dialkylboranes, 1,3-dimethyl-2-azaborolidine,[9] *bis*benzyloxyborane and trifluoroacetoxyborane[23] do not react.

2.2.3 Haloethenes

The same selectivity was observed for the non-catalytic and catalytic hydroborations of haloalkenes, the advantage of the latter being the low temperatures required which minimises rearrangements[25] (Table 3).

Table 3 Hydroboration of $R^1R^2C{=}CHX$ with catBH

$$R^1R^2C{=}CHX \xrightarrow[RhCl(PPh_3)_3]{catBH} R^1R^2CH\text{-}CHXBcat$$

entry	R^1	R^2	X	catalyst (mole %)	reaction time(h)[a]	%yield of **15**[b]
1	H	H	Br	0.1	38	73
2	Me	H	Br	0.1	8	82
3	Me	H	Br	0.0	24	76
4	$Me(CH_2)_3$	H	Br	0.5	48	54
5	Me	Me	Cl	0.2	24	70
6	Me	Me	Cl	0.0	18	66
7	Me	Me	Br	0.05	28	98
8	Me	Me	Br	0.0	4	82
9	Cl	H	Cl	0.5	72	0
10	Cl	H	Cl	0.0	72	0
11	Br	H	Br	0.1	24	65
12	Br	H	Br	0.0	30	80
13	$ClCH_2$	H	Cl	0.2	30	71
14	$ClCH_2$	H	Cl	0.0	24	79
15	$BrCH_2$	H	Br	0.1	5	79
16	$BrCH_2$	H	Br	0.0	8	76
17	Ph	H	Br	0.1	30	87
18	Ph	H	Br	0.0	20[c]	59

[a]All uncatalysed reactions were done at 80-90°C using neat reagents. All catalysed reactions were at 20°C in benzene. [b]Isolated, purified yields. [c]Ultrasonic bath for 2h.

Reactions were slower for chloroalkenes than for the corresponding bromoalkenes (entries 13 and 15, 9 and 10, 6 and 8) and 1,2-dichloroethene does not react at all. In all cases, even the substituted styrenes (entries 17 and 18), the reactions are highly regioselective and place the boron atom on the same carbon atom as that bearing the halogen.

2.2.4 Arylethenes

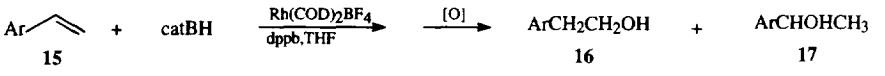
Dramatic changes in regioselectivity are seen in the catalysed and uncatalysed hydroboration of arylethenes, **15**.

Table 4 Hydroboration of styrene

Catalyst	Ratio of products	
	$PhCH_2CH_2OH$	$PhCHOHCH_3$
None	92	8[3]
$Rh(COD)_2BF_4/PPh_3$	<1	>99[26]
$Rh(COD)_2BF_4$/dppb	<1	>99[26]
$RhCl(PPh_3)_3$	90	10[26]
$Rh(COD)_2BF_4$	43	57[26]
$0.5[RhCl(COD)]_2$	73	27[26]
$RhCl(N_2)(P^iPr_3)_2$	95	5[27]

Exclusive formation of the secondary alkylborane was evidenced by cationic rhodium complexes that have phosphine ligands. The reaction was relatively unsensitive to substitution on the benzene ring but was influenced by steric effects (Table 5).

Table 5 Hydroboration of styrenes catalysed by the cationic complex generated from $Rh(COD)_2BF_4$ and dppb[a]



15 16 17

Styrene substituent	time (h)	16 : 17
4-Cl	1.0	<1 : 99
4-Me	0.5	<1 : 99
4-MeO	0.5	<1 : 99
3-Cl	0.5	<1 : 99
2-Cl	1.0	<1 : 99
2-MeO	0.5	<1 : 99
2,4,6-Trimethyl	16.0	37 : 63

[a]Reactions in THF at 25°C in presence of 1 mol% of cationic Rh complex

Ethenylferrocene also undergoes a highly selective reaction (**16**:**17** = 3 : 97) but 2-naphthylethene is less selective (**16**:**17** = 35:65). 2-Pyridylethene did not react at all.[26]

The regioselectivities of hydroboration of disubstituted styrenes and indene, using the same conditions as in Table 5, are given in Figure 2.

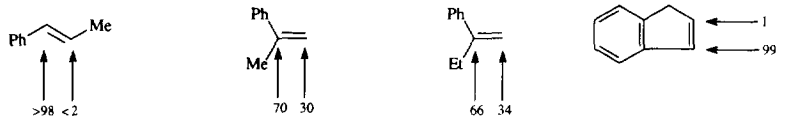


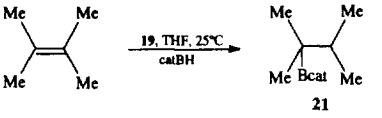
Figure 2

Change of catalyst can overcome some of the difficulties.[27] Thus 2-naphthylethene with **19** or **20**, derived from **18**, give >99% of the internal alcohol.

18

19 P_2 = DIPPE (1,2-bis (diisopropylphosphino)ethane)
20 P_2 = DPPB

2-Phenylpropene rapidly added catecholborane at 25°C to give only the internal alcohol using **19**. Unfortunately the products of borane addition are also present. However **20**, gives a 95:5 mixture of internal and terminal alcohol with no products from BH_3 addition. It is noteworthy that the catalyst **19**, even allowed hydroboration of tetramethylethene (2,3-dimethylbut-2-ene)(see section 2.2.2.), though $t_{½}$ was 40h at 25°C. Nevertheless the formation of **21** (Scheme 7) was quantitative.

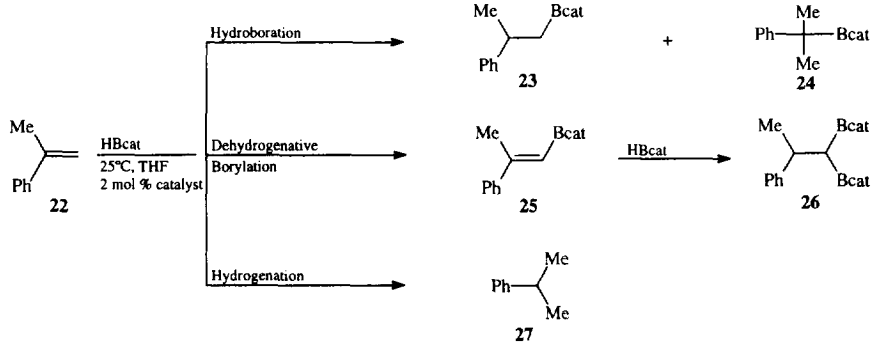


Scheme 7

At this time there are some disagreements in the literature. Thus it has been reported,[28] in contradiction to references 22 and 29, that Wilkinson's catalyst gives internal hydroboration with high selectivity for a range of substituted styrenes. The same authors report that the addition of 4 mol % of a Lewis acid such as $SnCl_2$, $Ti(OR)_4$, $ZnCl_2$ or BF_3, may enhance the 'reversed' regioselectivity.[28] When $[RhCl(COD)]_2$ was used as catalyst, the ratio of **16** : **17** was 67 :33. On addition of 4 mol % of triphenylphosphine the ratio reversed to 2 : 98!

Hydroboration of styrenes to give the internal alcohols **17** introduces a chiral centre, and clearly chiral induction with optically active chiral ligands becomes an important target. This is discussed later.

With hindered styrenes, hydroboration is not the only reaction to be taken into account. A detailed study has been made of the catalytic hydroboration of 2-phenylpropene **22** with catecholborane.[30] The reactions delineated are shown in Scheme 8 and the results in Table 6.



Scheme 8

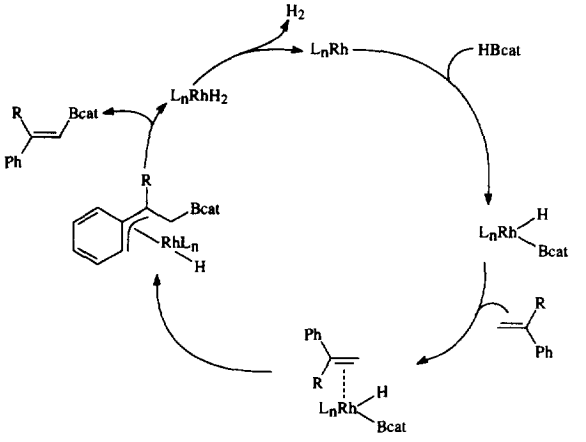
Table 6 Catalysed hydroboration of **22** according to Scheme 8

Entry	Catalyst	**23**	**24**	**25**	**26**	**27**
1	$[RhCl(COE)_2]/PPh_3$	**98**	--	--	--	2
2	$Rh(COD)(DPPB)BF_4$	30	70	--	--	--
3	$Rh(\eta^6\text{-Bcat})(DPPB)$	5	**95**	--	--	--
4	$RhCl(PPh_3)_3$	14	3	53	27	3
5	$RhCl(PPh_3)_3/10PPh_3$	10	1	70	18	1
6	$[RhCl(PPh_2oTol)_2]_2$	15	--	**76**	8	1

The variation of product with catalyst is obvious, and in particular when a bulky catalyst is used for this more hindered alkene, then 76% of alkenylborane results (entry 6). The result with a large excess of free

triphenylphosphine suggests that the ligating phosphine, in that case, was displaced, perhaps by oxidation. A slight variation of the cycle suggested is shown in Scheme 9.

It was suggested[30] that **25** and **26** arise by insertion of alkene into the Rh-B bond, rather than the Rh-H bond. The insertion is followed by β-hydride elimination leading to production of hydrogen. This process of 'dehydrogenative borylation' is catalytic (Scheme 9).



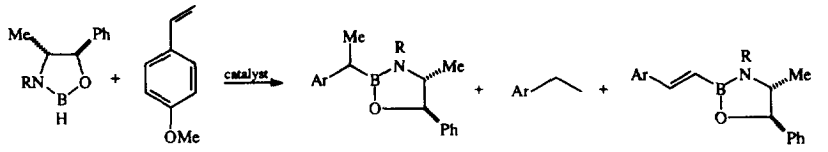
Scheme 9

In this case a η^3-benzyl Rh complex, in which Rh is bonded to H, not B, is invoked as a participant in the catalytic cycle.[26] An insertion into the Rh-B bond has been demonstrated.[31]

Observations of the production of vinylboranes from monosubstituted alkenes have been made in other cases such as the $PdBr_2$ catalysed hydroboration of alkenes with borazine[33] or pentaborane.[34] Additionally it was noted[32] that the catalysed hydroboration of a silyl ether with catBH gave, after oxidative work-up, an aldehyde, derived from a vinylborane. A mechanism which involved regiospecific Rh-B addition to the double bond of the allyl ether followed by reductive elimination was postulated.

That both the nature of the catalyst and the borane are important in the composition of the products was underlined in studies of the hydroboration of 4-methoxystyrene **28** (Scheme 10) by boranes **29** and **30**.[35,36] With **29**, the major product was the internally borated alkene **31**, when catalyst **34** was used. With the same catalyst but with the somewhat more hindered borane **30**, reduction product **32** and the vinylborane **33** appeared. If the catalyst **34** was deliberately exposed to oxygen so that the phosphine ligand was lost prior to use, then no hydroboration product was produced and instead a 1 : 1 mixture of **32** and **33** resulted. *The effect of oxygen is important and helps explain some of the discrepancies in the literature.* In the light of the oxidation result, complex **35** was used as catalyst and it also gave only a 1 : 1 mixture of **32** and **33** with a number of substituted styrenes. That the nature of the catalyst is of particular importance is clear as using catecholborane (*vide infra*) and **35**, the hydroboration product was a minor product, the rest being reduction

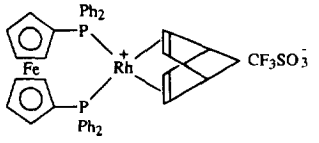
product and vinylborane. Catecholborane has little hindrance α to the boron atom and hence the *steric situation on the catalyst* must make a very large contribution to the result.



29, R=Me
30, R=Pr^i

28 **31** **32** **33**

For (**29**) + (**34**)	82	4	<1
For (**30**) + (**35**)	0	50	50



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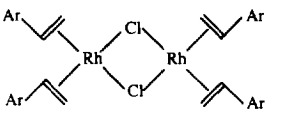
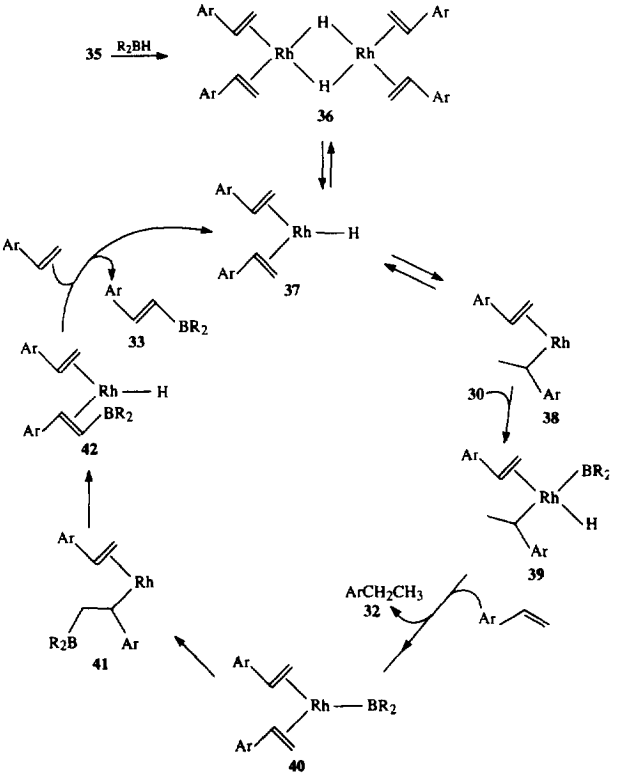


35

Scheme 10

The authors propose the mechanism shown in Scheme 11.

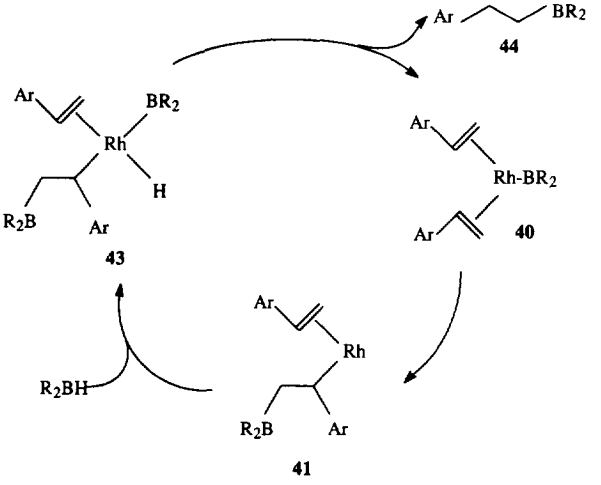


Scheme 11

In the preliminary phase the dichloride **35** is reduced to the dihydride **36** which undergoes a reversible dissociation to yield **37**, the entry point to the catalytic cycle. This converts to the σ-complex **38** which adds the borane to give the key intermediate **39**, which undergoes alkylhydride elimination and incorporation of alkene to give **40**. This is a complex analogous to **37**, with hydride replaced by R_2B, which migrates in a regiospecific fashion to give the σ-complex **41**. This rearranges to the π-complex **42** from which vinylborane is displaced to give back **37**.

This cycle is in accord with deuterium isotope experiments and a kinetic model was successfully set up, in which the conversion of **38** to **39** was rate limiting for catalysis.

The reaction of catecholborane **1** with **28** using **35** as catalyst[36] was examined in detail. A very rapid reaction led to a 1 : 1 : 1 mixture of hydroborated borated and reduction products. The hydroborated product was entirely *primary* borane! Similar reactions had, of course, been previously examined from the viewpoint of regiochemistry using Wilkinson's catalyst, and it was known that the outcome depended on the quality of the catalyst. Commercial $RhCl(PPh_3)_3$ can contain peroxides[37] and Rh(II) impurities[38], which are absent from freshly prepared samples.[39] It would seem that this explains the discrepancy between the results of Männig,[9] Westcott[27] and Evans[23] on the one hand and Hayashi[26] and Burgess[40] on the other, a view accepted by Burgess.[32] Pre-exposure of the catalyst to oxygen lowers the regioselectivity a phenomenon countered by addition of PPh_3. This is similar to the findings in the case of vinylborane production, though the previous authors did not report the production of vinylboranes. In order to explain their findings with catecholborane a modified version of the previous cycle was proposed in which **41** adds R_2BH (catBH) to give **43** which yields primary borane **44** with regeneration of **40** which again yields **41** (Scheme 12).



Scheme 12

For the recently introduced hydroborations of alkenes with pinacolborane using rhodium and nickel catalysts, see section 2.7.3.

2.2.5 1,3-Dienes

Catecholborane rapidly hydroborates a variety of a cyclic conjugated dienes in a 1,4-fashion,[53] under catalysis by $Pd(PPh_3)_4$. Rhodium complexes are ineffective in the cyclic series but are useful for cyclohexa-1,3-diene. Results are given in Figure 3.

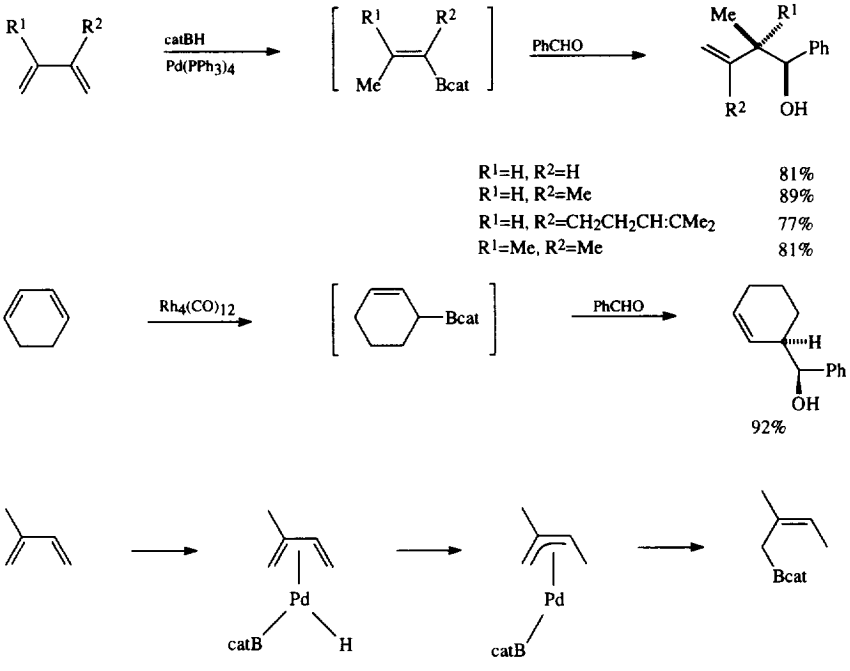


Figure 3

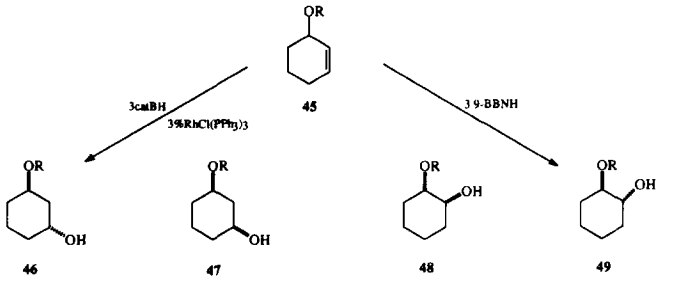
The allylborane intermediates in the reactions were not isolated but were carried through, by aldehyde insertion, to the alcohols on which the yields are given. The authors propose the pathway shown in Figure 3 to explain their results. Reactions with 1,3-enynes are detailed in Section 2.5.3, which deals with transition metal catalysed hydroborations of alkeynes.

2.2.6 Substrate influenced hydroborations

2.2.6.1 Non ligating substituents

Catalysed hydroboration of cyclohex-2-en-1-ol and derivatives with catBH has been contrasted with the uncatalysed process using 9-BBNH.[23] The results are shown in Table 7.

Table 7 Hydroboration of cyclohex-2-en-1-ol derivatives

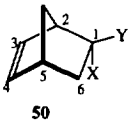


(a) R=H; (b) R=CH_2Ph; (c) R=$SiBu^tMe_2$

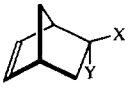
substrate	conditions	46	47	48	49	yield %
45a	catalysed	72	9	1	18	84
45b	catalysed	72	13	8	7	87
45c	catalysed	86	11	1	2	79
45a	uncatalysed	5	10	2	83	86
45b	uncatalysed	13	19	0	68	73
45c	uncatalysed	10	15	0	75	70

In each case the catalysed reaction gives a predominance of the 1,3-*anti* isomer **46**, the selectivity being particularly high with the bulky $SiBu^tMe_2$ substituent **45c**. The uncatalysed reaction also gives a predominance of *anti*-isomer, but this time the 1,2-*anti* predominates. The latter effect is presumably due to electronic factors plus a steric influence to give *anti*-isomer. The catalysed reactions would seem to be greatly influenced simply by the bulk of the HRhB moiety, the actual hydroborating agent.

In searching for methods of directing attack by boron on substituted norbornene derivatives (**50**) and (**51**), both catalysed and uncatalysed hydroborations were studied.[41] In all cases only *exo*-attack was noted, suggesting that the *endo*-substituents did not co-ordinate with the hydroborating agents. However changes in regiochemistry were marked (Scheme 13).



50



51

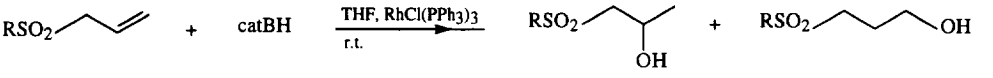
	3-OAc : 4-OAc	3-OAc : 4-OAc
X=SO_2Ph, Y=H		
Catalysed	13 : 87	57 : 43
Uncatalysed	56 : 44	63 : 37
X=CH_2NBn, Y=H		
Catalysed	20 : 80	50 : 50
Uncatalysed	50 : 50	---
X=$NHCO_2Bn$, Y=CO_2Et		
Catalysed	22 : 78	
Uncatalysed	62 : 38	--- : ---
		--- : ---

Scheme 13

In many cases, catalysed hydroborations of **50** were selective to place boron mainly at C-4, whereas uncatalysed reactions gave relatively random placement. The *exo*-substituent at C-1, had little effect in either the catalysed or uncatalysed reactions. The mechanistic features of these reactions remain to be clarified.[41]

2.2.6.2 Ligating substituents

The catalysed (3% $RhCl(PPh_3)_3$) hydroborations of sulfone derivatives of allyl alcohol **52** have been studied.[42] In all cases the reaction is selective to give, on oxidation, the 2-ol, **53**, rather than the 1-ol, **54** (Scheme 14).

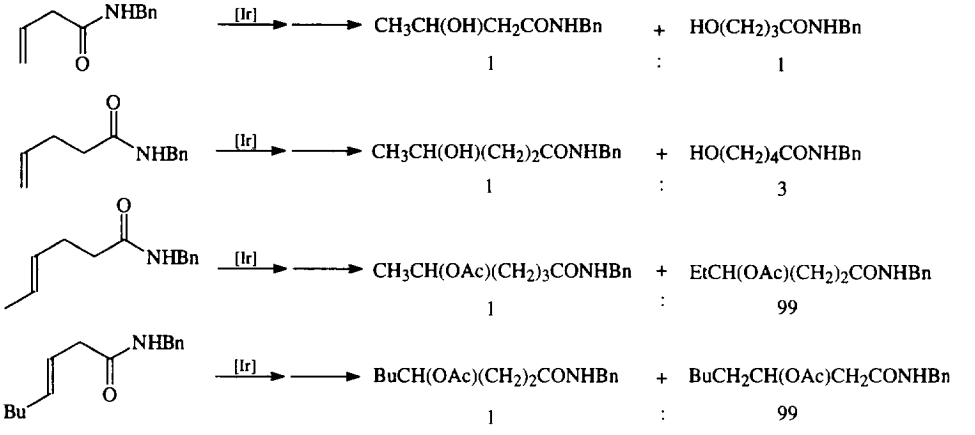


52 **53** **54**

R=Ph	Catalysed	87	13
R=Ph	Uncatalysed(9-BBNH)	0	100
$R=CH_2Ph$	Catalysed	90	10
$R=CH_2Ph$	Uncatalysed(BH_3)	59	41

Scheme 14

Secondary amide groups are not readily reduced by catBH and have strong directing effects in both acylic (Scheme 15) and cyclic systems.[23] Catalytic quantities of $Rh(nbd)(dppb)BF_4$ or, better, 5% $Ir(COD)(PCy_3)PF_6$ ([Ir]) can be used with yields, after oxidation and acetylation, of 73-78%.

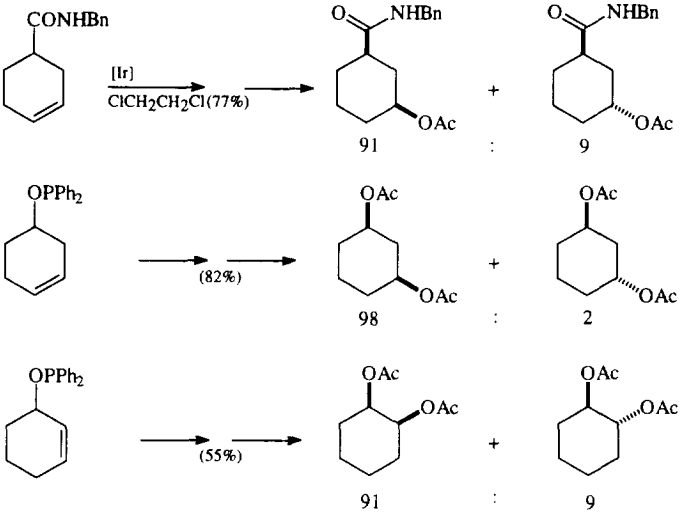


Scheme 15

There is excellent selectivity for disubstituted alkenes in which the double bond is separated from the amide by one or two carbon atoms. The selectivity is considerably lowered for similarly substituted terminal alkenes.

The diphenylphosphinate group also has a strong directive effect, but has the disadvantage that stoichimetric quantities of metal complex are required and that yields may be moderate.

For substituted cyclohexenes delivery of the boron is regioselective and mainly *syn* to the directing group (Scheme 16).[23]



Scheme 16

Amide delivery of the hydroborating species is supported by the regio- and stereo-selectivity and by the enhanced reactivity of substrates containing an amide group. In addition the selectivity is lowered greatly when donating ether solvents are used rather than non-complexing 1,2-dichloroethane. In ether solvents there is, presumably, a competition for the metal between the directing group and the solvent. Potassium alkoxides, esters, urethanes and benzyl ethers were ineffective as directing groups in the systems tried. The subject has been briefly reviewed.[43]

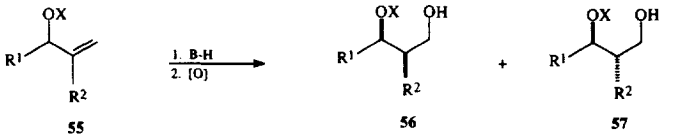
2.3 The diastereoselectivity of catalysed hydroborations of alkenes

2.3.1 Acyclic alkenes

As diastereoselectivity is determined by a combination of electronic and steric factors, both of which are different for uncatalysed and catalysed hydroboration, it would be expected that the two processes would give different results with the same substrate. In a complementary fashion, changes in the substrate might strongly effect the outcome of any particular type of hydroboration.

Table 8 summarises the results of three studies[23,44,45] of substrates **55**.

Table 8 Stereoselectivity in the hydroboration of **55**



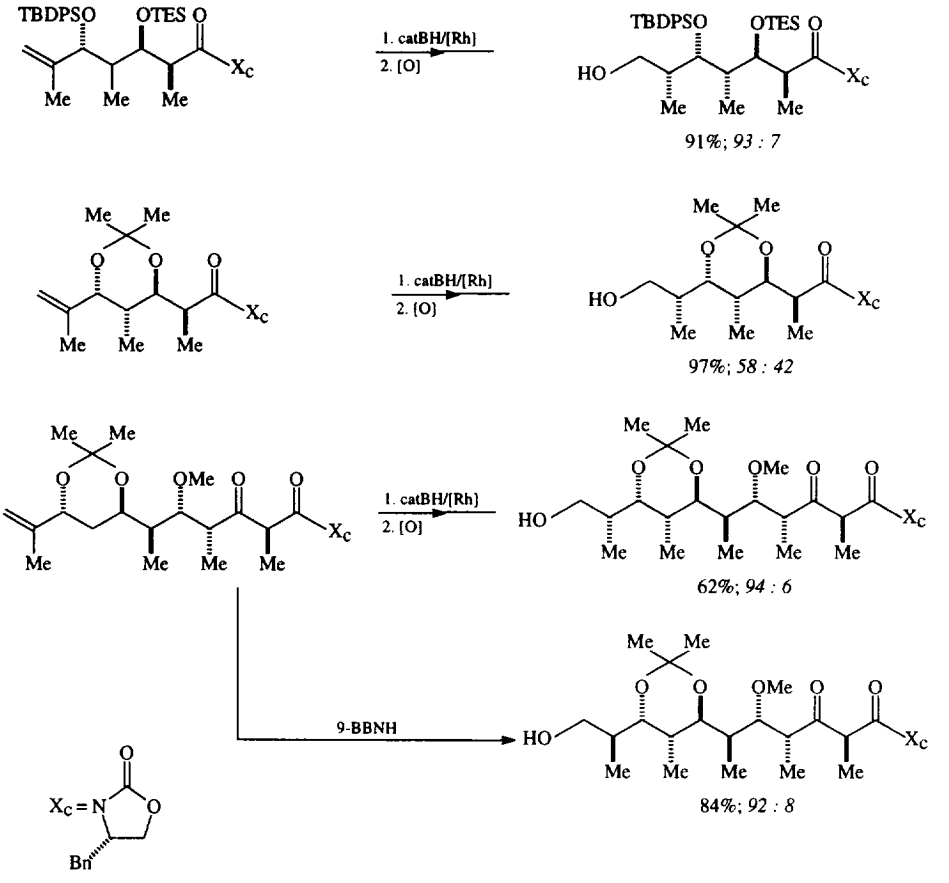
55 **56** **57**

entry	X	R	R	catalyst	reagent	**56 : 57**	ref
1	H	Bu	Me	$[RhCl(COD)]_2$[a]	catBH	69 : 31	44
2	Ac	Bu	Me	$[RhCl(COD)]_2$	catBH	73 : 27	44
3	$CONMe_2$	Bu	Me	$[RhCl(COD)]_2$	catBH	71 : 29	44
4	$COCF_3$	Bu	Me	$[RhCl(COD)]_2$	catBH	88 : 12	44
5	$COBu^t$	Bu	Me	$[RhCl(COD)]_2$	catBH	87 : 13	44
6	THP	Bu	Me	$[RhCl(COD)]_2$	catBH	89 : 11	44
7	CPh_3	Bu	Me	$[RhCl(COD)]_2$	catBH	95 : 5	44
8	$SiBu^tMe_2$	Me	Pr	$RhCl(PPh_3)_3$[b]	catBH	93 : 7	23
9	$SiBu^tPh_2$	Me	Pr	$RhCl(PPh_3)_3$	catBH	93 : 7	23
10	H	Me	Pr	$RhCl(PPh_3)_3$	catBH	81 : 19	23
11	H	Me	Pr	$Rh(nbd)(dppb)BF_4$[b]	catBH	50 : 50	23
12	CH_2Ph	Me	Pr	$RhCl(PPh_3)_3$	catBH	80 : 20	23
13	CH_2Ph	Me	Pr	$Rh(nbd)(dppb)BF_4$	catBH	50 : 50	23
14	H	Bu	Me	-------	9-BBNH	8 : 92	45
15	Ac	Bu	Me	-------	9-BBNH	12 : 88	45
16	$COCF_3$	Bu	Me	-------	9-BBNH	7 : 93	45
17	$COBu^t$	Bu	Me	-------	9-BBNH	6 : 94	44
18	THP[c]	Bu	Me	-------	9-BBNH	21 : 79	44
19	CPh_3	Bu	Me	-------	9-BBNH	15 : 85	45
20	$SiBu^tMe_2$	Pr^i	Me	-------	9-BBNH	5 : 95	23
21	$SiBu^tPh_2$	Pr^i	Me	-------	9-BBNH	5 : 95	23
22	H	Pr^i	Me	-------	9-BBNH	4 : 96	23
23	H	Me	Pr	-------	9-BBNH	17 : 83	23
24	CH_2Ph	Me	Pr	-------	9-BBNH	25 : 75	23

[a]1 mol %, [b]3 mol %, [c]THP=tetrahydropyranyl

From Table 8 it is clear that the catalysed hydroborations yield the *syn*-isomers **56** as the major products and, in a useful complementary fashion, the *anti*-isomers **57** are the major products from uncatalysed hydroborations. Both processes are not strongly influenced by variation in *alkyl* groups R^1 and R^2 (though substitution of R^1=Bu by R^1=$PhCH_2$ does double the stereoselectivity)[46] but strongly affected by the electronic (entry 4) and steric (entries 5, 7) nature fo the allyic oxygen substituents. Both factors work together in the case of bulky $OSiR_3$ substituents to give the excellent diastereoselectivities observed (entries 8, 9). Somewhat surprisingly exactly the same observations apply to the non-catalysed hydroborations but in the opposite direction (entries 16, 17, 19, 20, 21). Another point is that a cationic rhodium complex was far less effective than a non-cationic complex (entries 11, 13). It has been argued that complexation to alkene is an important factor and competitive rate studies[47] tend to support this. When R^1 is an aryl group then diastereoselectivity drops quite markedly,[44] though this may be overcome by use of a bulky $OSiR_3$ group.[23]

The process has been applied in model studies on the synthesis of loncomycin (Scheme 17).[48]

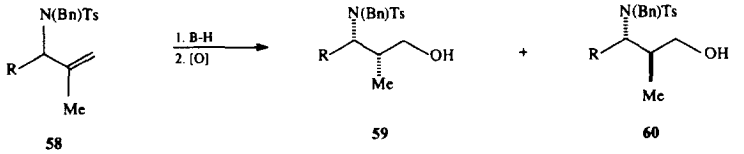


Scheme 17

A comparison of the reactions of the last two substrates in Scheme 18 shows that the factors governing reaction stereoselectivity can be rather subtle.

High discrimination in favour of the *syn*-product is also evidenced in the catalysed hydroboration of allylic tosylamides and phthalimides.[49] Unfortunately the phthalimido group is partly reduced and so cannot be used synthetically. The effects of the TsNH group can be strongly enchanced by benzylating it to give the TsNBn group which gives the diastereoselectivities shown in Table 9.

Table 9 Diastereoselectivities of hydroborations of allylic N-benzyltosylamides



58 59 60

entry	R	method	59	:	60
1	$PhCH_2$	[Rh][a], catBH	18	:	1
2	$PhCH_2$	9-BBNH	13	:	1
3	$PhCH_2$	BH_3.THF	1	:	17
4	Bu	[Rh], catBH	10	:	1
5	Bu	9-BBNH	7	:	1
6	Bu	BH_3.THF	1	:	21
7	Pr^iCH_2	[Rh], catBH	6	:	1
8	Pr^iCH_2	9-BBNH	25	:	1
9	Pr^iCH_2	BH_3.THF	1	:	20
10	$Bu^tO_2CCH_2$	9-BBNH	5.3	:	1
11	$Bu^tO_2CCH_2$	BH_3. THF	1	:	52

[a] [Rh]=2 mol % of $[RhCl(COD)]_2$. $4PPh_3$

In this case, though not with the simple NHTs derivatives, the diastereoselectivity of the catalysed reaction and the reaction with 9-BBNH are in the same direction, to give the *syn*-isomers **59** as major products. However quite remarkable reverses of diastereoselectivity are seen when using borane itself and again the two processes are complementary.

Unfortunately the reaction is very sterically sensitive and when the methyl on the double bond of **58** is replaced by either a *n*-butyl or a phenyl group, the catalysed reaction is either very slow or does not occur at all.[50]

Burgess[44] has concluded, on the assumption that complexation of the alkene to catB-Rh-H occurs irreversibly or the complex reacts relatively rapidly, that the diastereoselectivity will be determined *via* the diastereofacial selectivity of coordination to the alkene. Considerations of secondary orbital effects indicate that the best electron withdrawing group (EWG) will be oriented *anti* to the pathway of approach of the metal. Steric considerations indicate that the largest group will be similarly oriented and the outcome of a reaction depends on the balance of these factors. When they work together then the situation is optimal (OR = $OSiBu^tR_2$) (Table 8, entries 8, 9). Relative to the CH_3COO group, the CF_3COO is of similar size but a better EWG and selectivity increases (Table 8, entries 2, 4). A pivaloate is larger than an acetate but electronically similar, and once again there is an increase in selectivity (Table 8, entries 2, 5). The general steric effect is shown in **61** (Figure 4), whilst the situation with allylic oxygen substituents is shown in **62**.

le produit de départ reste inchangé. Le mélange réactionnel est alors chauffé à 60°C durant une nuit. On ajoute à nouveau 23,1 mg (1,9 éq.) de composé **14** et 12,6 mg (2 éq.) de DCC. Puis 5h après, on ajoute 14,4 mg (2,3 éq.) de DCC et on maintient l'agitation 1h supplémentaire. Le milieu réactionnel est alors dilué avec CH_2Cl_2, filtré et concentré à sec sous pression réduite. La purification par CCM (Heptane/AcOEt : 6/4) fournit 11,7 mg de **15** (Rdt. = 44%).

Composé 15. $C_{50}H_{65}NO_{13}$ (M = 887). Amorphe. $[\alpha]_D$ + 44 (c = 0,2, $CHCl_3$). IR : 3375, 3020, 1720, 1700, 1255, 1170 cm^{-1}. SM (IC) : 888 (MH^+), 489, 429, 371. RMN ^1H (300 MHz) : 7,41-7,31, (m, 7H, Ph-H et PMP), 6,88 (d, J = 8,5 Hz, 2H, PMP) ; 6,31 (s ép., 1H, H, PMP) ; 6,05 (m, 1H, H-13) ; 5,39 (m ép., 1H, H-3') ; 4,86 (d ép., J = 9 Hz, 1H, H-5) ; 4,53 (d, J = 9,5 Hz, 1H, H-10) ; 4,52 (d, J = 5 Hz, 1H, H-2') ; 4,43 (d, J = 9 Hz, 1H, H-20) ; 4,39 (d, J = 9 Hz, 1H, H-20) ; 4,17 (d, J = 9,5 Hz, 1H, H-9) ; 3,99 (d, J = 5 Hz, 1H H-2) ; 3,79 (s, 3H, C<u>H</u>$_3$-O) ; 2,27 (d, J = 5 Hz, 1H, H-3) ; 2,18 (dd, J = 9 et 15,5 Hz, 1H, H-14) ; 1,76 (dd, J = 7,5 et 15,5 Hz, 1H, H-14) ; 1,54 (s, 3H, CH_3) ; 1,53 (s, 3H, CH_3) ; 1,42 (s, 6H, 2xCH_3) ; 1,38 (s, 3H, CH_3); 1,31 (s, 6H, 2xCH_3) ; 1,29 (s, 3H, CH_3) ; 1,02 (s, 9H, [C<u>H</u>$_3$]$_3$-C).

*Déprotection des positions 2' et 3' : **15** —> **10***. À 7,8 mg (0,008 mmol) de **15** mis en solution dans 0,1 ml de MeOH, on ajoute, à 0°C, 0,98 ml (1,1 éq. d'APTS) d'une solution d'APTS dans le MeOH 0,01M préalablement refroidie à 0°C. Après 45 mn à 0°C, puis 1h15 à température ambiante, le mélange réactionnel concentré est traité par plaques CCM (Heptane/AcOEt : 5/5). On obtient 3,9 mg de **10** (Rdt. = 58%) .

Composé 10. $C_{42}H_{59}NO_{12}$ (M = 769). Amorphe. $[\alpha]_D$ + 55 (c = 0,3, $CHCl_3$). IR : 3020, 2995, 1720, 1230, 1170 cm^{-1}. SM (IC) : 770 (MH^+), 712, 489, 431, 429 , 373, 371, 313. RMN ^1H (300 MHz) : 7,29-7,23 (m, 5H, Ph-H) ; 6,04 (m, 1H, H-13) ; 5,67 (d ép., J = 9 Hz, 1H, NH) ; 5,28 (d ép., J = 9 Hz, 1H, H-3') ; 4,91 (d, J = 8,5 Hz, 1H, H-5) ; 4,59 (d, J = 10 Hz, 1H, H-10) ; 4,55 (m, 1H, H-2') ; 4,47 (s, 2H, 2xH-20) ; 4,21 (s ép., 1H, OH) ; 4,18 (d, J = 10 Hz, 1H, H-9) ; 4,09 (d, J = 5 Hz, 3H, H-2) ; 2,44 (d, J = 5 Hz, 1H, H-3) ; 2,35 (dd, J = 10 et 15,5 Hz, 1H, H-14) ; 2,06 (s, 3H, C<u>H</u>$_3$-COO) ; 1,78 (dd, J = 5 et 15,5 Hz, 1H, H-14) ; 1,58 (s, 6H, 2xCH_3) ; 1,54 (s, 3H, CH_3) ; 1,44 (s, 3H, CH_3) ; 1,39 (s, 3H, CH_3) ; 1,38 (s, 9H, [C<u>H</u>$_3$]$_3$-C) ; 1,34 (s, 3H, CH_3) ; 1,30 (s, 3H, CH_3) ; 1,26 (s, 3H, CH_3).

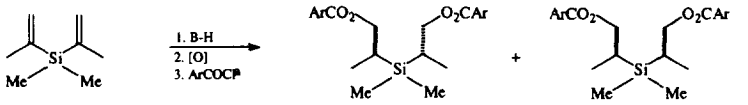
Préparation du 2-débenzoyl-1,2-O-isopropylidène-7-déshydroxy-10-acétyldocétaxel 16

*Protection des hydroxyles en positions 9, 10 de **18** par acétone/H_2SO_4 —> **20***. À 5,56 g (11,2 mmol) de **18** mis en solution dans 16 ml d'acétone à 0°C, on ajoute 16 gouttes d'acide sulfurique concentré. La réaction est laissée 5h sous agitation, puis le milieu réactionnel est neutralisé avec une solution saturée de bicarbonate de sodium. Après extraction par CH_2Cl_2, la phase organique est lavée avec une solution saturée de NaCl, séchée sur $MgSO_4$ et le solvant distillé. Le résidu est séparé par chromatographie sur colonne de silice avec l'éluant Heptane/AcOEt : 8/2. On isole 4,05 g de produit **20** (Rdt. = 64%) et 0,61 g de **19** (Rdt. = 9%).

*Protection des hydroxyles en positions 9, 10 de **18** par le 2,2-diméthoxypropane —> **20***. À 3,18 g (5,93 mmol) de produit **18** solubilisés dans 188 ml de THF anhydre, on ajoute 8 ml (10 éq.) de 2,2-diméthoxypropane, à 0°C, puis 1,22 g (1 éq.) d'APTS. Après 15 min, le bain de glace est retiré, le milieu réactionnel est agité 3h30 à température ambiante. La réaction est arrêtée avec une solution saturée de $NaHCO_3$. Après extraction par CH_2Cl_2, la phase organique est lavée par une solution saturée en NaCl, séchée sur $MgSO_4$ puis concentrée à sec sous pression réduite. Le produit est séparé par chromatographie sur colonne de silice à l'aide du mélange de solvants (Heptane/AcOEt : 8/2) : 2,92 g de produit **20** (Rdt. = 84%) et 0,37 g de produit de départ **18** (Rdt. = 10%) sont isolés.

Composé 20. $C_{32}H_{40}O_7$ (M = 536). Amorphe. $[\alpha]_D$ + 206 (c = 0,54, $CHCl_3$). UV [λmax nm (ε)] : 204 (8800), 216 (9000), 279 (13600). IR : 2930, 1720, 1670, 1130 cm^{-1}. SM (IC) : 537 (MH^+), 519, 479, 389, 331, 313. RMN ^1H (250 MHz) : 7,73 (m, 2H, Ph-H) ; 7,63 (d, J = 16 Hz, 1H, H-3") ; 7,42 (m, 3H, Ph-H); 6,35 (d, J = 16 Hz, 1H, H-2") ; 5,45 (s, 1H, H-20) ; 5,35 (s, 1H, H-20) ; 5,31 (s ép., 1H, H-5) ; 4,90 (d, J = 9 Hz, 1H, H-10) ; 4,27 (d, J = 9 Hz, 1H, H-9) ; 4,06 (d, J = 6 Hz, 1H, H-2) ; 3,25 (d, J = 6 Hz, 1H, H-3) ; 2,74

Table 10 Hydroborations of **63**



63 **64** **65**

reagent	catalyst	64	:	65
Ipc_2BH[b]	-----	65[c]	:	35
catBH	$Ph_2P(CH_2)_5PPh_2$/[Rh]	52	:	48
catBH	$Ph_2P(CH_2)_4PPh_2$/[Rh]	8.5	:	91.5
catBH	$Ph_2P(CH_2)_3PPh_2$/[Rh]	20	:	80
catBH	$Ph_2P(CH_2)_2PPh_2$/[Rh]	35	:	65
catBH	$Ph_2P(CH_2)PPh_2$/[Rh]	38	:	62
catBH	Ph_3P/Rh	46	:	54

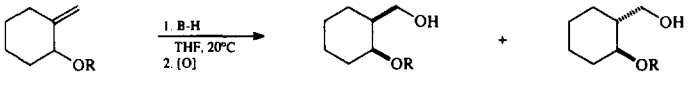
[a] Ar=4-BrC_6H_4, [b] Ipc=isopinocampheol, [c] e.e=75%

It is interesting that the diastereoselectivity achieved varies with the length of the chain connecting the two diphenylphosphine groups. This would suggest that the rhodium is complexed to both double bonds throughout, and that the strength of the complex is determined by the P-Rh-P angle, itself controlled by the length of the connecting chain.[51]

2.3.2 Cyclic alkenes

exo-Methylenecyclohexanes **66** with an allylic oxygen substituent yield *cis*-diols as the major components of the reactions products.[23] The uncatalysed reaction with 9-BBNH shows little selectivity (Table 11).

Table 11 Hydroboration of 2-methylenecyclohexanol derivatives **66**



66 **67** **68**

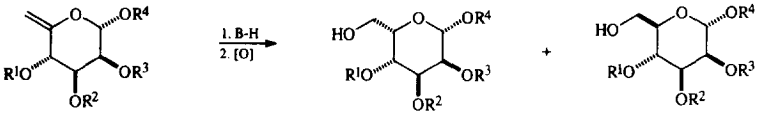
entry	R	conditions	67	:	68	yield (%)
1	H	9-BBNH	54	:	46	83
2	H	3%$RhCl(PPh_3)_3$[a]	91	:	9	93
3	H	3%[Rh(nbd)(dppb)]BF_4[a]	48	:	52	80
4	$SiBu^tMe_2$	9-BBNH	39	:	61	81
5	$SiBu^tMe_2$	3%$RhCl(PPh_3)_3$[a]	93	:	7	87
6	$SiBu^tMe_2$	3%[Rh(nbd)(dppb)]BF_4[a]	93	:	7	92

[a] All catalytic hydroborations use catBH

As regards the catalysed reactions, when R=H, a cationic complex shows no selectivity (entry 3) in contrast with a neutral complex (entry 2). However in the presence of a bulky substituent both complexes show good selectivity (entries 5, 6).

No studies seem to have been made of simple 2-methylenepyrans, but investigations[52] of complex derivatives[69] show that, whilst the reactions may be highly diastereoselective, it is difficult to predict the sense of the selectivity (Table 12). It should be noted that, as the substrates **69** are homochiral, structures **70** and **71** represent the absolute configurations of products.

Table 12. Hydroborations of substituted 2-methylenepyrans



69 **70** **71**

entry	R^1	R^2	R^3	R^4	reductant	**70**	:	**71**	yield (%)
1	TBS	CMe_2		Me	catBH/[Rh][a]	0	:	100	---
2	TBS	Bn	Ac	Me	catBH/[Rh]	50	:	50	---
3	Ac	Ac	Ac	Me	9-BBNH	37	:	63	85
4	Bn	Ac	Ac	Me	catBH/[Rh]	95	:	5	78
5	Bn	Ac	Ac	Bn	catBH/[Rh]	95	:	5	---
6	H	Bn	Ac	Bn	catBH/[Rh]	98	:	2	82

[a] $RhCl(PPh_3)_3$ used for all catalytic hydroborations

In this case it is surprising that increasing the bulk of the substituent on the allylic oxygen substituent actually *decreases* the diastereoselectivity (entries 2, 6). The substituent on the hemiketal oxygen, R^4, seems to have little effect (entries 4, 5) and R^2 can be changed from acetyl to benzyl with no change in selectivity. It would seem that having R^3 as acetyl is important, though the effect seems to be neutralised by a TBS group (entry 2). There is a striking change of stereoselectivity in an isopropylidene derivative (entry 1), which could be due simply to the TBS group effect predominating, or else to a conformational change in the pyran ring in the bicyclic isopropylidene derivative. If the TBS group is the dominant feature, then its effect is the opposite to that in cyclohexanes, *i.e.* it tends to give *trans*-products. Clearly more work on simple 2-methylenepyrans would be illuminating.

The diastereoselectivity of hydroborations of cyclohex-2-en-1-ol and cyclohexen-3-en-1-ol derivatives has been dealt with in Section 2.2.4.1 at the same time as the regioselectivities were considered.

2.4 Enantioselectivity of catalysed hydroborations of alkenes

2.4.1 Introduction

Three approaches to the problem of inducing enantioselectivity in catalysed hydroborations of alkenes can be used.

The first is to apply reactions of good stereoselectivity to homochiral substrates. This has been done in the case of allylic N-benzyltosylamides (section 2.3.1) derived from homochiral α-amino acids.[50] The

hydroboration of chiral allylic alcohol derivatives has been applied in a similar fashion (section 2.3.1),[48] and the reactions of methylene sugar derivatives (Section 2.3.2)[52] also fall into this category.

The second approach, so far little explored, is to produce a cheap chiral analogues of catecholborane and use uncomplicated non chiral catalysts such as $RhCl(PPh_3)_3$.

The third and very promising approach is to incorporate chirality into the ligands attached to the metal. If there is a high turnover number and regio- and diastereo-selectivity are retained, then there can be a high chiral multiplication factor. Summaries of earlier work in this field have been made.[10, 54]

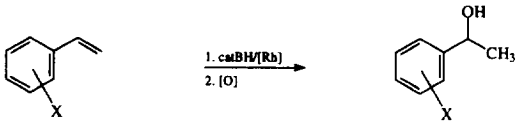
In particular Burgess and Ohlmeyer[54b] have emphasised that all factors must be examined if high chiral induction is to be achieved. Thus norbene gives *exo*-norbornanol with 23% e.e. using $[RhCl(COD)]_2$ and (*R*,*R*)-DIOP with **1** in benzene at 40°C. In THF at -40°C with the same catalyst and hydroborating agent the e.e. was raised to 55%.[54a] A change of catalyst to $[RhCl(COD)]_2$ and (*R*)-BINAP at -25°C in THF gave 64% e.e.

To obtain good enantiomeric syntheses the regiochemistry of the reaction must be as high as in the equivalent reactions without chiral ligands. However the ligand very frequently influences the outcome of the reaction. Thus the hydroboration of 2-phenyl-1-butene with $[RhCl(COD)]_2$, and (*S*,*S*)-BDPP gives a ratio of primary to tertiary alcohol of 53 : 47 with an e.e. of 30% and 84% respectively. When $Rh(COD)_2BF_4$, and (*R*,*R*)-DIOP is used the ratio becomes 73 : 27 with an e.e. of 13% and 43% respectively. The ratio of ligand to rhodium can strongly influence the regiochemistry and hence the usefulness of a reaction. Hydroboration of 2-phenylpropene with one equivalent of $[RhCl(COD)]_2$ and one equivalent of (*R*,*R*)-DIOP gave a ratio of primary to tertiary alcohol of 9 : 1, which changed to 1 : 8 when two equivalents of the same ligand were used. 'Asymmetric amplification' experiments provided no evidence for there being more than one phosphine ligand per catalyst molecule, but the data did not eliminate the possibility.

2.4.2 Monosubstituted ethenes

Studies of this group of compounds are restricted to substituted styrenes for reasons of regiochemistry (Section 2.2.4). In these cases use of cationic rhodium complexes allows internal attack to give, on oxidation, 1-arylethanols with almost complete regioselectivity.[29,55] A systematic study of the hydroboration of styrene with catecholborane using catalysts derived from $Rh(COD)_2BF_4$ and a chiral ligand showed that low temperatures (-78°C) and dimethoxyethane as solvent were advantageous. The best ligand was BINAP, the (*R*)-isomer giving (*R*)-1-phenylethanol with 96.2% e.e. and the (*S*)-isomer giving (*S*)-1-phenylethanol with 92.3% e.e. These conditions were applied to a variety of substituted styrenes with the results shown in Table 13.[55]

Table 13 Asymmetric hydroboration of substituted styrenes with catecholborane catalysed by rhodium (*R*)-BINAP complex[a]



entry	X configuration	Solvent	temp(°C)	yield(%)[b]	% e.e.	
1	4-Cl	DME	-78	98	90.5	(*R*)
2	4-Me	DME	-78	77	93.8	(*R*)
3	4-OMe	THF	-30	74	85.1	(*R*)
4	4-OMe	THF/DME	-78	54	88.5	(*R*)
5	3-Cl	DME	-78	99	84.6	(*R*)
6	2-Cl	DME	-50	30	72.1	(*R*)
7	2-OMe	DME	-30	84	81.5	(*R*)
8	2,4,6-Me_3	DME	-30	5	---	---

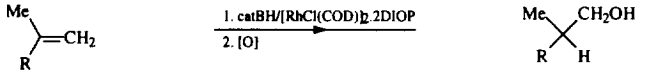
[a]% of complex generated from $Rh(COD)_2BF_4$ and (*R*)-BINAP. Alkene:catBH:$Rh(COD)_2BF_4$: BINAP=1.0 : 1.1 : 0.010 : 0.011., [b]Isolated yield.

Both 4- and 3-substituted styrenes gave good yields of products with high e.e.'s. However 2-substitution lowered the selectivity somewhat, and 2,6-disubstitution inhibited reaction. The best conditions may have to be a balance between chemical yield and chiral yield. Thus 4-methoxystyrene (entry 4) reacts at -78°C to give the corresponding 1-arylethanol with 88.5% e.e. but the yield goes down to 54% as compared to 74% at -30°C (entry 3).

2-Ferrocenylethane gives the (*R*)-1-arylethanol in 81% yield with e.e. of 58%. Surprisingly 2-naphthylethene gives (*S*)-1-(2-naphthyl)ethanol in 36% yield and 13.2% e.e.

2.4.3 1,1-Disubstituted ethenes

The asymmetric hydroboration of 1,1-disubstituted alkenes remains a problem for stoichimetric hydroboration with reagents such as Ipc_2BH.[56] In the first investigation of asymmetric hydroboration,[22] alkenes **72-74** were examined (Scheme 18).



72 R=Ph
73 R=Pr^i
74 R=Bu^t

75 R=Ph
76 R=Pr^i
77 R=Bu^t

Scheme 18

With (*R*,*R*)-DIOP, (*R*)-**75** with 27% e.e. resulted from **72**. Compound **73** gave (*S*)-**76** with 12% e.e. when(*S*,*S*)-DIOP was used and **74** gave (*R*)-**77** with 69% e.e. with (*R*,*R*)-DIOP.[20,54] Suzuki[57] also studied **74** but obtained only 12% e.e.

2.4.4 1,2-Disubstituted ethenes

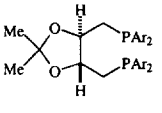
In general these compounds give low enantiomeric excesses. Thus 3-hexene gives 3-hexanol with 10% e.e.,[57a] (*E*)-stilbene and (*Z*)-stilbene give 1,2-diphenylethanol with 7% e.e. and 19% e.e. only,[20,22,55] using the DIOP complex. (*E*)- and (*Z*)-1-phenyl-1-propene give good yields (79%, 86%) of (-)-1-phenyl-1-propanol (*S,S*-DIOP) with 47% and 41% e.e.'s respectively. Alkenylboronic esters such as (*E*)-2-(2-phenylethenyl)-1,3,2-dioxaborolane react with catecholborane in the presence of rhodium diphosphine catalysts to give 1,2-diboryl-1-phenylethenes in poor to moderate yields.[57b] Use of chiral catalysts gives low chemical yields and moderate chiral induction.

2.4.5 Cyclic alkenes

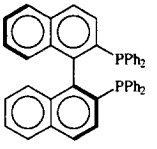
Indene reacts with cationic rhodium complexes to place boron entirely at the benzylic position. The complex with (*R*)-BINAP gave the (*S*)-alcohol but with only 13.1% e.e.[55] However with (*S,S*)-DIOP, (*R*)-1-indanol was obtained in 91% yield and 74% e.e.[56] In the same conditions 1,2-dihydronaphthalene gave (*R*)-tetralol with 14% e.e.[57] while norbornene gave (1*S*, 2*S*, 4*R*)-*exo*-norborneol with 59% e.e.[57] The e.e.'s using BINAP as ligand were much lower.[22,56] The initial report[22] on the catalysed hydroboration of norbornene gave an e.e. of 62% (at -25°C) using RhCl(COD).2(*R*)-BINAP and 55% with RhCl(COD).2(*R.R*)-DIOP.

Norbornadiene gave (1*S*,2*R*)-*exo*-1,4-dihydroxynorbornane with 76% e.e. using RhCl(COD).2(*R.R*)-DIOP and catecholborane.[22] However this product was accompanied by appreciable quantities of *meso*-1,3-dihydroxynorbornane.

Burgess[58] synthesised a series of (*R,R*)-DIOP derivatives which were chiral not only in the carbon backbone but also at phosphorus. Using these he was able to produce *exo*-norbornanol with an e.e. of 84%. However, regardless of the chirality at phosphorus, the chirality of the product was the same. This was also true for the production of 1-indanol and 1-phenylethanol, and therefore it is the chirality of the carbon backbone that controls the chirality of the reaction. There was no correlation in these experiments between the chirality at phosphorus and that at carbon and attempts to produce 'matched' and 'mismatched' catalysts were unsuccessful. The common chiral reagents used are shown in Figure 6.

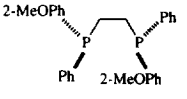


Ar=Ph; (*R,R*)-DIOP
Ar = 2-MeOPh; (*R,R*)-2-MeODIOP
Ar = 3-MeOPh; (*R,R*)-3-MeODIOP

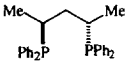


(*S*)-BINAP

(*R,R*)-CHIRAPHOS



(*S,S*)-DIPAMP

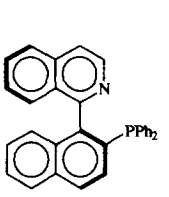


(*S,S*)-BDPP

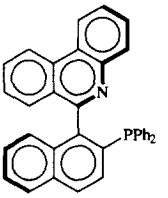
Figure 6

2.4.6 *Use of specially designed ligands*

Brown[59,60] has synthesised isoquinolyl (QUINAP) **78** and phenanthridyl **79** analogues of binaphthyl ligands in which a phosphorus group of the BINAP series is replaced by a ring nitrogen atom.



(S)-**78**



(R)-**79**

Table 14 shows the results of catalysed hydroborations of alkenes with catecholborane **1**. In general the results follow the known trends but it is of interest that enantioselectivities change little from 0°C to 40°C. In some cases respectable chemical yields are obtained to give products with >90% e.e's (entries 1, 4, 7, 8, 9, 10).

Table 14 Hydroboration of arylalkenes with **1** catalysed by Rh(COD)(*S*-QUINAP)CF_3SO_3 (**80**) and Rh(COD)(R-**79**)CF_3SO_3 (**81**)

entry	reactant	product	catalyst	e.e.% config.,	yield %[a]
1	$PhCH{=}CH_2$	$PhCHOHCH_3$	**80**	91 *S*	71
2	$PhCH{=}CH_2$	$PhCHOHCH_3$	**81**	67 *R*	70
3	$PhCH{=}CH_2$	$PhCHOHCH_3$	Rh-BINAP	96	
4	$4\text{-}MeOC_6H_4CH{=}CH_2$	$ArCHOHCH_3$	**80**	94 *S*	57
5	$4\text{-}ClC_6H_4CH{=}CH_2$	$ArCHOHCH_3$	**80**	78 *S*	56
6	$2\text{-}ClC_6H_4CH{=}CH_2$	$ArCHOHCH_3$	**80**	55 *S*	59
7	(*E*)-PhCH=CHMe	PhCHOHEt	**80**	95 *S*	64
8	(*E*)-PhCH=CHMe	PhCHOHEr	**81**	91 *R*	60
9	(*Z*)-PhCH=CHMe	PhCHOHEt	**80**	93 *S*	60
10	indene	1-indanol	**80**	91 *S*	58
11	indene	1-indanol	**81**	64 *R*	59
12	1,2-dihydronaphthalene	α-tetralol	**80**	37 *S*	68
13	1,2-dihydronaphthalene	α-tetralol	**81**	84 *R*	69
14	Δ^2-chromene	4-chromanol	**80**	52 *S*	21[b]
15.	Δ^2-chromene	4-chromanol	**81**	74 *R*	57
16.	1-(2-naphthyl)ethene	1-(2-naphthyl)ethanol	**80**	89 *S*	64
17.	1-(2-naphthyl)ethene	1-(2-naphthyl)ethanol	Rh-BINAP	13	
18.	$PhC(Me){=}CH_2$	$PhCHMeCH_2OH$	**80**	'low e.e.'	42
19.	norbornene	*exo*-1-bornanol	**80**	52 S	

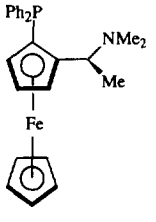
[a]Isolated yield, [b]3-OH isomer also produced.

Both **80** and **81** are effective catalysts for the hydroboration of 1-phenylpropene (entries 7, 8, 9). It is interesting that both the (*E*)- and (*Z*)-isomers give the same alcohol, as this implies that the Rh-H addition step in the catalytic cycle is reversible, as also shown by the isomerisation of the (*Z*)- to the (*E*)-isomer.

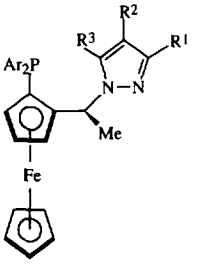
There are marked differences in the results using **80** and **81** (derived from **78** and **79** respectively). With styrene (entries 1, 2) and indene (entries 10, 11) **81** gives less asymmetric induction than **80** and with 1-phenylpropene (entries 7, 8, 9) both are highly effective. With 1,2-dihydronaphthalene (entries 12, 13) **81** is far more effective than **80**, as it is with Δ^2-chromene (entries 14, 15), with which it is also more regioselective.

Thus steric effects in both the ligand and the substrate are important in determining the stereoselectivity of catalytic asymmetric hydroboration. A model which on steric grounds correctly predicts the stereochemical outcome of the reactions was proposed.[60] However the detailed differences between **80** and **81** require further elucidation.

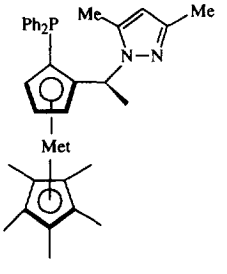
The phosphine-amine ferrocenyl ligand **82** was only effective for the rhodium catalysed hydroboration of styrene with **1**. No other alkene reacted at -78°C and at higher temperatures there was little asymmetric induction.[61]



(*S,R*)-**82**



(*S,R*)-**83**



(*S,R*)-**84**, a, Met=Fe
b, Met=Ru

A related series of pyrazolyl ligands **83** was produced[62] and Ar, R^1, R^2 and R^3 were systematically varied and tested for the catalysed hydroboration of styrene, using the cationic complex $Rh(COD)_2BF_4$ as the source of rhodium. An immediate and serious problem is that, despite using a cationic complex, the reactions are not highly regioselective, the *p*-alcohol : *sec*-alcohol ratios varying between 64 : 36 to 79 : 21 and many reagents were hardly regioselective at all. Optimal substitution on the pyrazole ring comes when R^1=R^3=Me; R^2=H. (e.e. of 1-phenylethanol=95.1%) and this is enhanced when Ar changes from phenyl to 4-$CF_3C_6H_4$ (98.0% e.e). When an electron withdrawing group is placed on the pyrazolyl ring at R^1 or R^1, R^3 the e.e. of the product is reduced. However increase of steric hindrance of R^1, R^3 by making them isopropyl groups has little effect. The results were not explicable by steric effects nor by partial dissociation of the ligands from the metal. An interesting concept of 'electronic asymmetry' at the metal centre was introduced and remains to be explored.

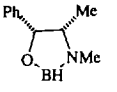
The pentamethyl analogue **84a**[63] reacted with 76% regioselectivity with styrene to give (*R*)-1-phenylethanol with 94% e.e. The corresponding ruthenium compound **84b** reacted with 67% regioselectivity to give product with 87% e.e. A variety of other diphosphinylruthenocene and ferrocene complexes were tested but none gave both good regioselectivity and asymmetric induction.

The synthesis of an electron poor biphenyldiphosphinyl ligand has been reported.[64] It offers no advantage in the hydroboration of 4-methoxystyrene as regards regiochemistry (78 : 22) or asymmetric induction (e.e. 78%).

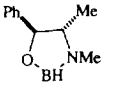
TADDOL derived cyclic phosphonites, with phosphorus attached to two oxygen atoms gave little asymmetric induction in the catalysed hydroboration of styrene.[65]

2.4.7 Use of chiral hydroborating agents

The combination of chiral hydroborating agent and a metal complex allows the investigation of the role of the structure of the hydroborating agent in catalysed hydroborations. In conjunction with chiral ligands studies can be made of the combined roles of ligand and borane and whether enantioselectivities can be enchanced by a judicious choice of both. Borane reagents **85** and **86** derived from ephedrine and pseudoephedrine have been examined[66] for their reactions with 4-methoxystyrene.



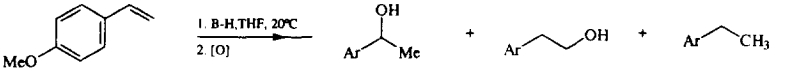
85



86

The uncatalysed reaction of **86** is sluggish at 100°C and gave >90% of the primary alcohol. Additions of 1 mol % of either $RhCl(PPh_3)_3$ or $HRh(PPh_3)_3$ in THF leads to smooth reaction at ambient temperature. Oxidative work up led to a mixture of 1-phenylethanol, 2-phenylethanol and ethyl benzene with modest selectivity. However the secondary alcohol **87** (Ar=Ph) was produced with an e.e. of 17% (*S*) using **85** and 55% (*R*) using **86**. *Thus a chiral borane on its own is able to induce chirality in a transition metal catalysed hydroboration.* Some representative results are given in Table 15.

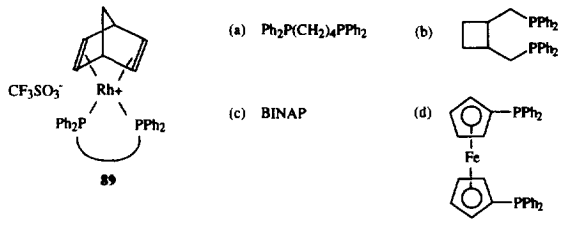
Table 15 Hydroboration of 4-methoxystyrene 28 with chiral oxazaborolidines



28 **87** **88** **32**

entry	borane	catalyst	**87** (e.e., config.)	**88**	**32**
1	**84**	$Ph_3P/RhCl(PPh_3)_3$	36 (17, (*S*))	28	36
2	**84**	$Ph_3P/RhCl(PPh_3)_3$[a]	63 (31, (*S*))	25	12
3	**84**	**89a**	95 (5, (*S*))	5	0
4	**84**	**89b** (*S*)	75 (31, (*R*))	13	12
5	**84**	**89c** (*R*)	32 (86, (*S*))	37	31
6	**84**	**89c** (*S*)	25 (8, (*S*))	38	38
7	**85**	$PPh_3/RhCl(PPh_3)_3$	53 (55, (*R*))	24	23
8	**85**	**89a**	96 (6, (*S*))	2	2
9	**85**	**89c** (*R*)	low	low	major
10	**85**	**89c** (*S*)	42 (83, (*R*))	28	30
11	**85** (4R, 5R)	**89d**	82 (76, (*S*))	14	4

[a]Glyme as solvent



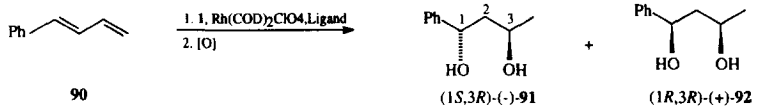
Unfortunately those catalysts that give good regioselectivity give low asymmetric induction (entries 3, 8), the best compromise being that in entry 11. That the chirality of the ligand as well as the borane can be influential is shown by comparing entry 5 with 6 and entry 9 with 10. Solvent also has an effect, induction increasing in glyme as compared with THF (entries 1, 2).

2.4.8 Chiral hydroboration of 1,3-dienes

Rhodium catalysed hydroboration of 1-phenyl-1,3-butadiene **90** with catecholborane **1** can be carried out to give double hydroboration and, on oxidation, to give 1-phenyl-1,3-butanediols **91** and **92**. With $RhCl(PPh_3)_3$ the *anti* : *syn* ratio is 10 : 1.[67] It is somewhat unusual to catalyse diene reactions with Wilkinson's catalyst due to the strength of the complexes with dienes.[14]

Attempts to make the reaction chiral[67] were complicated in that the ratio of *anti* : *syn* products fell from 3 : 1 to 2 : 1. Again, yields and enantiomeric excesses opposed each other and no really satisfactory conditions were found to give high yields of either the *anti*- or *syn*-isomers (Table 16).

Table 16 Asymmetric hydroboration of **90** catalysed by chiral rhodium complexes



90 (1*S*,3*R*)-(-)-**91** (1*R*,3*R*)-(+)-**92**

entry	ligand	solvent	temp°C	Yield (**91**+**92**)	**91** : **92**	**91** (%e.e.)[a]	**92** (%e.e.)[b]
1	(*R*)-BINAP	THF	20	62	3 :1	40	44
2	(*R*)-BINAP	THF	0	77	3 : 1	48	43
3	(*R*)-BINAP	THF	-20	42	3 : 1	61	35
4	(*R*)-BINAP	DME	20	57	3 : 1	46	40
5	(*R*)-BINAP	C_6H_6	20	68	3 : 1	47	36
6	(*R*)-BINAP	CH_2Cl_2	20	60	3 : 1	55	11
7	(*R*)-BINAP	CH_2Cl_2	-20	36	3 : 1	67	11
8	(*R*,*S*)-BPPFA	C_6H_6	20	65	2 : 1	2	15
9	(*S*,*S*)-DIOP	C_6H_6	20	62	2 : 1	8	2

[a]Product **91** was always (1*S*,3*R*), [b]Product **92** was always (1*R*,3*R*)

For the *anti*-isomer, lower temperatures (entries 1, 2, 3) and solvents of low polarity (entries 5, 6, 7) gave higher e.e.'s. Neither statement applies to the *syn*-isomer. A model to explain the favoured production of the *anti*-isomer has been proposed.[67]

2.5 The catalytic hydroboration of alkynes

2.5.1 Introduction

The stoichiometric hydroboration of alkynes has been well explored and reagents have been developed that add either once or twice to the triple bond and which are also very sensitive to the steric environment on each side of the triple bond.[3,4,68] In general the reactions are more facile than hydroboration of double bonds and stereospecifically add the BH in a *syn* fashion. Therefore in order for the catalytic process to be useful it must, in some way, complement the known reactions. This section deals with Rh(I) catalysis. See sections 2.6.4, 2.6.5 and 2.6.6 for titanium, zirconium and Rh(III) catalysed hydroborations of alkynes.

2.5.2 Catalysed hydroboration of phenylethyne

The rhodium mediated hydroboration of phenylethyne has been studied[32] using 2 equivalents of **1** and 1 mol % of catalyst. The results, which vary with time and amount of triphenylphosphine, are presented in Figure 7.

$PhC{\equiv}CH \xrightarrow[2.\ [O]]{1.\ [Rh],\ 1}$ PhCHOHMe, $PhCH_2CH_2OH$, PhCOMe, $PhCH_2CHO$, $PhCHOHCH_2OH$

$RhCl(PPh_3)_3$ (1h)	9	12	32	47	trace
$RhCl(PPh_3)_3$ (12h)	20	9	10	3	58
$RhCl(PPh_3)_3 + PPh_3$ (1.5h)	2	2	35	60	trace
$RhCl(PPh_3)_3 + PPh_3$ (15h)	29	9	16	12	29
$[RhCl(COD)]_2 + 8PPh_3$ (12h)	54	19	trace	trace	27

Figure 7

The reactions are not particularly regioselective, even in the presence of a large excess of triphenylphosphine.[28] Reduction products, 1- and 2-phenylethanol, increase with time presumably due to a build up of rhodium hydride species from the degradation of **1** (section 5.2). The increase of phenylglycol with time suggests that the alkenylboronate intermediates can themselves be hydroborated.

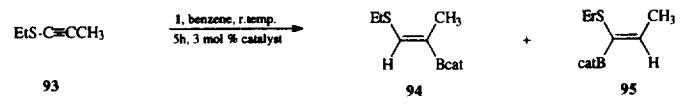
For the hydroboration of alkynes with $Cp_2Zr(H)Cl$ and pinacolborane see section 2.6.5. For the hydroboration of alkynes with pinacolborane catalysed by rhodium and nickel catalysts see section 2.7.3.1.

2.5.3 Catalysed hydroboration of alkylthioethynes

The non-catalysed hydroboration of thioalkynes by dialkylboranes shows a strong preference for placement of boron on the carbon atom bearing the sulfur group.[69] A study[70] of the transition metal catalysed coupling of 1-(methylthio)propyne with catecholborane, **1** showed that rhodium catalysis was inefficient both in terms of chemical yield and regioselectivity (Table 17, entries 4, 5, 6). Some palladium catalyts (Table 17, entries 1, 3) were effective in placing the boron atom on C-2, β to the sulfur atom but yields were only moderate. Nevertheless palladium catalysts are useful as they can then be used in a one pot procedure which involves first catalytic hydroboration and then coupling of the vinylboronate with unsaturated halides.[71] In fact with a variety of methylthioalkynes the isolated yields on the overall hydroboration-coupling process ranged from 72-90%, showing that the yield on ethylthiopropyne might have been somewhat misleading as regards the potential of palladium catalysis. Finally, excellent yields and regioselectivities in the catalysed hydroboration were obtained with bidentate phosphine ligands on nickel chloride (Table 17, entries 8, 9), in marked contrast

to the uncatalysed reaction (Table 17, entry 10).

Table 17 Catalysis of hydroboration of 1-ethylthio-1-propyne **93** with catecholborane



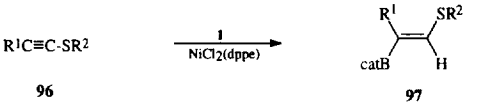
93 94 95

entry	catalyst	% yield[a]	**94** : **95**
1	$Pd(PPh_3)_4$	54	98 : 2
2	$PdCl_2(PPh_3)_2$	29	66 : 34
3	$PdCl_2$(dppf)	69	96 : 4
4	$RhCl(PPh_3)_3$	40	58 : 42
5	$Rh(Cp)(PPh_3)_2$	12	91 : 9
6	$[Rh(COD)(PPh_3)_2]_2PF_6$	45	74 : 26
7	$NiCl_2(PPh_3)_2$	19	52 : 48
8	$NiCl_2$(dppe)	100	>99 : 1
9	$NiCl_2$(dppp)	97	98 : 2
10	None	20	50 : 50

[a]g.c. yields

The conditions used in entry 8 were then applied to a variety of thioalkynes (Table 18).

Table 18 Nickel catalysed hydroboration of thioalkynes with catecholborane **1**



96 97

Entry	R^1	R^2	%yield of **97**[a]
1	H	Ph	93[b]
2	Me	Et	99
3	Bu	Me	93
4	Chx[c]	Me	92
5	Ph	Me	95
6	vinyl	Me	63
7	MeS	Me	78

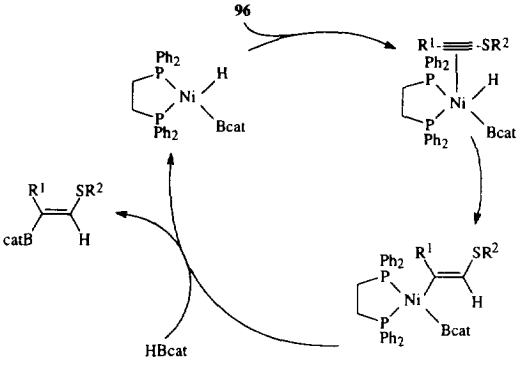
[a]Isolated yields by distillation, [b]$NiCl_2$(dppp).3 mol % used, [c]Chx=cyclohexyl

All reactions proceeded smoothly even when R^1 was bulky (entry 4), although uncatalysed hydroborations seem more sensitive to steric than to electronic effects.[69] The conjugated enyne tried (entry 6) underwent 1,2-addition to the triple bond in strong contrast to 2-methyl-1-buten-3-yne which undergoes 1,4-addition (*vide infra*). Phenylthioethyne gave only 30% yield with $NiCl_2$(dppe), but satisfactory reaction with $NiCl_2$(dppp) (entry 1). A phenyl group (entry 5) and a methylthio group on the triple bond were successfully accommodated (entry 7).

1-Ethoxy-1-propyne gave the *cis*-2-boronate in 98% yield, the reaction proceeding in an analogous fashion to the alkylthioalkynes. Uncatalysed hydroborations with borane[72] or catecholborane[73] also place boron β to the oxygen substituent.

The catalysed reaction of catecholborane with 1-phenyl-1-propyne is not particularly regiospecific (66 : 34 ratio of placement of boron on C-2 compared to C-1), indeed slightly less so than the uncatalysed reaction.[72]

Based upon the much greater efficacy of bidentate phosphine ligands (Table 17, entries 8, 9) as compared with monodentate ligands (Table 17, entry 7), a saturated five-co-ordinate nickel complex, formed with elimination of a phosphine ligand, was proposed as a key intermediate in the catalytic cycle (Scheme 19).

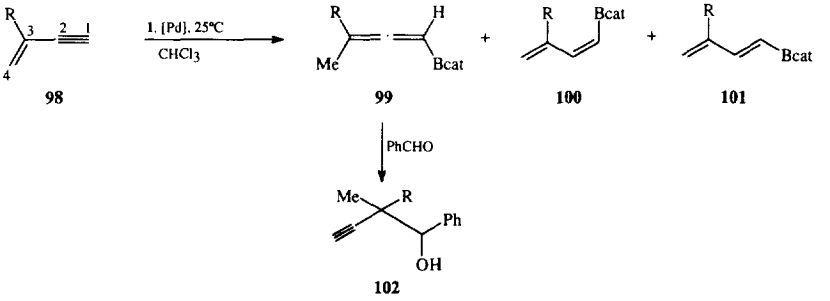


Scheme 19

2.5.4 Catalysed hydroboration of 1,3-enynes

There are three possible modes of mono-addition of catecholborane to a 1,3-enyne. The borane can add in a 1,2-fashion across either the double or triple bond or it can add in a 1,4-fashion across the complete system. In practice 1,2-addition across the double bond is not observed but both other modes occur in proportions which depend on the specific substrate and conditions.

In the presence of $Pd(PPh_3)_4$, catecholborane **1** adds to 3-methylbut-3-en-1-yne **98**, R=Me, by 1,4-addition to give an allenic borane that was characterised by benzaldelyde addition (Scheme 20).[53] This observation was followed up by a detailed study[74] the results of which are given in Table 19.



Scheme 20

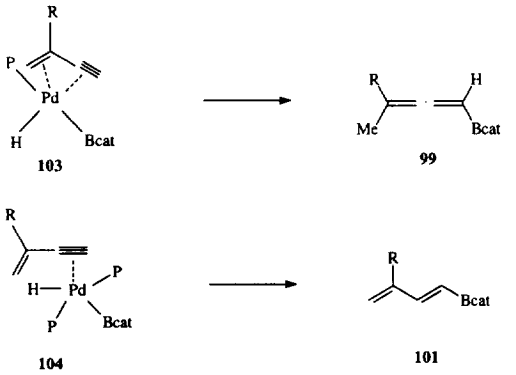
Table 19 Hydroboration of 3-alkylbut-3-en-1-ynes with **1**, catalysed by palladium-phosphine complexes according to Scheme 21

Entry	R	catalyst[a]	yield[b]	**99**	:	**100**	:	**101**
1	Me	$Pd(PPh_3)_4$	75	60	:	34	:	6
2	Me	[Pd][c] $5PPh_3$	86	38	:	37	:	25
3	Me	[Pd] $4PPh_3$	75	41	:	53	:	6
4	Me	[Pd] $2PPh_3$	70	62	:	38	:	0
5	Me	[Pd] $1.5PPh_3$	63	84	:	16	:	0
6	Me	[Pd] PPh_3	22	92	:	8	:	0
7	Me	[Pd]	0			----------		
8	Me	[Pd]dppe	39	0	:	0	:	100
9	Me	[Pd]dppb	61	0	:	0	:	100
10	Me	[Pd]dppf	89	0	:	0	:	100
11	Me	[Pd] $2PPh_2(C_6F_5)$	73	83	:	17	:	0
12	*n*-Pentyl	[Pd] $2PPh_2(C_6F_5)$	74	88	:	12	:	0
13	*t*-Bu	[Pd] $2PPh_2(C_6F_5)$	89	83	:	4	:	13

[a]Reactions in $CHCl_3$ at 25°C with 1.25-1.5 equiv. of **1** and 2 mol % of catalyst, [b]Isolated yield by distillation, [c][Pd]=$0.5Pd_2(dba)_3.CHCl_3$

Entry 1 shows that a simple palladium catalyst induces hydroboration in good yield but with little selectivity. Experiments 2-7 are interesting in that they show the effect of the amount of triphenylphosphine present on the selectivity of the reaction. Experiment 6 gives the highest selectivity of any tried and, though the yield was poor all the reactions of entries 2-7 were done for 0.5h only and if left longer entry 6 could lead to a preparative procedure. The need for a phosphine ligand is shown by entry 7. The substitution of a C_6F_5 group for a C_6H_5 group enchances the stereoselectivity (compare entries 4 and 11) and offers a rapid preparative procedure for compounds **99**. The use of bidentate phosphine ligands (entries 8, 9 and 10) radically alters the stereoselectivity of the process and 1,2-addition product **101** is the sole result of the reactions.

The authors' explanation of these results is given in Scheme 21.



Scheme 21

The key intermediate giving **99** would be **103** with only one co-ordination site occupied by a phosphine ligand, in line with experiments using 1-2 equivalents of a monodentate ligand. Intermediate **104** could be

formed from a bidentate ligand. It can provide only one co-ordination site for the enyne and therefore catalyses 1,2-addition to the triple bond to produce 1,3-(*E*)-dienylborane, **101**.

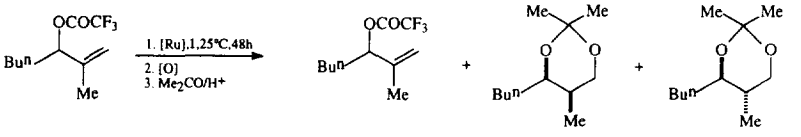
It should be noted that allene production proceeds only for 3-substituted 1,3-enynes. Compounds such as 4-phenyl-3-buten-1-yne undergo selective 1,2-hydroboration at the triple bond to give *E*-dienylboranes even with $PPh_2(C_6F_5)$[Pd] as catalyst. Alkyl substitution at the 1-position inhibited reaction.

The reactions of the allenylboranes with benzaldehyde proceed at -78°C in chloroform to give **102** without need to isolate the allenes, as the dienylboranes do not react.

2.6 Catalysed hydroborations with catalysts other than rhodium or iridium complexes

2.6.1 Ruthenium based catalysts

Männig and Nöth[9] early reported that $RuH(Cl)(CO)(PPh_3)_3$ showed low activity as a catalyst in hydroboration. Later a systematic study of ruthenium complexes was made by Burgess and Jaspers.[75] They tested $RuCl_2(PPh_3)_4$, $RuCl_3(PPh_3)_2$.MeOH, $RuH(Cl)(PPh_3)_3$, $RuH_4(PPh_3)_3$ and $RuH(Cl)(DIOP)_2$ with catecholborane **1** and oxazaboroline **29**. All the complexes were shown to be catalysts for the hydroboration of alkynes and unhindered alkenes. There are however some drawbacks to the use of ruthenium complexes. The first is that competing hydrogenations occur in all cases and with both boranes used. Thus hydroboration/oxidation of dec-1-yne gave dec-1-ene and decane as well as decan-1-ol, decan-2-ol and decaldehyde as an inseparable mixture. Secondly the reactions are slower than those with rhodium catalysis and give lower regioselectivities (Scheme 22).



$RuCl_2(PPh_3)_4$	32	:	41	:	28
$RuCl_3(PPh_3)_2$.MeOH	41	:	33	:	24
$RuH(Cl)(PPh_3)_3$	27	:	40	:	32

Scheme 22

Thirdly, though reaction occurs predominantly by the addition of **1**, an analysis of the reaction of cyclohexene with **1** catalysed by $RuCl_3(PPh_3)_2$.MeOH showed that there is some disproportionation of catecholborane to BH_3 which rapidly adds in an uncatalysed reaction.

Styrene and norbonene react relatively rapidly (*ca.* 6h). The major product from styrene tends to be 2-phenylethanol, through with $RuH_4(PPh_3)$ and **29**, the secondary alcohol is 71% of the product mixture. However the hydrogenation product, ethylbenzene is always present and can be the major component of the mixture. Norbornene gives *exo*-norbornanol, though again accompanied by starting material and norbornane.

In summary, ruthenium complexes currently offer no advantages as compared with rhodium and iridium complexes for catalysed hydroborations.

2.6.2 *Lanthanide based catalysts*

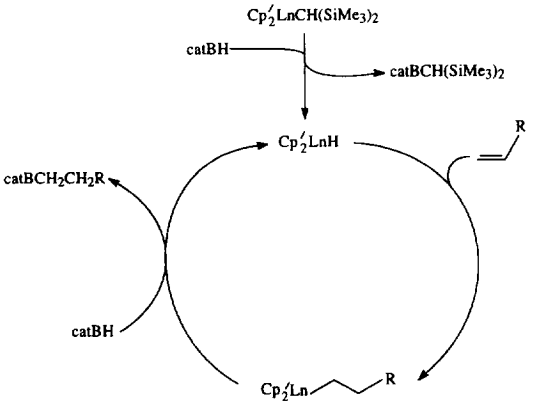
Pentamethylcyclopentadienyl (Cp′) complexes of lanthanum and samarium efficiently catalyse the hydroboration of alkenes with **1**.[76] Complexes Cp'_2LnR (Ln=La,Sm; R=H, $CH(SiMe_3)_2$), Cp''_2LnR($Cp'' = \eta^5$-C_5Me_4, Ln = Sm, R = $CH(SiMe_3)_2$) and $Cp'_2Sm(THF)$ were studied. Hydroborations were carried out at 20°C for 14h in benzene, and the product mixtures were then oxidised. Results are presented in Table 20.

Table 20 Organolanthanide catalysed alkene hydroboration with **1**

Entry	substrate	product	yield(%)[a]
1	$CH_3(CH_2)_3CH=CH_2$	$CH_3(CH_2)_4CH_2OH$	78
2	4-$MeOC_6H_4CH=CH_2$	4-$MeOC_6H_4CH_2CH_2OH$	89
3	$EtC(Me)=CH_2$	$EtCH(Me)CH_2OH$	71
4	cyclohexene	cyclohexanol	25
5	norbornene	*exo*-norbornanol	71
6	1-methylcyclohexene	*trans*-2-methylcyclohexanol	79
7	1-methylcyclopentene	*trans*-2-methylcyclopentanol	73
8	(*E*)-stilbene	1,2-diphenylethanol	61

[a]Isolated yields

The hydroborations occur in an *anti*-Markovnikov sense, as with uncatalysed hydroborations and without hydrogenation. Trisubstituted alkenes can be hydroborated (entries 6, 7) and it will be interesting to examine chirality induction in such systems. No reaction was observed with tetramethylethene (2,3-dimethyl-2-butene), the rates in general being in the order terminal > terminal disubstituted > internal disubstituted > trisubstituted alkenes. Larger metal ions and more ligation increase the rate of reaction, in particular $N_t(La) \approx 10N_t(Sm)$. For R = $CH(SiMe_3)_2$, NMR studies reveal that production of $catBCH(SiMe_3)_2$ precedes catalytic turnover. That the conveniently prepared $Cp_2'Sm(THF)$ is an efficient precatalyst argues that binuclear substrate activation provides access to the catalytic manifold. Moreover labelling studies with catB-D (entries 1, 2, 4 and 5) show that reactions occur with no scrambling and with delivery of deuterium to C-2, β-to boron in the organylborane. The cycle shown in Scheme 23 accommodates the experimental findings.



Scheme 23

It was later found[77] that simple trivalent lanthanide derivatives also catalyse hydroborations of alkenes with **1**. (Table 21).

Table 21 Hydroboration/oxidation of 1-decene with LnX_3 using catecholborane **1**

entry	catalyst[a]	conversion[b]	*prim* : *sec*
1	SmI_3	98	50 : 1
2	$Sm(OBu^t)I_2$	94	46 : 1
3	$Sm(OPr^i)_3$	98	42 : 1
4	ScI_3	69	43 : 1
5	PrI_3	92	21 : 1
6	LuI_3	84	11 : 1
7	$Eu(tfc)_3$	92	22 : 1

[a]10 mol % used, [b]conversion after 18h at 25°C

Hydroboration in the case of all entries proceeds to give the *anti*-Markovnikov product as the major, sometimes almost the exclusive product. However SmX_3 (X=Br, Cl, F, OTf) all failed to catalyse the reaction.

Very interestingly it was shown that for the hydroboration of dec-1-ene the ratio of 1-decanol : 2-decanol varied with time; 3 : 1 after 3h (8% conversion); 3.5 : 1 after 7h (40% conversion) and 50 : 1 after 18h (98% conversion). Therefore either the formation of the boronate is reversible or the catalyst is being chemically modified. There is also an increase in rate as the reaction proceeds and the SmI_3, which is only slightly soluble in THF, eventually dissolves in the presence of **1**, and 1-decene. Thus SmI_3 may not be the actual catalyst.

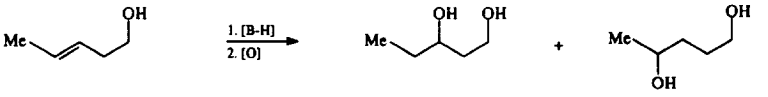
The SmI_3 mediated reaction was tested with a variety of alkenes as in Table 22.

Table 22 SmI_3 catalysed hydroboration of alkenes with **1**

entry	substrate	product	(conv.%)[a],	yield %[b]	ratio
1	$CH_3(CH_2)_7CH{=}CH_2$	$CH_3(CH_2)_8CH_2OH$	(98)	79	50 : 1[c]
2	$PhCH{=}CH_2$	$PhCH_2CH_2OH$	(59)	47	5 : 1[c]
3	$PhC(Me){=}CH_2$	$PhC(Me)CH_2OH$	(91)	81	>99 : 1[d]
4	norbornene	*exo*-norbornanol	(97)	78	27 : 1[e]
5	(*E*)-PhCH=CHPh	$PhCH_2CHOHPh$	(80)	67	---
6	1-phenylcyclohexene	*trans*-1-phenylcyclohexanol	(85)	64	>99 : 1[f]
7	α-pinene	isopinocampheol	(79)	61	[g]

[a]conversion after 18h, [b]purified product after 18h, [c]*prim* : *sec* alcohols, [d]*prim* : *tert* alcohols, [e]*exo* : *endo*, [f]*trans* : *cis*, [g]one product only.

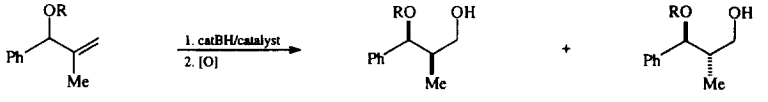
As shown in Scheme 24, the catalysed reaction has greater regioselectivity than uncatalysed reactions in hydroxy directed hydroboration.



10 mol% SmI_3,catBH	11	:	1	73%
$ThxBH_2$	3	:	1	56%
9-BBNH	3	:	1	62%

Scheme 24

A preliminary assessment of acyclic reaction diastereoselectivity was made as shown in Scheme 25.



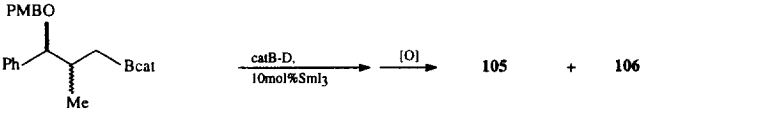
105 **106**

SmI_3; R=H;	conversion after 18h., 99%	2	:	1
SmI_3; R=PMB*;	conversion after 7h., 21%	1.8	:	1
SmI_3; R=PMB;	conversion after 18h., 95%	2.1	:	1
NdI_3; R=PMB;	conversion after 7h., 9%	1	:	9
NdI_3; R=PMB:	conversion after 18h., 98%	1	:	1.4

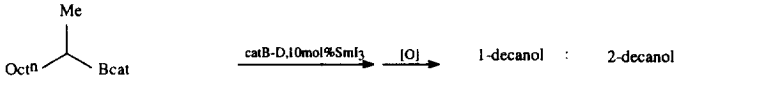
*PMB=*para*-methoxybenzene

Scheme 25

The ratios of *syn* : *trans* products varied with time in the cases tested, and so the question of reversibility was important. To test this the experiments shown in Scheme 26 were carried out.[76]



107 *syn* : *anti*=1.2.8 2 : 1 (No D incorporation)

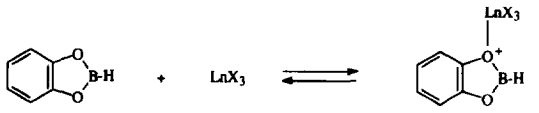


108 48 : 1 (No D incorporation)

Scheme 26

The *syn* : *anti* ratio of **107** changed without deuterium incorporation, and the pure 2-boronate **108** gave mainly the 1-ol, again without deuterium incorporation. It would appear that a non-dissociating alkene complex is formed in the reaction mixture. Olefins such as 1-phenylcyclohexene (Table 22, entry 6) give boronates that do not isomerise even over extended periods.

The authors point out that though it is reasonable to conclude that catalysis could proceed *via* a lanthanide hydride, there is also the possibility that LnX_3 activate catecholborane by Lewis acid complexation, that would increase the Lewis acidity of the boron centre. This should, in turn, elevate the hydroboration capacity of catecholborane (Scheme 27).



1

Scheme 27

The authors stated that $Zr(OEt)_4$, Cp_2ZrCl_2, $Ti(OPr^i)_4$ and Cp_2TiCl_2 also act as catalysts for the hydroboration of alkenes by **1** but no details were given.[77]

A survey[78] was carried out of early transition metal complexes as catalysts for the hydroboration of 1-hexene with **1**. In all cases except Cp_2TiMe_2(93 : 7) and Cp_2ZrMe_2(95 : 5), 1-hexanol, the *anti*-Markovnikov product, was produced with a regioselectivity of >99 : 1.

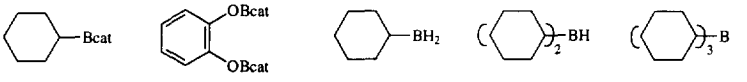
Most complexes had some catalytic activity, but the most effective was $Cp'_2LaCH(SiMe_3)_2$.[76] Many catalysts were rapidly deactivated and some catalysts such as $Cp'_2YCH(SiMe_3)_2$ led to the decomposition of **1**.

In general catalytic activity depended on the metal and the stabilising auxiliary ligand system present. For bis(pentamethylcyclopentadienyl) complexes the highest activity is found for lanthanum, the largest metal. For smaller metal centres (Y, Zr, Ti) activity is low.[78]

2.6.3 Niobium based catalysts

An investigation was made into the hydroboration of alkenes with **1** catalysed by dimesitylniobium (Mes_2Nb).[79] The reactions were clean and rapid with regio- and stereo-selectivities similar to those of borane.

^{11}B NMR investigation of the reaction mixture from cyclohexene, **1** and Mes_2Nb revealed that the expected boronate ester **109** was not the major product. An intense resonance was observed corresponding to **110** and peaks corresponding to **111**, **112** and **113** were also present.



109 **110** **111** **112** **113**

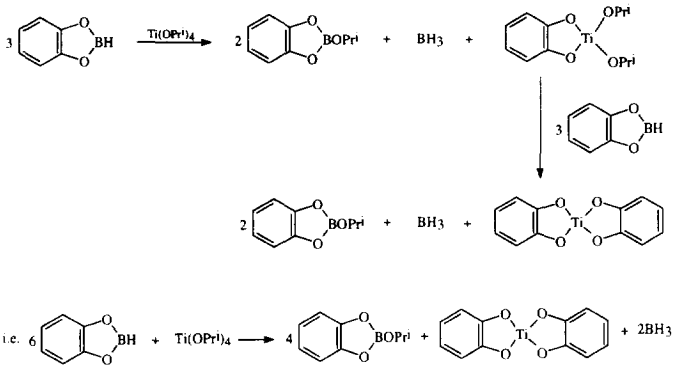
It was shown that Mes_2Nb does not cause disproportionation of **109**. Therefore BH_3 is the active hydroborating agent, and the role of Mes_2Nb is to establish an equilibrium between **1** and **110** which yields borane itself in a rate limiting step. The need for multinuclear NMR monitoring of catalysed hydroborations using **1** has previously been stressed.[27,80]

2.6.4 Titanium based catalysts

The promotion of the hydroboration of alkenes by borohydrides using Cp_2TiCl_2[81] and $TiCl_3$[82] has been recently re-investigated.[83]

Titanium trichloride causes rapid dismutation of $LiBH_4$ to borane which is the active hydroborating agent. The Cp_2TiCl_2 complex also serves to produce borane via $Li[Cp_2Ti(BH_4)_2]$, and in some circumstances the Cp_2TiH can, in fact, add across a double bond.[83]

Titanium tetraisopropoxide catalysed the hydroboration of akenes by catecholborane, **1**.[83] This is also due to the production of borane, as in Scheme 28.



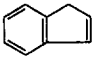
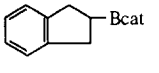
Scheme 28

With hindered alkenes such as cyclohexene the pathway shown in Scheme 29 is followed and trialkylborane results from the borane generated. The situation can however be more complex as monoalkylboranes can react with catecholborane/$Ti(OPr^i)_4$ to give RBcat. There remains some possibility that terminal alkenes may participate in a genuine catalytic pathway, but this is not proven.

Surprisingly, an ^{11}B NMR investigation of the hydroboration of cycloheptene with **1** and $Ti(OPr^i)_4$ showed only $(C_6H_4O_2)B(C_7H_{13})$ with no other compounds containing a C-B bond. The same was true for Cp_2TiCl_2.[84]

However it has been shown that dicarbonyltitanocene $(Cp_2Ti(CO)_2)$ **114** is an efficient and selective catalyst for alkyne hydroborations by **1** and that dimethyltitanocene (Cp_2TiMe_2) **115** is equally effective for alkene hydroborations. Both types of reaction proceed in an anti-Markovnikov fashion.[85]

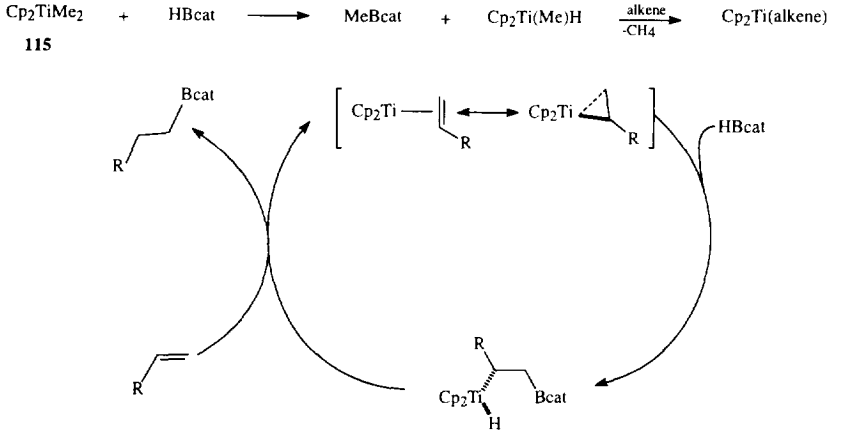
Table 23 Hydroborations with **1** of alkynes and alkenes catalysed by **114** and **115**

entry	substrate	catalyst[a]	products[b]	temp°C,	time(h)	%yield[c]
1	*p*-TolC≡CH	**114**	*p*-TolCH:CHBcat	25	2	96
2	BuC≡CH	**114**	BuCH:CHBcat	25	2	97
3	PhC≡CPh	**114**	$PhCH_2COPh$	25	2	91
4	MeC≡CPh	**114**	$MeCH_2COPh$ (67) $MeCOCH_2Ph$ (33)	25	2	89
5	*p*-TolCH=CH_2	**115**	*p*-TolCH_2CH_2OH	25	10	89(96[d])
6	BuCH=CH_2	**115**	$BuCH_2CH_2OH$ (66) $BuCHOHCH_3$ (33)	25	10	85
7	Bu(Me)C=CH_2	**115**	Bu(Me)$CHCH_2$Bcat (85) $Me_2BuCBcat$ (15)	55	48	87
8	cyclopentene	**115**	cyclopentanol	25	10	77
9		**115**		55	48	96

[a]4 mol % used, [b]some reactions were oxidised, [c]yield of oxidised product is given where appropriate, [d]yield of alkylborane

The reactions with alkynes give excellent yields (entries 1-4) but show little selectivity for disubstituted alkynes (entry 4). Alkenes require longer reaction times and sometimes also need heating (entries 7, 9). The lack of regioselectivity with 1-hexene (entry 6) lowers the synthetic value of the procedure, as does the lack of regioselectivity shown in entry 7.

Vinylboronates are not produced in the hydroborations of alkenes, which is remarkable in view of the report that addition of **1** to the ethene complex of permethyltitanocene does yield B-ethenylcatecholborane.[86] It has also been reported that dimethyltitanocene induces decomposition of **1** and catalyses addition to alkenes[87] and it is currently difficult to reconcile all the results. Multinuclear NMR studies[85] of the catalytic addition of **1** to *p*-tolylethyne and 4-methylstyrene indicate high yields of vinyl- and alkylboranes *without* significant decomposition of **1**. Borane has not been implicated in these reactions and the mechanism proposed[85] is shown in Scheme 29.

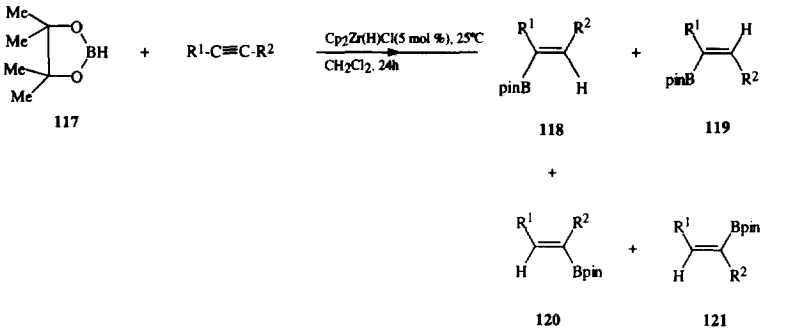


Scheme 29

Evidence to support Scheme 29 is as follows. There is analogy for the metathesis of an H-B with a Ti-C bond,[87] one of the key steps in Scheme 29. Titanium(III) complexes are excluded as, although they catalyse hydroborations, they do so at a much slower rate than found in the reactions considered. Also the reaction of **1** with **115** does in fact give catBMe and methane, as proposed, and isolated $Cp_2Ti(CO)(PhC{\equiv}CPh)$ reacts immediately with **1** to give the vinylboronate in quantitative yield. It should be noted that **114** is commerically available and that **115** can be prepared *in situ* from cheap, readily available Cp_2TiCl_2.

2.6.5 Zirconium complex catalysed hydroborations of alkynes

The zirconocene derivative $Cp_2Zr(H)Cl$ (**116**) is an effective catalyst for the high yield, selective hydroboration of alkynes by pinacolborane (pinBH or PBH) (**117**) (see Section 2.7).[88] Possible products are shown in Scheme 30.



Scheme 30

The results of a wide ranging investigation are shown in Table 24.

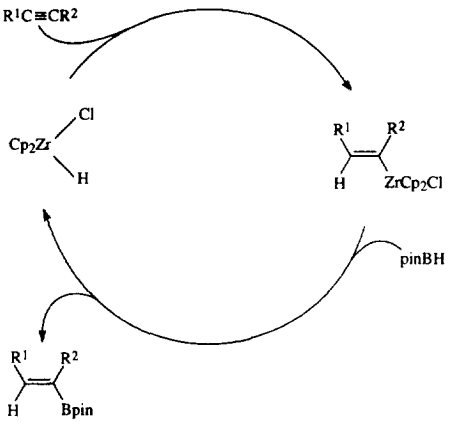
Table 24 Hydroboration of alkynes with pinacolborane **117** catalysed by **116**

entry	R^1	R^2	**118**	**119**	**120**	**121**	yield(%)[a]
1	*n*-Hex	H	98	2	0	0	93
2	$Cl(CH_2)_3$	H	96.8	2.4	0	0.8	94
3	Me_3Si	H	90.3	2.2	3.2	4.3	87
4	cyclopentyl	H	97.5	0.7	0	1.8	94
5	Me_3C	H	100	0	0	0	95
6	Ph	H	97.2	0.8	0.7	0.9	94
7	$Ph(CH_2)_3$	H	98.3	1.7	0	0	87
8	*i*-Pr	Me	96.9	2.2	0	0.9	94
9	Me_3C	Me	100	0	0	0	92
10	Et	Et	100	0	0	0	93
11	$(EtO)_2CH$	H	81.9	10.8	7.3	0	82
12	$MeOCH_2$	H	95.0	2.5	2.5	0	87
13	$Me_3SiC{\equiv}CCH_2$	H	96.3	2.5	0.8	0.4	82

[a]Isolated yields

With most terminal akynes, the yields and regioselectivity are excellent. The regioselectivity however drops seriously with trimethylsilylethyne (entry 3) presumably due to an electronic effect (compare with entry 5). More marked is the drop in regioselectivity with an acetal substituent (entry 11) when only 82% of the expected product **118** is formed, and the *trans*-product **119** is 11% of the product mixture together with 7% of regioisomer **120**. This may be due to co-ordination to the oxygen atoms of the acetal function.[89] In general however by-products are few. The regiochemistry of the hydroboration of disubstituted ethynes warrants further investigation, as the two examples included (entries 8, 9) usually give reasonable regioselectivity. It would be interesting to test R^1=Ph, R^2=Me and R^1=*n*-alkyl, R^2=Me.

Zirconocene dichloride is ineffective as a catalyst and actually retards the reaction. However the alkenyl groups from 1-alkenylzirconocene chlorides ($Cp_2Zr(Cl)CH{=}CHR$) readily transfer to B-chlorocatecholborane[90] and it therefore appears that pinacolborane does not reduce zirconocene dichloride, a hypothesis confirmed by ^{11}B NMR studies. An abbreviated cycle to explain the results is shown in Scheme 31.



Scheme 31

Compound **116** has also been shown[91] to catalyse hydroborations of alkenes using pinacolborane. The yields however are consistently lower than those obtained using Wilkinson's catalyst. The *anti*-Markovnikov product is invariably obtained and when *trans*-4-octene was used the product was B-(1-octyl)pinacolborane. This is consistent with hydrozirconation as the initial step followed by rapid isomerisation to place zirconium on the least hindered carbon atom. This is then followed by replacement of zirconium by boron.[88]

The properties of PBH are dealt with in Section 2.7.3.

2.6.6 Hydroboration of alkenes catalysed by a rhodium(III) complex

The combination of $NaBH_4$, O_2 and rhodium(III) octaethylporphyrin (OEP) is an efficient system for the reduction of carbonyl compounds.[92] The same system has been applied[93] to the hydroboration of alkenes and alkynes and is unique in that on hydrolysis, alcohols are produced directly from either alkenes or alkynes. The system is cheap and easy to use as there is no need for an inert atmosphere or for dry solvents.

Oct-1-ene yields octan-1-ol and octan-2-ol in a ratio of 91 : 9. Methylcyclohexene gives *trans*- and *cis*-2-methylcyclohexanol in a ratio of 93 : 7 when 1.2 mol % of catalyst is used and 97 : 3 when 12 mol % is present. The hydroboration of styrene shows little regioselectivity, the ratio of primary to secondary alcohol being 61 : 39. 1-Heptene gives 1-heptanol and 2-heptanol in a ratio of 82 : 18. The processes of this reaction are by no means clear. It is possible that (OEP)Rh(III)BH_4 acts as a source of borane plus (OEP)RhH. The latter could react with oxygen to give (OEP)RhOOH which could behave like $^-$OOH to oxidise alkylboranes. When 2-methylcyclohexene is hydroborated (BH_3) and then oxidised with oxygen in the presence of either aqueous NaOH or $NaBH_4$, then *trans*- and *cis*-2-methylcyclohexanols are isolated in a ratio of 80/20 in contrast to the catalysed oxidation. Thus there is present an oxidising species that is not oxygen and which does not give rise to radicals.

2.6.7 Rh(II) catalysed hydroborations

Rhodium(II) carboxylates and carboxamides have high catalytic activity for the hydroboration of alkenes with catecholborane.[94] Reactions are carried out in refluxing dichloromethane with 0.5 mol % of catalyst, usually

$Rh_2(OAc)_4$. Tetrahydrofuran coordinates with dirhodium(II) compounds and inhibits hydroborations. Table 25 shows some results.

Table 25 Hydroboration-oxidation of alkenes catalysed by $Rh_2(OAc)_4$ and $(Ph_3P)_3RhCl$

entry	alkene	catalyst	product	selectivity	yield(%)[a]
1	bicyclo[2.2.1]hept-2-ene	$Rh_2(OAc)_4$	bicyclo[2.2.1]heptan-2-ol	99 : 1[b]	80
2	bicyclo[2.2.2]oct-2-ene	$Rh_2(OAc)_4$	bicyclo[2.2.2]octan-2-ol	----	45
3	styrene	$Rh_2(OAc)_4$	2-phenylethanol	95 : 5[c]	60
4	styrene	$RhCl(Ph_3P)_3$	1-phenylethanol	50 : 1[d]	80
5	indene	$Rh_2(OAc)_4$	2- and 1-indanol	30 : 70	45
6	indene	$RhCl(Ph_3P)_3$	2- and 1-indanol	63 : 37	75
7	2-phenylpropene	$Rh_2(OAc)_4$	2-phenylpropanol	e	78
8	2-phenylpropene	$RhCl(Ph_3P)_3$	2-phenylpropanol	e	66

[a]isolated yields, [b]*exo* : *endo*, [c]2-ol : 1-ol, [d]1-ol : 2-ol, [e]one product only reported.

Rhodium(II) diacetate can isomerise alkenes. For example allylbenzene in the presence of 1.0 mol % $Rh_2(OAc)_4$ and catecholborane (3.0 mol %) underwent complete isomerisation to a mixture of (*E*)- and (*Z*)-1-phenylpropene (81 : 19). Neither $Rh_2(OAc)_4$ nor **1** alone caused isomerisation, indicating the involvement of a rhodium hydride species.

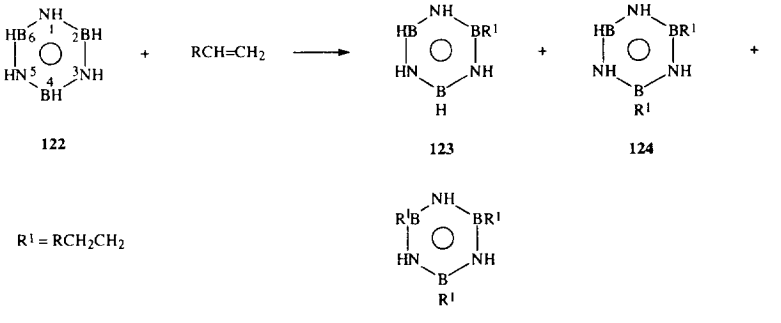
Dirhodium tetraacetate (2.0 mol %) catalyses the hydroboration of phenylethene by **1** to give, on iodinative work-up, exclusively (*E*)-1-iodo-2-phenylethene in 71% isolated yield. This suggests exclusive *cis*-hydroboration under these conditions, in contrast to rhodium(II) catalysed hydrosilation.[95]

2.7 Alternative hydroborating agents

2.7.1 Borazine and derivatives

In the course of making polyborazylenes as ceramic precursors a systematic investigation was made of the rhodium catalysed hydroboration of alkenes and ethyne with borazine, **122**[33,96]. The work centred on RhH $(CO)(PPh_3)_3$ which is the catalyst used for all the work described in this section. Indeed this catalyst appears to be highly efficient, with high turnover numbers (14000 in 1h, ~ 4/sec.) and can be used in 10^{-2}-10^{-1} mol % concentrations, with no solvent present.

The reactions may proceed to give mono, di, or trialkylated products **122**, **124** and **125** (Scheme 32).



122 **123** **124** **125**

Scheme 32

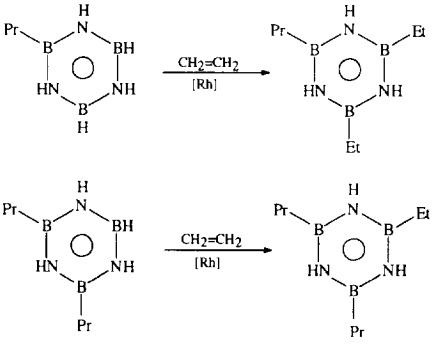
By use of a large excess of borazine, the monoalkyl products **123** can be synthesised in almost quantitative yields. By use of three equivalents of alkene, the trialkylated borazines **125** are readily produced. With propene about 44% of **124** was produced. The ratios of products are dependent also on the quantity of catalyst used. Thus with ethene: borazine in a 3 : 1 ratio, 0.14 mol % of catalyst gave 92% yield of product that was 100% **125** (R^1=Et). At 1.5 x 10^{-4} mol % catalyst the product mix in the same conditions was **123**, 71%, **124**, 24% and **125** only 5% (R^1=Et).

The reactions proceed in an *anti*-Markovnikov fashion, even for styrene, in contrast to the products obtained from styrenes using catecholborane **1**. The alkenes used were ethene, propene, 1-butene, *cis*- and *trans*-2-butene, 3,3,3-trifluoropropene ($CF_3CH{=}CH_2$), styrene α-methylstyrene, and 4-allylanisole. They reacted with rates in the order of ethene > 1-butene > *cis*-2-butene > *trans*-2-butene, and electron withdrawing substituents as in 3,3,3-trifluoropropene and styrene, slowed the reaction down.

From the 2-butenes only the terminal *n*-butyl product resulted. This is similar to the findings that the *n*-pentylsilane is the only product of the reaction of $PhMe_2SiH$ with *cis*-2-pentene in the presence of a rhodium catalyst[97] and also similar to the results of zirconium catalysed hydroboration of alkenes with pinacolborane.[70] These results are generally assigned to the greater stability of the primary metalloalkyl compared to the secondary metalloalkyl.[98]

It was further shown that the catalyst could be used at least three times without decreasing yields or turnover number.

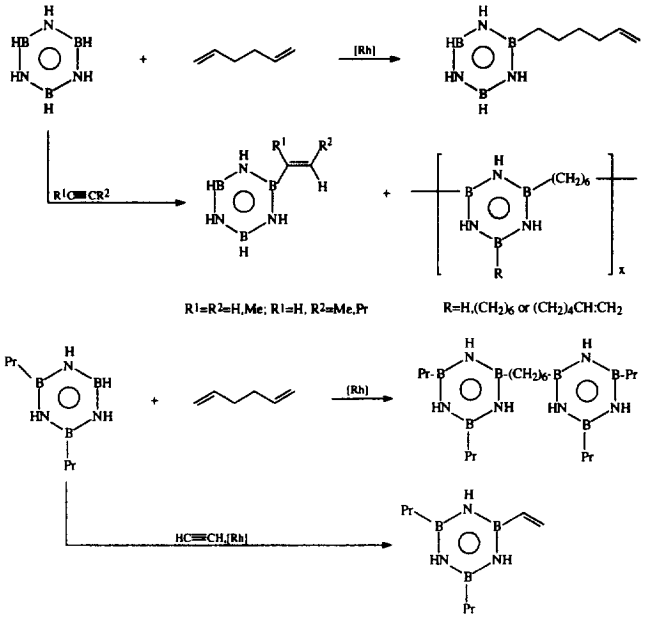
The mono- and di-alkylated borazines are still hydroborating agents, and can be used to give very specifically substituted borazines (Scheme 33).



Scheme 33

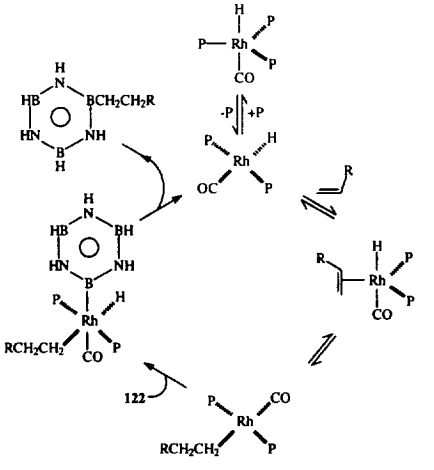
The catalysed reaction of **122** with 1,3-butadiene gave a mixture of monoorganyl products consisting of 1,2- and 1,4-addition products as well as B-1,3-butadienylborazine.

With 1,5-hexadiene, reactions with **122** gave simple 1,2-Markovnikov product plus a polymer. With **124** a 63% yield of the hydroborated product was isolated (Scheme 34).



Scheme 34

Acetylene underwent reaction with **124** (R=Pr) to give di-B-propyl-B-vinylborazine but the reaction was comparatively slow (~2 turnovers/day). Borazine itself reacts with acetylene, propyne, 1-butyne and 2-butyne to give the corresponding mono-B-vinylborazines (Scheme 34).[33,99] The catalyst turnover rate is ~50/h and the reaction is readily stopped at the monoalkenyl stage. The reactions are carried out at room temperature since higher reaction tempertures result in the formation of polymers. Palladium bromide also catalyses the addition of alkynes, but some alkylboranes result from overreaction.[99] The catalytic cycle proposed[96] for the rhodium catalysed hydroboration of alkenes is shown in Scheme 35.



Scheme 35

2.7.2 *Polyhedral boranes and carboranes*

The reactions of alkynes with pentaborane give alkenylpentaboranes when $IrCl(CO)(PPh_3)_2$ and $Co_2(CO)_6(R_2C_2)$ are used as catalysts.[100-102] The reactions of alkenes with pentaborane proceed at 0°C and also give alkenylpentaboranes using Pd(II) salts as catalysts (Section 2.2.3).[33] The products are mainly 1- and 2-alkenylpentaboranes in a ratio of *ca* 3 : 1, and very little (1-3%) alkylpentaboranes are formed.

Platinum(II)bromide and chloroplatinic acid catalyse the room temperature insertion of $RCH{:}CH_2$ (R=H, Me, Et, Pr) into decaborane to yield the corresponding 6,9-dialkyldecaboranes.[103]

The carborane complex $[Rh(Ph_3P)_2][7,8\text{-}\mu\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]$, has been used to catalyse the insertion of *n*-butyl acrylate into the terminal B-H bond of the carborane ligand.[104] 2-Butyne undergoes hydroboration with *nido*-$2,3\text{-}Et_2C_2B_4H_6$ in reactions promoted by $Ru_3(CO)_{12}$.[105] However $Ru_3(CO)_9(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$ give the insertion product *nido*-4,5-dimethyl-7,8-diethyl$C_4B_4H_4$ almost exclusively.

Earlier work on small, polyhedral boranes and carboranes has been summarised.[106]

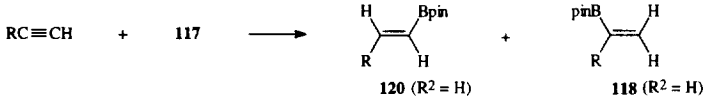
2.7.3 *Pinacolborane*

A simple preparation of pinacolborane, **117** (PBH) (section 2.6.5) from pinacol and borane-dimethyl sulfide has been given.[107] This borane has been reported[88a,91] as being considerably more stable than catecholborane, **1** in metal catalysed hydroborations. As a consequence it can be used in slight excess rather than the 1.5 - 2.0 equivalents of **1** that have to be used to take account of its degradation. Moreover the products of PBH hydroboration are air and moisture stable and can be separated by chromatography.[88a,91] This is in sharp contrast to boronates derived from catechol which are very moisture sensitive and cannot be chromatographed.

Hydroborations of alkynes using **117** and a zirconium catalyst have been considered in section 2.6.5.

Very recently pinacolborane **117** has been shown to hydroborate both alkynes and alkenes[88b] using either rhodium or nickel catalysts. Some results for alkynes are given in Table 26.

Table 26. Rhodium and nickel catalysed hydroboration of alkynes with **117**[a]



entry	R^1	catalyst[b]	**120 : 118**	entry	R^1	catalyst[b]	**120 : 118**
1	hex	A	71 : 29	10	*i*-Pr	A	79 : 21
2	hex	B	99 : 1	11	*i*-Pr	B	99 : 1
3	hex	C	99 : 1	12	*i*-Pr	C	99 : 1
4	Ph	A	48 : 52	13	*t*-Bu	A	99 : 1
5	Ph	B	98 : 2	14	CH_2OMe	A	30 : 70

6	Ph	C	98 : 2	15	CH_2OMe	B	99 : 1
7	$ClCH_2CH_2CH_2$	A	40 : 60	16	CH_2OMe	C	99 : 1
8	$ClCH_2CH_2CH_2$	B	99 : 1	17	$Me_3SiC{\equiv}CCH_2$	A	59 : 41
9	$ClCH_2CH_2CH_2$	C	99 : 1	18	$Me_3SiC{\equiv}CCH_2$	B	99 : 1
				19	$Me_3SiC{\equiv}CCH_2$	C	98 : 2

[a]1 equiv. of **117**, 1 mol % catalyst, 0.5M in CH_2Cl_2 at 25°C; 1h for rhodium and 18h for nickel. All yields were 98-99% isolated products, [b]A = $RhCl(PPh_3)_3$; B = $RhCl(CO)(PPh_3)_2$; C = $CpNiCl(PPh_3)$.

Wilkinson's catalyst $RhCl(PPh_3)_3$ shows little selectivity (entries 1, 4, 7, 10, 14, 17) except when R^1 is a bulky *t*-butyl group (entry 13). However replacement of one PPh_3 group by a carbonyl group favourably affects the stereoselectivity so that *anti*-Markovnikov attack prevails with every substrate. This is true also for catalysis by the cheaper $CpNi(PPh_3)Cl$. The reactions of 1-trimethylsilyl-1,3-pentadiyne were chemoselective and reaction occurred only on the less hindered triple bond, in the cases of catalysts B and C to give exclusively the terminal alkenylboronate.

For alkenes the use of Wilkinson's catalyst for the hydroboration of (*E*)-4-octene with **117** gives only 1-octanol on oxidation. However either catalyst B or C gives almost entirely 4-octanol in excellent yield. The hydroboration of styrene using $RhCl(PPh_3)_3$ gives *prim*-boronate (50%), *sec*-boronate (35%) and alkenylboronate (15%). Use of either catalyst B or C gives almost exclusively the primary boronate. Vinyl bromide however gives EtBpin and 1-bromo-1-propene gives PrBpin, both in 50% yield. This implies that a facile reduction has occurred that utilises 50% of **117**. Enol ethers, trimethylsilylenol ethers and enol acetates hydroborate so as to place boron β- to the oxygen atom.

2.7.4 Oxazaborolidines

The homochiral reagents (4*S*, 4*R*)-ephedrineborane **85** and (4*S*, 5*S*)-pseudoephedrine **86** have been described in section 2.4.7. They are readily produced by reaction of the appropriate amino-alcohol with either borane-dimethyl sulfide or with an alkylboronate, $RB(OR^1)_2$ until two equivalents of hydrogen or R^1OH have been evolved.[108] The preparation of the N-isopropyl analogue of **86** has been described.[36]

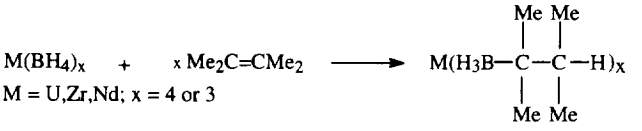
2.7.5 Lithium borohydride with UCl_4, $ZrCl_4$ or $NdCl_3$

The addition of 10^{-2} equivalent of uranium tetrachloride to a solution of $LiBH_4$ in THF in the presence of tetramethylethene catalyses hydroborations at room temperature (t½=1h) to yield lithium thexylborohydride.[109] Zirconium tetrachloride is almost as efficacious but neodymium trichloride, though active, is less efficient than the other two chlorides. It would seem from the viewpoint of handling and price that zirconium tetrachloride would be an attractive catalyst.

The order of reactivity of alkenes is the *inverse* of that normally found for hydroboration with boranes. The most reactive of the alkenes tried was tetramethylethene (2 days at room temperature for complete reaction), followed by the trisubstituted alkenes α-pinene (18 days), 2-methyl-2-pentene (20 days) and 1-methylcyclohexene (42 days). Oxidation of the reaction mixtures gave isopinocampheol, a 95 : 5 mixture of 2-methyl-3-pentanol and 2-methyl-2-pentanol, and *trans*-2-methylcyclohexanol in almost

quantitative yields. The reactions therefore proceed in the classical *anti*-Markovnikov fashion for the hydroboration of alkenes with boranes. Disubstituted alkenes cyclohexene and 2-methylpropene and monosubstituted alkene 1-hexene were inert towards the UCl_4-$LiBH_4$ system.

In an effort to understand the reactions the metal borohydrides $M(BH_4)_x$ were prepared and were reacted with tetramethylethene. In each case, in a new reaction, the corresponding monothexylborohydrides were produced in excellent yields and fully characterised (Scheme 36).



Scheme 36

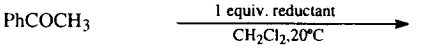
Despite the facile reaction shown in Scheme 36, it is unlikely that the neutral borohydrides are the true hydroborating species in the metal catalysed reactions since it is known[110] that the metal borohydrides react rapidly with $LiBH_4$ to give, for example, $Li[Zr(BH_4)_5]$. Moreover although the alkenes showed the same unusual reactivity sequence with $U(BH_4)_4$, the rates of their hydroborations were distinct from the catalytic system.

It is speculated that the selectivity of these hydroborations reflects high cationic character on the alkenic carbon atoms of the intermediates or transition states. The difference in reactivity between tetramethylethene and 2-methylpropene is similar to that encountered in their bromination in which a three centre cationic intermediate is involved.[111]

3. CATALYSED REDUCTIONS OF CARBONYL COMPOUNDS AND IMINES

3.1 Reductions of ketones

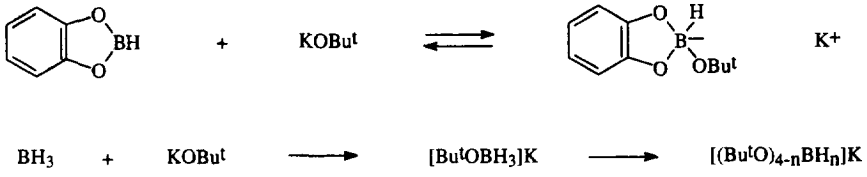
The reductions of ketones by **1** and by borane THF can be dramatically accelerated by catalytic quantities of $Ti(OPr^i)_4$, $Al(OPr^i)_3$ and $Zr(OPr^i)_4$.[84] (Scheme 37).



reductant	reaction time	
	uncatalysed	0.1 equiv. $Ti(OPr^i)_4$
1	24h	30 min (93%)
BH_3.THF	30min	<1 min (95%)
$HB(OPr^i)_2$	4h	---

Scheme 37

The combination of **1** and $Ti(OPr^i)_4$ has already been discussed (section 2.6.4). In the present case[84] it was thought that $HB(OPr^i)_2$ could be the active reductant, but in fact it is only a modestly better reducing agent than **1** (Scheme 37). The authors assign the cause of the acceleration of catecholborane reduction by metal alkoxides to its Lewis basicity, and not to its Lewis acidity. This is founded on the observation that $KOBu^t$ is as good as $Ti(OPr^i)_4$ in accelerating reduction by both catecholborane **1** and borane. With **1**, presumably the borohydride is formed directly (Scheme 38) and with borane an intermediate monoalkoxyborohydride would be formed that would disproportionate to other alkoxyborohydrides and eventually potassium borohydride.

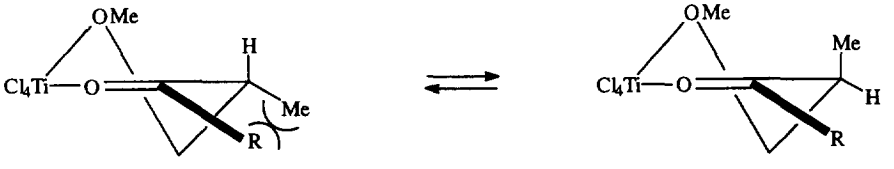


Scheme 38

An interesting observation was that the order of mixing of the reagents was important for borane reductions, but not for reductions with **1**. When ketone and $Ti(OPr^i)_4$ are mixed before addition of BH_3.THF, reduction takes less than 1min. When a solution of $Ti(OPr^i)_4$ is treated first with BH_3.THF followed by addition of ketone, the reduction rate is the same as the uncatalysed reaction. It would seem that in the absence of ketone, the intermediate borohydride $[Ti(OPr^i)_3][Pr^iOBH_3]$ is destroyed by excess borane to give an inactive species.

It is worth mentioning that $TiCl_4$ in stoichiometric quantities directs the boron reagent reduction of β-ketoesters and 3-alkoxyketones so that *syn* products result.[112] The reductants vary from borohydrides ($Et_4N.BH_3CN$) to strongly complexed boranes ($Ne_3N.BH_3$) to weakly complexed boranes (BH_3.THF) and in all cases *syn* : *anti* ratios are normally high (Table 25).

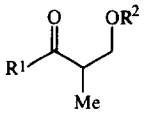
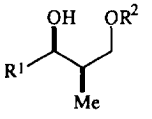
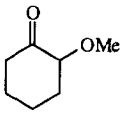
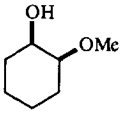
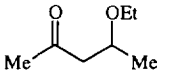
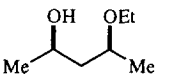
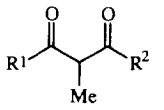
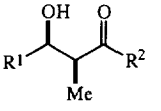
The effect is put down to chelation of the functionalised ketone by $TiCl_4$. The chelate can exist in two conformations **126** and **127** (Figure 8), the first being discouraged except when R is small (Table 27, entry 5).



126 **127**

Figure 8

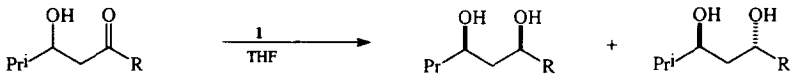
Table 27 Reductions of ketones by $TiCl_4$ and $Et_4N\,BH_3CN$

entry	substrate	major product	R^1	R^2	*syn* : *anti*	yield (%)
1)			Ph	MOM	98 : 2	86
2)			Ph	Bn	96 : 4	94
3)			Ph	TBDS	92 : 8	84
4)			But	Me	97 : 3	89
5)			Me	Me	58 : 42	90
6)			Ph	OBz[a]	89 : 11	91
7			--	--	94 : 6	91
8			--	--	78 : 22	--
9)			But	OEt	98 : 2	91
10)			Me	pip[b]	98 : 2	92

[a]Bz = benzoyl, [b]pip = piperidyl

The presumed chelated intermediates have 5-,6- and possibly 7-membered (entry 6) chelate rings, but all give good diastereoselectivity. In those cases in which it was lowered (entries 5, 8) both substituents were methyl or methyl and hydrogen, so making **126** a reasonably populated conformation. Methoxy (entries 4, 7), ethoxy (entries 8, 9), benzyloxy (entry 2) and *t*-butyldimethylsilyl (entry 3) all proved to be good directing groups even though silyl ethers are generally recognised as having poor coordinating and chelating abilities.[113] Esters and amides may also act as directing groups (entries 9, 10).

Rhodium complexes may also be used to enhance diastereoselectivity in the reduction of 1,3-hydroxyketones by **1**.[114] Some examples are given in Scheme 39.



R=Pr^i; -35°C,	catalysed,	20	:	1
	uncatalysed,	6	:	1
R=Hex^n; -10°C,	catalysed,	10	:	1
	uncatalysed,	3	:	1

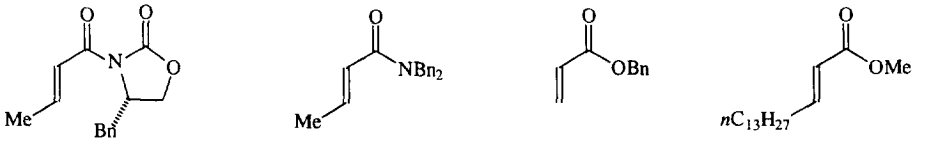
Scheme 39

It is suggested that the increase in stereoselectivity is concerned with the known[114] ability of Wilkinson's catalyst to promote borate formation between catecholborane and alcohols.

Rhodium(III)octaethylporphyrin (section 2.6.6) in the presence of O_2 catalyses the reduction of ketones by $NaBH_4$.[92]

3.2 Reductions of αβ-unsaturated carbonyl compounds

Catecholborane **1** readily reduces αβ-unsaturated ketones in a 1,4-fashion in the presence of a variety of functional groups.[115] In the absence of a catalyst αβ-unsaturated imides, esters and amides are unreactive at room temperature to 1,4-addition of **1**. However addition of 2 mol % of $RhCl(PPh_3)_3$ (Wilkinson's catalyst) results in conjugate reduction of these compounds under very mild conditions (-20°C, 12h).[115] Some results are shown in Figure 9.



70%[a] 55%(95%)[b] 82% 73%(80%)

Figure 9

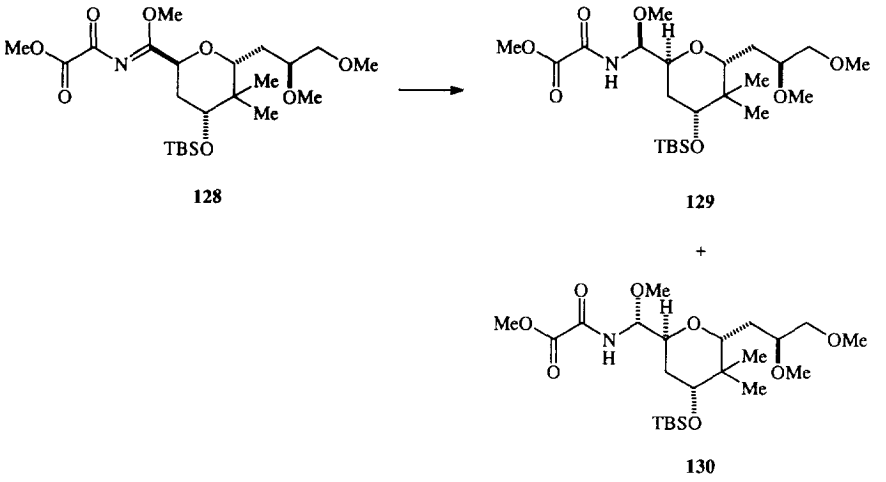
a)all yields are unoptimised, isolated yields. b)yields in parentheses are based on recovered starting material.

The mechanism of rhodium catalysis is not clear. The rhodium may simply fulfil the role of a Lewis acid, but against this is that conjugate addition is not catalysed by $BF_3.OEt_2$. Alternatively the mechanism may involve oxidative addition of **1** to rhodium. In favour of the latter proposal is that $RhCl(PPh_3)_3$ catalyses conjugate reduction by **1** and **2** but not by 9-BBNH. It was early shown[9] that **1** and **2** oxidatively add to $RhCl(PPh_3)_3$ but that 9-BBNH does not.

The rhodium catalysed conjugate reduction of benzyl acrylate gives a single product (^1H NMR), said to be the (Z)-boron enolate. However addition of this species to benzaldehyde gives both *syn* and *anti* alcohol products in a ratio of 2 : 1.

3.3 Reductions of imines by catecholborane

The transition metal catalysed hydroboration of simple imines is currently unexplored. However, in a synthesis of pederin the key step was the stereoselective reduction of imidate **128** to **129** (Scheme 40).[116]

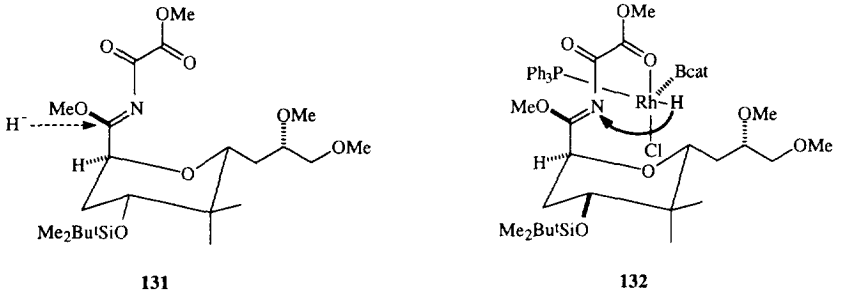


128 129 + 130

Scheme 40

A wide variety of reagents either failed to reduce **128** (e.g. Pd-C/H_2; $RhCl(PPh_3)_3/H_2$) or were not selective (50 metal hydride reductants) or caused rearrangement (L-selectride). However $RhCl(PPh_3)_3$ together with **1** gave 70% of a 10 : 1 mixture of **129** and **130**.

Good stereocontrol had previously only been obtained for the production of **130**. It is postulated that the favoured rotamer **131**, which normally is reduced as shown in Figure 10 to give **130**, undergoes hydride delivery in complex **132** to give **129**.



131 132

Figure 10

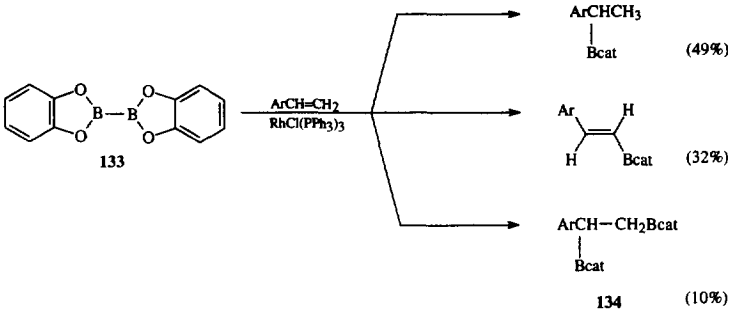
Conformation **131** is favoured by the bulky Me_2Bu^tSi protecting group, and if this is changed for a benzoyl group the reaction is much less stereoselective.

4. CATALYSED DIBORATIONS OF ALKENES AND ALKYNES

This section is included as, though it does not deal with catalysed hydroborations it is relevant to the mechanisms of a variety of reactions that may be postulated as proceeding through insertion into a Met-B bond rather than a Met-H bond.

4.1 Alkenes

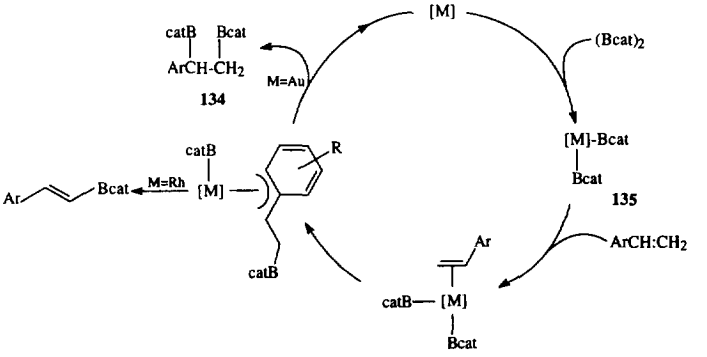
*bis*Catecholborane **133**[117] reacts with 4-methoxystyrene ($ArCH{:}CH_2$) in the presence of $RhCl(PPh_3)_3$ to give a mixture (Scheme 41) containing *ca* 10% of diborylated product **134**.[118,119]



Scheme 41

In order to avoid β-hydrogen eliminating pathways, rhodium complexes containing bisphosphine ligands were used, and indeed the zwitterionic complex $Rh(dppb)(\eta^6\text{-}B(cat)_2)$ gave a 46% yield of **134**, the highest observed for any rhodium system. Unfortunately there was also present 23% of $ArCH(CH_3)Bcat$ and $ArCH_2C(Bcat)_3$(22%).

Catalysis by gold complexes was tried[118] on the basis that alkene gold complexes are known to be labile and there are no known mononuclear gold hydrides.[120] Therefore alkyl gold species will be stabilised relative to the alkene metal hydride. The complexes $AuCl(PR_3)_n$(R = Et,Ph and n = 2,3) have little activity but the addition of two equivalents of the bulky bisphosphine ligand, dcpe (bis(dicyclohexylphosphino)ethane) to commercially available $AuCl(PEt_3)$ generates a catalyst system that leads *exclusively* to 1,2-bisboronate esters **134**, even with Ar = 4-$CF_3C_6H_4$. The reaction is not confined to arylalkenes as allylbenzene also produces the bisborylated product. The reaction pathway proposed is shown in Scheme 42.[118]



Scheme 42

The cycle includes the formation of [M]-$(Bcat)_2$ **135** and the transfer of Bcat from gold to carbon, both steps being of interest for the mechanisms of catalysed hydroborations.

4.2 Alkynes

Bis(pinacolato)diboron (pinB-Bpin), **136**, and tetrakis(methoxy)diboron, **137** add in a *syn* fashion to both terminal and internal alkynes in the presence of a catalytic quantity of $Pt(PPh_3)_4$ to yield *cis*-bis(boryl)alkenes such as **138** in excellent yields (Figure 11).[120,121]

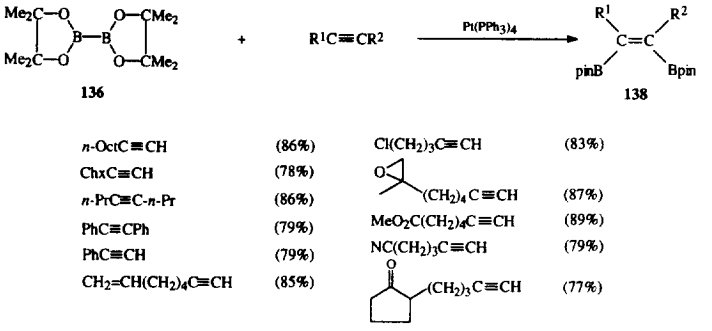


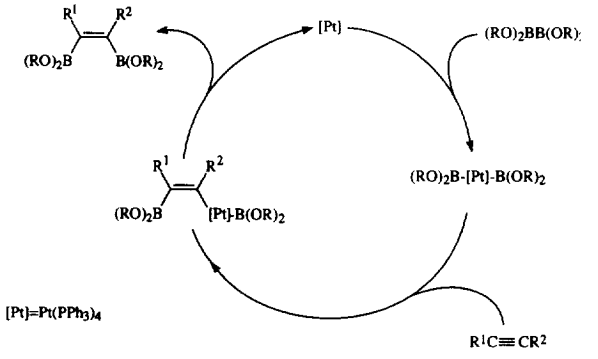
Figure 11

A wide range of potential catalysts was surveyed but only $Pt(PPh_3)_4$ and $Pt(CO)_2(PPh_3)_2$ showed useful activity. Reactions could be carried out in DMF at 80°C for 24h, the conditions used in Figure 11 or in hexane at 50°C. The catalyst $Pt(PPh_3)_4$ was not soluble in hexane but high yields may still be obtained.

Figure 11 shows that the reaction is exceptionally chemoselective in that it proceeds in good yields in the presence of vinyl, chloro, ester, epoxy, nitrile and keto groups. Phenylethyne reacted very slowly at 80°C but gave a good result at 120°C.

Compound **137** reacts in a very similar fashion to **136** but tetrakis(dimethylamido)diboron is relatively inert to alkynes. None of the diboron reagents reacted with alkenes.

It was shown that **136** reacted with $Pt(PPh_3)_4$ to give a crystalline complex $Pt(Bpin)_2(Ph_3P)_2$ **139**. Complex **139** reacted rapidly with alkynes at 50°C for 6h to give **138** in excellent yields, but did not react with alkenes. The catalytic cycle proposed is shown in Scheme 43.[122a]

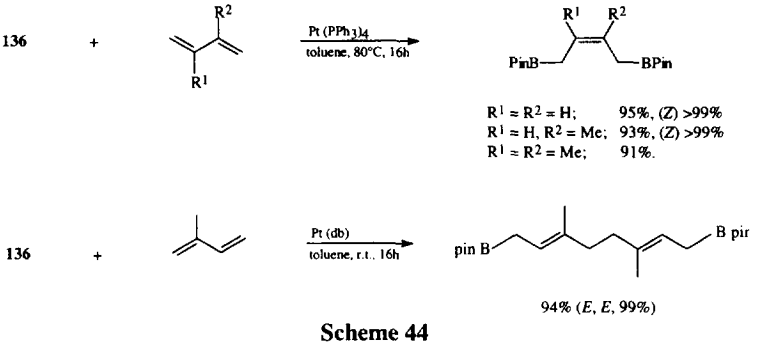


Scheme 43

4.3 1,3-Dienes

Bis(pinacolato)diboron **136** adds to 1,3-dienes under the influence of 3 mol% of $Pt(PPh_3)_4$ to give the (*Z*)-1,4-

di-adducts with an isomeric purity of >99% and with good chemical yields (Scheme 44).[122b] When the catalyst was changed to $Pt(dba)_2$ dimerisation preceded addition and good yields of the (*E,E*)-dimer (isomeric purity 89%) were obtained.



Scheme 44

5. SOME MECHANISTIC CONSIDERATIONS OF CATALYSED HYDROBORATIONS

5.1 Introduction

Although the topic of transition metal catalysed hydroboration is comparatively young,[9] great attention has been paid to mechanistic considerations, and as much is known as in the more mature fields of hydrosilation and hydroformylation.

Metal catalysed hydroboration is a multi-step process, catalysed by a wide variety of complexes and applicable to many different types of substrate. Broad generalisations must therefore be treated with caution. The nature of the catalyst,[26,28,29,30,32,34,35,59,60] the steric and electronic constitution of the substrate,[10,28,44,45] (sections 2.2.3; 2.2.4; 2.3.1), the nature of the stabilising ligand (section 2.2.4, Tables 4, 6), the solvent and temperature[55] (section 2.4.2, Table 13), can, and do affect the mechanism of transition metal catalysed hydroboration. The catalyst may alter during a reaction,[54b] so that the mechanism may not be constant even within a single reaction, and also the history of the catalyst is important,[123] in particular its exposure to oxygen. Probably it is best in all cases to use highly purified, freshly prepared catalysts. The most usual hydroborating agent, catecholborane, **1**, is always used in excess to allow for its degradation, which may lead to the production of borane and metal dihydride species which may react with the substrate to yield products that complicate analysis and interpretation. It has been noted that pinacolborane, **117**, is stable to the conditions of metal catalysed hydroborations and[50] does not need to be used in excess. Possibly use of **117** could simplify mechanistic investigations, although its steric requirements are very different from **1**, and so **117** could itself perturb the 'normal' system used.

5.2 Degradation of catecholborane

Attention has been drawn to the need to understand the reactions of catecholborane, **1** with a variety of catalysts[27,32] and several studies have been made of the reactions of **1** with rhodium,[32,80,92] titanium[83] (section 2.6.4) and niobium[79] complexes. In all cases, given time, breakdown occurs to give a variety of boron

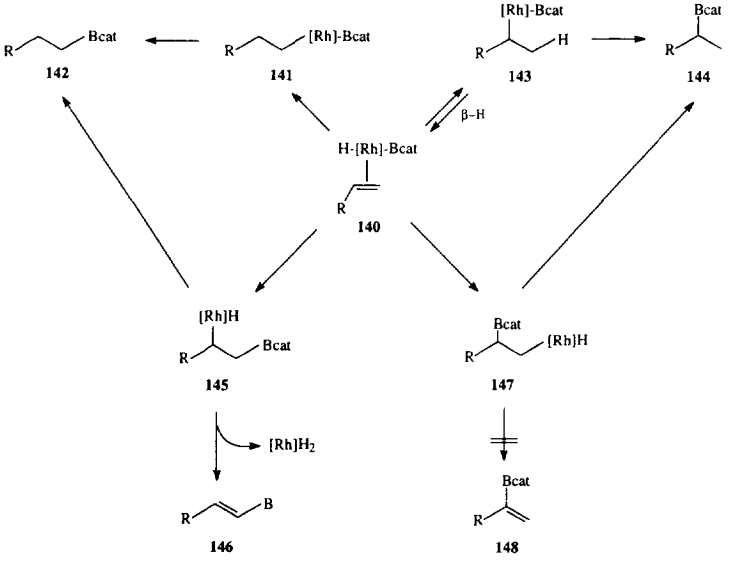
products such as **110**, plus borane plus metaldihydrido species such as $Rh(H)_2Cl(PPh_3)_3$.[32] Titanium tetra*iso*propoxide rapidly gives cat_2Ti and borane,[83] whilst dimesitylniobium is a catalyst for the breakdown of catecholborane to **110** plus borane.

Triphenylphosphine can trap borane as $Ph_3P.BH_3$ but it can also promote the formation of **110** and related compounds.[80] This depends on the nature of the phosphine ligands and rhodium complexes. In particular cationic rhodium dihydrides $[RhH_2(dppp)]^+[B(cat)_2]^-$ and $[RhH_2(PMe_3)_3]^+\{LB(cat)_2]^-$ were observed. In the case of $RhCl(dppp)_2$ about 30% had been converted into $[RhH_2(dppp)]^+[B(cat)_2]^-$ upon completion of catalysis. The production of rhodium dihydrido species may account for hydrogenation products such as alkylbenzenes in the hydroborations of styrenes. Catecholborane degradation was negligible only for a chlororhodium complex containing a basic monodentate phosphine. This also gives a high selectivity for primary alcohol in the catalysed hydroboration of 4-methoxyanisole, which ties in well with observations that high selectivity for the secondary alcohol is occasioned by the use of cationic rhodium complexes.

5.3 Alkylethenes

5.3.1 Monoalkylethenes

Two general mechanisms can be considered. For both, catBH adds to the rhodium catalyst to yield an H-[Rh]-Bcat species which then complexes alkene to give a generalised intermediate **140** (Scheme 45).



Scheme 45

In the first mechanism complex **140** *undergoes Rh-H insertion* to yield either **141** or **143** from which **142** and **144** respectively are derived. In the second mechanism Rh-B insertion occurs to give **145** and **147** from which **146** and **148** can be derived by β-hydride elimination to give $[Rh]H_2$ or from which **142** and **144** can also be produced.

Detailed thermochemical data on bond dissociation energies, to help to analyse the situation are rare and this lack, due mainly to problems of isolating the intermediates in catalysed hydroborations, leads to the use of *average* bond dissociation energies (BDEs) which are often very different from first BDEs.[123] Hartwig has carried out calculations of bond dissociation energies for a number of boron compounds including catecholborane **1**. Borane (gas) impressively shows the problem. The first BDE is 106.6 kcal mol^{-1} and is like that of methane or benzene. However the second BDE is 78.5 kcal mol^{-1} whilst the average BDE is 89-90 kcal mol^{-1}. For **1** the first BDE is 111.3 kcal mol^{-1}, and this should be applicable in solution chemistry as **1** does not form solvent adducts, even with THF. The enthalpy of the addition of **1** to *trans*-$IrCl(CO)(PPh_3)_2$ to give *trans*-$IrCl(Bcat)(H)(CO)(PPh_3)_2$[124] was measured and from this an estimate of 66 kcal mol^{-1} for the strength of the Ir-Bcat bond was made. This value greatly exceeds the 35 kcal mol^{-1} for the Ir-CH_3 bond in *trans*-$IrCl(Me)(CO)(PPh_3)_2$. From this, estimations may be made of the enthalpies for the various possible reactions that could make up the process of iridium catalysed hydroboration (Table 28).

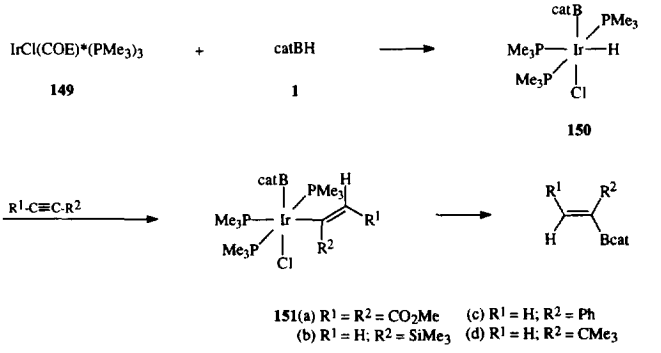
Table 28 Iridium mediated hydroboration of alkenes

entry	reaction			ΔH ($kcalmol^{-1}$)
1	[Ir][a]+HBcat	→	[Ir](H)(Bcat)	-15.1
2	[Ir](H)(Bcat) + C_2H_4	→	Ir](CH_2CH_3)(Bcat)	2
3	[Ir](H)(Bcat) + C_2H_4	→	[Ir](H)(CH_2CH_2Bcat)	-6
4	[Ir](CH_2CH_3)(Bcat)	→	[Ir] + CH_3CH_2Bcat	-11
5	[Ir](H)(CH_2CH_2Bcat)	→	[Ir] + CH_3CH_2Bcat	-3
6	HBcat + C_2H_4	→	CH_3CH_2Bcat	-24

[a] [Ir]=*trans*-$IrCl(CO)(PPh_3)_2$

Comparison of entries 2 and 3 shows that insertion into the Ir-Bcat bond is favoured over insertion with the Ir-H bond by 8kcal mol^{-1}. However reductive elimination from [Ir](CH_2CH_3)(Bcat) is favoured, also by 8 $kcalmol^{-1}$, over reductive elimination from [Ir](H)(CH_2CH_2Bcat). This implies that kinetic factors will dominate the selectivity between these two competing pathways.[30,32,33,35]

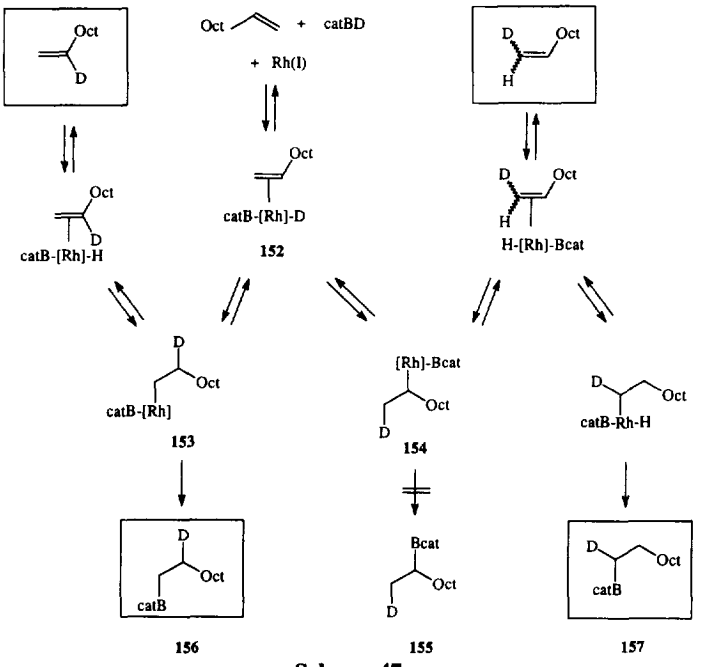
The reactions in Scheme 46 have been described as a possible analogy to a catalytic hydroboration.[125]



Scheme 46

Iridium complex **149** reacts with **1** to give **150**, which was isolated and fully characterised. Compound **150** reacted with dimethylacetylene dicarboxylate to give **151a** by insertion into the Ir-H bond. Compound **151a** was fully characterised but **151b-d** could not be isolated, though observable in solution by NMR. Compounds **151b-d** readily underwent reductive elimination to the corresponding alkenylboronates suggesting a catalytic system for hydroboration. Indeed six turnovers were observed in a period of 2 days, and reaction is faster than for the uncatalysed system.[125] As written by the authors, the iridium atom is always at the more hindered end of the alkenyliridiums **151b-d** showing Markovnikov addition. No characterisations of the corresponding alkenylboranes were given. However, the most important point is that all of the alkynes formed an Ir-C bond by Ir-H insertion and not by Ir-B insertion.

Evans[126,127] studied the hydroboration of 1-decene with deuterio-**1** catalysed by Wilkinsons catalyst. The 1-decanol that was produced had 85% deuterium incorporation at C-1 but, unexpectedly also had 15% deuterium incorporation at C-2 and deuterium was also incorporated in recovered 1-decene. The ratio of 1-decanol : 2-decanol is 99 : 1. The authors explain their results as shown in Scheme 47.



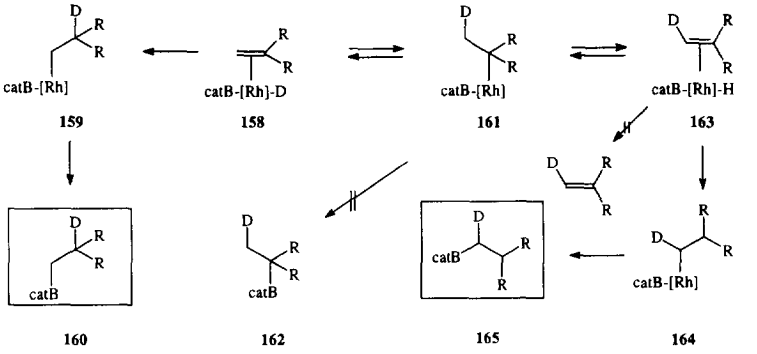
Scheme 47

The key intermediate **152**, of type **140**, undergoes B-D insertion to give **153** and **154** from which **156** and **157** respectively are derived as are 2- and 1-deuterio-1-decene. The authors explain the high regioselectivity of the reaction on the basis that reductive elimination from the secondary alkylrhodium complex **154** is considerably slower than reductive elimination from the primary alkylrhodium complex, **153**, *e.g.* it is reductive elimination rather than addition that is responsible for regioselectivity. It is somewhat difficult to understand this as, in the case of styrene, in which the C-2 addition product equivalent to **154** is stabilised

(*vide infra*), reductive elimination does in fact occur. On steric grounds the formation of **153** rather than **154** would be favoured and this would explain the regioselectivity observed on the basis of addition rather than elimination.

5.3.2 Dialkylethenes

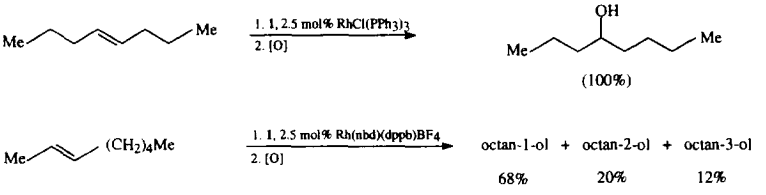
Reaction of 1,1-dialkylethenes gives somewhat different results using catBD.[126,127] Incorporation of deuterium into the product alcohols was very similar to that of monoalkylethenes but there was no incorporation of deuterium into starting alkene. This is explained by the sequence shown in Scheme 48.



Scheme 48

π-Complex **158** will give mainly **159** in a step that is *irreversible*, presumably on steric grounds, and this in turn leads to **160**. Insertion products **161** do not give **162** but revert to π-complexes **158** and **163** from the latter of which, *via* **164**, the α-deuteriated product **165** is derived. Complex **163** does not revert to free, deuteriated alkene.

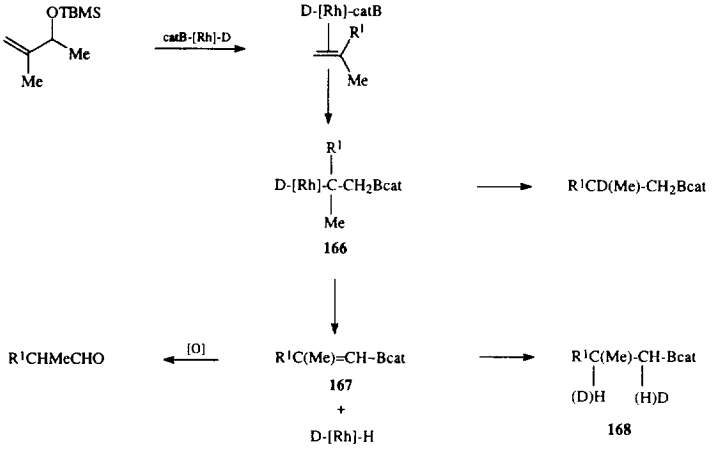
In view of the probability that **159** does not revert to **158**, it appears that β-elimination is sensitive to steric factors. This is supported by the fact that 4-octene gives only 4-octanol on hydroboration with **1** and Wilkinson's catalyst (Scheme 49). However the reaction of oct-2-ene using a cationic complex[23] as catalyst gave a mix of alcohols, presumably because elimination can give rise to a sterically favoured rhodium complex on C-1.



Scheme 49

Burgess *et al*[32] have proposed insertion into a Rh-B bond to explain deuteriation with catBD. They first observed that the hydroboration oxidation of silyl ether **55** ($R^1 = R^2 = Me$, $X = SiMe_2Bu^t$) (Table 4, entry 8), with **1** gave not only primary alcohol but also aldehyde and hydrogenation product. It was also found that the distribution of deuterium correlated with *syn/anti* diastereoselectivity. Their explanation (Scheme 50) is that

alkene inserts into a Rh-B bond to give **166** and that this is followed by elimination to yield an alkenylboronate **167** and [Rh](H)(D). Reduction then gives deuterium incorporation into the α and β positions of alkylboronate **168**. The final oxidation produces aldehyde from **167** and alcohols from the alkylboronates **168**. The vinylboronate **167** was converted to its pinacol derivative which was isolated and characterised.



Scheme 50

Intermediate **166** does not have diastereotopic methyl groups, as would the product from Rh-H insertion, and elimination can be directed to give only **167** and a [Rh](H)(D) species by which it is reduced to **168** with *no incorporation of deuterium into the methyl group*, in line with experimental findings. It was further demonstrated that **167** could in fact be hydrogenated under the reaction conditions. That β-deuterium incorporation predominates could be due to reductive elimination from **166** or to at least some insertion into Rh-H, as proposed previously.

5.4 Arylethenes

In contrast with the reactions of 1-decene with catBD (section 5.3.1), the hydroboration of styrene with catBD catalysed by $RhCl(PPh_3)_3$ followed by oxidation yields only 2-deuterio-1-phenylethanol. There was no incorporation of deuterium into recovered styrene.[126] This was interpreted as a regiospecific alkene insertion into the Rh-D bond of the usual π-complex followed by reductive elimination. The results demand a very simple pathway in which a single alkylrhodium species is formed irreversibly and also that the decomposition of the π complex back to alkene does not occur.[126]

Hayashi[26] proposed that the catalysed hydroboration of phenylethenes differed from that of alkylethenes in that a stabilised η^3-benzylrhodium complex is formed in the catalytic cycle (section 2.2.4, Scheme 9). The extra stability associated with this complex could explain the deuteration results.

With phosphine free rhodium catalysts the product of catalysed hydroboration of styrenes can be alkenylboronate, exclusively or for the major part.[35,36] This has been dealt with in detail in section 2.2.4 and it

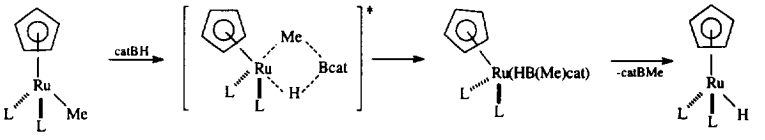
only remains to point out that the process invoked (section 2.2.4, Scheme 11) involves alkene addition into a Rh-B bond in a rather symmetrical cycle, one half of which involves alkene insertion into a B-H bond and the other half is based on Rh-B insertion.[36]

Insertion of an arylethene into a Rh-B bond is now well established. The insertion of 4-vinylanisole into $RhCl(Bcat)_2(PPh_3)_3$, the X-ray structure of which was known, proceeded to give $ArCH(Bcat)CH_2Bcat$, ArCH=CHBcat, and $ArCH(Bcat)CH_3$ in a ratio of 3 : 2 : 2. As before, β-elimination to give the alkenylboronate is accompanied by production of a catB-Rh-H species which adds across the starting alkene.

The diborylation of alkenes[117,118] (section 4.1) must, of necessity have a M-Bcat (M=Rh, Au) step in the process.

5.5 σ-Bond metathesis

The mechanisms previously discussed would apply to most of the hydroboration reactions of rhodium, ruthenium and iridium complexes as low valent, late transition metal complexes. However addition of catecholborane, **1** to $CpRu(PPh_3)_2Me$ was shown to lead quantitatively and by direct metathesis to catBMe and $CpRu(PPh_3)_2H$.[128] As the first B-H and B-Me bond energies are very similar it is the difference in the Ru-H, Ru-Me linkages that provides the thermodynamic driving force for the reactions. A detailed investigation of the deuterium isotope effect shows that it is too large to be a secondary effect (K_H/K_D= 1.62 ± 0.13) and emphasises the importance of a bridging hydride during the exchange process. All the data were consistent with a mechanism proceeding through a four centred transition state that involves partial cleavage of the B-H bond during formation of the B-C bond (Scheme 51).



Scheme 51

The initial reaction (section 2.6.2, Scheme 24) for lanthanide catalysis of hydroboration with **1**, is a direct metathesis of $Cp'_2LnCH(SiMe_3)$ with **1** to give Cp'_2LnH and $catBCHSiMe_3$. The lanthanide hydride reacts with the alkene substrate $RCH{=}CH_2$ to give $Cp'_2LnCH_2CH_2R$ which then undergoes another direct metathesis with catBH to regenerate Cp'_2LnH and yield $catBCH_2CH_2R$.[76]

5.6 *Ab initio* studies of metal catalysed hydroborations

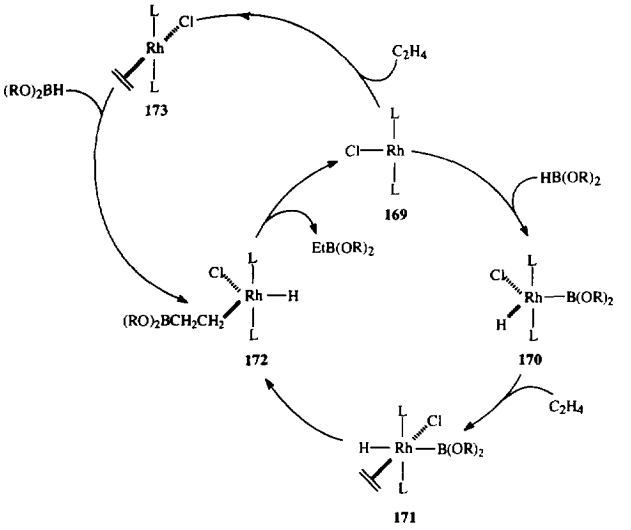
Morokuma *et al*, carried out an *ab initio* M.O. study of the mechanism of Rh(I) catalysed hydroboration of alkenes **129** using C_2H_4, $HB(OH)_2$ or $HB(O_2(CH_2)_3)$ and $RhCl(PH_3)_2$ **169** as model components suitable for computation (Scheme 52).[129]

$$HB(OH)_2 + C_2H_4 + RhCl(PH_3)_2 \longrightarrow RhCl(PH_3)_2 + C_2H_5B(OH)_2$$

$$HBO_2(CH_2)_3 + C_2H_4 + RhCl(PH_3)_2 \longrightarrow RhCl(PH_3)_2 + C_2H_5B(O_2(CH_2)_3$$

Scheme 52

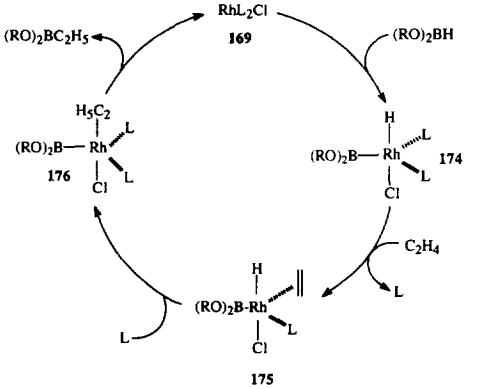
For both of the reactions in Scheme 51, computations indicated that the most favourable pathway involves addition of borane to the catalyst to give **170** followed by alkene co-ordination to give **171** which undergoes a highly favourable Rh-B insertion to give **172** from which **169** and $EtB(OR)_2$ are produced in a rate determining step (22.4 kcal mol^{-1}). An alternative cycle involves initial complexation of ethene to give **173** which, in a rate determining step (23.9 kcal mol^{-1}) involving σ bond metathesis to break BH and simultaneously form M-H and B-C, directly produces **172** (Scheme 53).



Scheme 53

The authors reject insertion into the Rh-H bond due to a high barrier of 46.7 kcal mol^{-1} for coupling of C_2H_5 and $B(OH)_2$.

Another paper[130] indicated that *insertion of alkene into Rh-H rather than Rh-B occurs in the key step.* The addition of BH_3 to C_2H_4 catalysed by $ClRh(PH_3)_2$ was the system chosen for computation, and is further removed from the standard $(RO)_2BH$ (catecholborane, pinacolborane) than the system previously studied. The cycle proposed (Scheme 54) is very close to the cycle proposed by Evans.[126]



Scheme 54

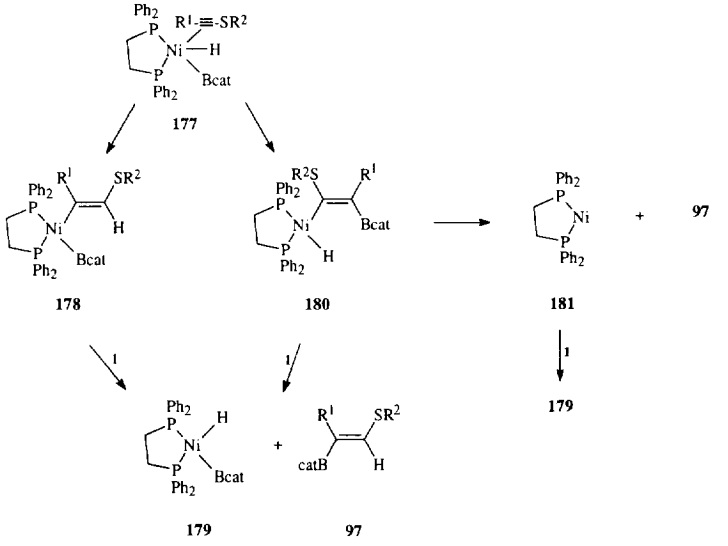
The first step is addition of $(RO)_2BH$ (in the Scheme, BH_3 in the calculations) to give **174** which then yields **175** *with loss of a ligand.* The intermediate between **174** and **175** is a 14-electron species. Species **175** can undergo alkene insertion between Rh-B and Rh-H, and in this case insertion into Rh-H to give **176** is favoured at all levels of computation.

5.7 Catalysed hydroborations of alkynes

The hydroboration of phenylethyne[32] has been previously discussed in section 2.5.2. However no mechanistic experiments were carried out.

A mechanism was proposed[69] for the nickel promoted hydroboration of 1-alkylthioalkynes (section 2.5.2, Scheme 20) which involved a five coordinated Ni(II) intermediate, **177**, produced without loss of a phosphine ligand. The key step was then a highly stereo- and regioselective insertion of the alkyne into the Ni-H bond of **177** to give **178** (Scheme 55), which with **1** yields **179** and **97**.

There remains the possibility of insertion into the Ni-B bond going with opposite regioselectivity (as with palladium-tin bonds[131]) to give **180** which in turn reacts with **1** also to give **179** and **97**.



Scheme 55

The mechanism for the conversion by **1** of **178** to **179** and **97** remains open. It could be oxidative addition followed by reductive elimination or direct metathesis. The same would be true for the conversion of **180** to **179** and **97** though additionally **180** could convert to **97** and **181** followed by reaction of **181** with **1** to generate **179**.

The highly effective hydroboration of alkynes by **1** catalysed by $Cp_2Ti(CO)_2$[85] has been discussed in section 2.6.4 and a mechanistic proposal which does not involve the intervention of Ti(III) intermediates for the hydroboration of alkenes using Cp_2TiMe_2 is given in Scheme 30. The mechanism of the alkyne reactions is not known, but again it would seem that Ti(III) intermediates are not involved. It is known[132] that alkynes

react with $Cp_2Ti(CO)_2$ with a single displacement of one carbonyl, and that reaction of $Cp_2Ti(CO)(PhC{\equiv}CPh)$ with catecholborane, **1**, gives quantitative and immediate production of (*Z*)-PhCH=C(Ph)Bcat. By ^{11}B NMR there was no indication of the formation of a stable intermediate with the boron interacting with a titanium hydride and therefore a mechanism analogous to that presented in Scheme 30 would be likely to apply.

A very similar mechanism to that in Scheme 30 has been presented for the hydroboration of alkynes with pinacolborane, **117**, using $Cp_2Ti(Cl)H$[88] (section 2.6.5, Scheme 31).

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Biographical Sketch

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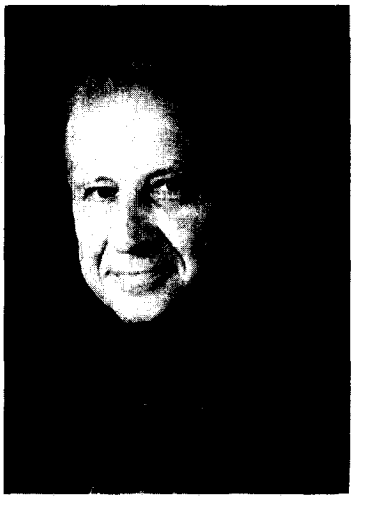

Andrew Pelter

Irina Beletskaya received her Diploma in 1955, her Ph.D in 1958 and her Doctor of Chemistry in 1963 from Moscow State University. The subject for the latter was "Electrophilic Substitution at Saturated Carbon." She became a full Professor in 1970 and in 1974 a Corresponding Member of the Academy of Sciences (USSR) of which she became a full member (Academician) in 1992. She is currently Head of the Laboratory of Organoelement Compounds, Department of Chemistry, Moscow State University.

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Andrew Pelter received his B.Sc and Ph.D degrees from Bristol University where he studied under Professors Wilson Baker and David Ollis. Later he was awarded a D.Sc from the same University. After his Ph.D. he moved to ICI Pharmaceuticals where he worked for one year under Professor F.L. Rose and then spent five years at the NIMR at Mill Hill with Nobel Laureate, Professor John Cornforth. With Cornforth he unravelled the vexed problem of the methyl shifts in cholesterol biosynthesis and worked on the synthesis of vitamin B_{12}. In 1962 he was appointed as Lecturer at Manchester University with Professor Arthur Birch and in 1967 was promoted to Senior Lecturer. In 1972 he was appointed as founder Professor of Organic Chemistry at the University of Wales Swansea, the position he currently holds.

Andrew Pelter was awarded the Tilden Medal of the Royal Society of Chemistry in 1981 and gave the R.S.C. sponsored Warren Lecture in South Africa in 1993. He is the author of more than 300 articles about 100 of which are on organoboron chemistry. His current interests are centred on; (i) organoboron chemistry; (ii) two electron oxidation of phenols; (iii) the use of chiral [2:2] paracyclophane derivatives as reagents, catalysts and chiral auxiliaries.