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Ligand Controlled Diastereoselectivity in the Rhodium Catalysed Hydroboration of Divinylsilanes

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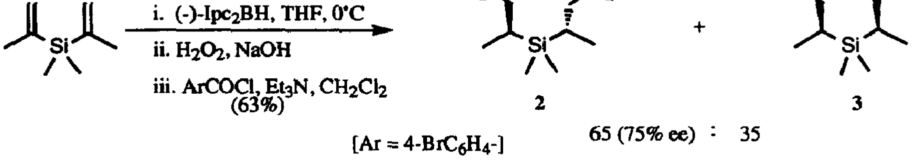
Abstract: The diastereoselectivity of the rhodium catalysed hydroboration of divinylsilanes is found to vary according to the length of the tether between the two phosphine ligands. Maximum diastereoselectivity is observed for butanodiphosphines and this may be related to the stability of a *cis* divinylsilane-diphosphine rhodium complex.

In the course of a project aimed at the synthesis of some chiral cyclic, silicon containing compounds, we had recourse to study the asymmetric hydroboration of divinylsilanes.[1] The cyclic hydroboration of these compounds has been the subject of a series of publications by Soderquist and co-workers enroute to metallocycloalkanones.[2] However, there are no reports as to the asymmetric hydroboration of this class of substrate. In this paper we report that these divinylsilanes undergo a double rhodium catalysed hydroboration in which the diastereoselectivity is controlled by the length of the carbon tether linking the two phosphine ligands. Although the double asymmetric hydrogenation of dienes, diketones and dienamides has been reported[3] the dependence of the diastereoselectivity on the gross structure rather than the chirality of the ligand is, to the best of our knowledge, unprecedented.

Prior to exploring the rhodium catalysed pathway, we examined the analogous stoichiometric hydroboration using both 9-BBN and (-)-diisopinocampheylborane, (Ipc_2BH), derived from R-(+)-pinene. Reaction of these reagents with di-(2-propenyl)dimethylsilane followed by oxidative workup afforded the silyldiol together with the oxidised alkyl ligand. In order to facilitate separation of these compounds and enable the diastereoselectivity of the process to be determined, the crude reaction mixture was treated directly with 4-bromobenzoyl chloride. The resultant silyldiester was stable to chromatography and could be isolated in good overall yield. Using the Tris[3-(heptafluoro-propylhydroxymethylene)-(+)-camphorato]-praseodymium [$Pr(hfc)_3$] chiral shift reagent and either ^1H, ^{13}C, or ^{29}Si[4] nmr the diastereoselectivity and, from the reaction using Ipc_2BH, Scheme 1, the enantiomeric excess[5] could be simply obtained.[6] These values were subsequently found to be in good agreement with those obtained using chiral HPLC.[7]



2

3

[Ar = 4-BrC$_6$H$_4$-]

65 (75% ee) : 35

Scheme 1

Asymmetric rhodium catalysed hydroboration[8] was then examined with a view to circumventing the problems of low diastereoselectivity and difficulty in the separation of the product from the chiral auxiliary. Although the catalysed hydroboration of 1-phenyl-1,3-butadiene occurs with high regio- and stereoselectivity,[9] to the best of our knowledge, there has not yet been any report on the stereoselectivity of the catalytic asymmetric double hydroboration of non conjugated diene substrates.[10]

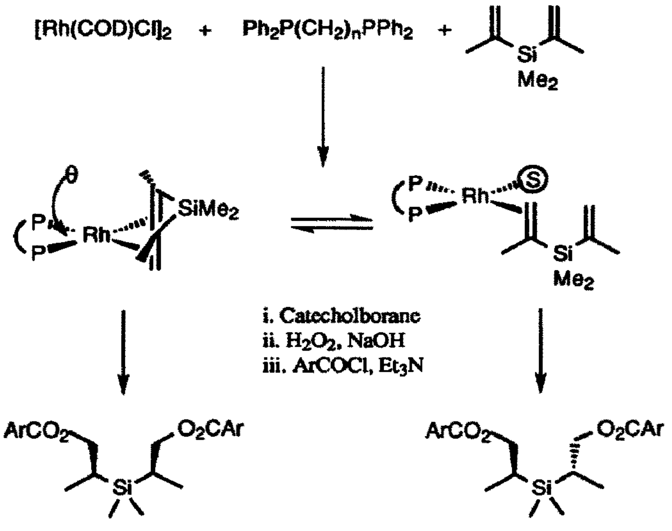
For our initial foray into this area we used (-)-DIOP as the chiral phosphine ligand and followed the standard procedure given below. Although the diol could be efficiently isolated, the crude reaction mixture was directly esterified to afford the silyl-di-4-bromobenzoyl ester in 67% overall yield. On examining the stereoselectivity of this process we found that, although high diastereoselectivity was obtained, the *syn* isomer was formed predominantly, 91.5 : 8.5, and furthermore, that the *anti* component was essentially racemic. On repeating this reaction with the achiral ligand diphenylphosphinobutane we obtained identical product ratios. This result suggested to us that the diastereoselectivity was controlled by the length of the tether between the two phosphines (or the related chelate bite angle). Consequently, we then studied a range of diphosphine ligands to see how the diastereoselectivity varied with changing tether length / bite angle. The results of this survey are given in the table below.

Table 1 Rhodium Catalysed Hydroboration of Di-(2-propenyl)dimethylsilane

Phosphine	Solvent	Yield[a]	Product Ratio[b] (anti) **2** : **3** (syn)
$Ph_2P(CH_2)_5PPh_2$	THF	35%	52 : 48
DIOP[f]	THF	67%	13 : 87[c]
DIOP	Toluene	64%	9.8 : 90.2
$Ph_2P(CH_2)_4PPh_2$	THF	45%	8.5 : 91.5
$Ph_2P(CH_2)_3PPh_2$	THF	55%	20 : 80
$CH_3C(CH_2PPh_2)_3$	THF	37%	18 : 82
$Ph_2P(CH_2)_2PPh_2$	THF: CH_2Cl_2[d]	14%	35 : 65
$Ph_2PCH_2PPh_2$	THF	< 5%[e]	38 : 62
PPh_3	THF	42%	46 : 54
NMDPP[f]	THF	75%	47 : 53[c]

(a) These yields quoted are those for the isolated di(4-bromobenzoyl)esters and are unoptimised reflecting the result obtained using a standard set of reaction conditions.[11] (b) As determined from ^{1}Hnmr using the chiral shift reagent $[Pr(hfc)_3]$ (c). In these cases the anti component was essentially racemic (d) An (8:1) mixture was used to ensure homogeneity (e) A large quantity of unreacted divinylsilane was recovered from the reaction mixture (f) DIOP = (RR)-4,5-bis(diphenylphosphino)methyl-2,2-dimethyldioxolane, NMDPP = (+)-neomenthyldiphenylphosphine.

The observed change in diastereoselectivity with changing tether length has not, as far as we are aware, been previously reported in rhodium catalysed hydroborations. The *syn* isomer is postulated to arise through a rapid hydroboration of a *cis* linked diphosphine-divinylsilane rhodium complex.[12] We speculate that with these substrates, the Männig-Nöth mechanism for catalysed hydroboration,[13] which involves oxidative addition of catecholborane, alkene ligand exchange followed by insertion of the alkene into metal hydrogen bond, is preceded by complexation of the diene. Consequently, the observed product ratios can be related, to some extent, to the relative stability of the monodentate and bidentate divinylsilane complexes, scheme 2.[14] This is, in turn, controlled by the bite angle, θ, created by the diphosphine tether. For di-(2-propenyl)dimethylsilane, maximum stability of the bidentate divinyl complex is achieved with a butano-tether.



Scheme 2

In an attempt to increase the amount of monodentate complex the use of a tripodal phosphine was examined to see if the third phosphine group would displace one arm of the silane. However, an identical ratio to that obtained with diphenylphosphinopropane was observed and this is not inconsistent with literature reports in which these tripodal ligands act as bidentate ligands through dissociation of one arm of the phosphine.[15]

In contrast, the monodentate phosphines and diphenylphosphinopentane do not exhibit pronounced diastereoselectivity. It is possible that, with these phosphines, a mechanism akin to that proposed by Männig and Nöth is followed. Alternatively, *trans* chelation of the metal centre[16] may be occurring which could preclude bidentate binding of the divinylsilane. With either of these possibilities, two discrete hydroboration steps may occur which would be consistent with the observed 1 : 1 ratio of *syn* : *anti* diastereoisomers.

In conclusion a high degree of diastereocontrol can be achieved in the rhodium catalysed hydroboration of divinylsilanes. We are currently examining both the hydroboration and other related transition metal catalysed reactions with a series of hydrocarbon dienes to see if similar trends can be observed. Although with these symmetrically substituted divinyl silanes the high *syn* diastereoselectivity observed is of little synthetic use, non symmetrical substrates cannot form a *meso* isomer and should therefore afford products of high enantioselectivity. Experiments designed to test this hypothesis are in progress.[17] The results of these and related studies on applications to synthetic projects will be reported in due course.

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1 The hydroboration of alkenylsilanes is a well established procedure. For a leading reference see J.A.Soderquist and H.C.Brown, *J.Org.Chem.*, **1980**, *45*, 3571.

2 J.A.Soderquist and A.Negron, *J.Org.Chem.*, **1989**, *54*, 2462; J.A.Soderquist, F.Y.Shiau, and R.A.Lemesh, *ibid*, **1984**, *49*, 2565; J.A.Soderquist and A.Hassner, *ibid*, **1983**, *48*, 1801 and references therein.

3 See for example J.C.Poulin and H.B.Kagan, *J.Chem.Soc., Chem.Commun.*, **1982**, 1261; H.Kawano, Y.Ishii, M.Saburi, and Y.Uchida, *J.Chem.Soc., Chem.Commun.*, **1988**, 87; H.Muramatsu, H.Kawano, Y.Ishii, M.Saburi, and Y.Uchida, *J.Chem.Soc., Chem.Commun.*, **1989**, 769; A.S.Carlström and T.Frejd, *J.Org.Chem.*, **1990**, *55*, 4175; C.S.Poss, S.D.Rychnovsky, and S.L.Schreiber, *J.Am.Chem.Soc.*, **1993**, *115*, 3360; L.Shao, H.Kawano, M.Saburi, and Y.Uchida, *Tetrahedron*, **1993**, *49*, 1997.

4 These spectra were run at 99.4 MHz with a relaxation decay of 60 minutes. The chemical shifts were *anti* isomer 6.05∂ and *syn* isomer 5.98∂. For an earlier example of the use of ^{29}Si nmr to determine enantiomeric purity see T.H.Chan, Q.J-Peng, D.Wang, and J.A.Guo, *J.Chem.Soc., Chem.Commun.*, **1987**, 325.

5 The major isomer is assigned the (S,S) configuration by analogy with literature precendent for the hydroboration of 1,1-disubstituted alkenes with this reagent. H.C.Brown, P.K.Jadhav, and A.K.Mandal, *Tetrahedron*, **1981**, *37*, 3547.

6 Using 9-BBN a 1:1 mixture of *syn* : *anti* isomers were obtained which indicates that with these reagents the result of the first hydroboration step has no bearing on the outcome of the second hydroboration. As stated above with (-) Ipc_2BH the the enantiomeric excess of the major diastereomer was 75±2%. Although this only represents ~45% enantioselectivity in each hydroboration this is still one of the highest values recorded for this class of olefin (α,α disubstituted) / reagent combination. (K.Smith and A.Pelter in Comprehensive Organic Synthesis, Eds. B.M.Trost and I.Fleming, Pergammon Press, Oxford 1991, Vol 8, Ed I.Fleming, Chapter 3.10, pp 721-723.)

7 Carried out using a CHIRALCEL OD column, eluting 2% EtOH / Hexane. RT(mins) Major enantiomer 5.88, syn diastereoisomer (6.79), minor enantiomer (8.47). We thank Mr. Steven Jackson, Glaxo Group Research, Ware for carrying out this determination for us.

8 For a recent review see K.Burgess and M.J.Ohlmeyer, *Chem. Rev.* , **1991**, *91*, 1179. Other leading references D.A.Evans, G.C.Fu, and A.H. Hoveyda, *J.Am.Chem.Soc.*, **1992**, *114*, 6671; D.A.Evans, G.C.Fu, and B.A.Anderson, *ibid*, **1992**, *114*, 6679; K.Burgess and M.J.Ohlmeyer, *Adv. Chem.*, **1992**, *230*, 163.

9 Y.Matsumoto and T.Hayashi, *Tetrahedron Lett.*, **1991**, 3387.

10 Catalytic cyclic hydroboration of 1,6-diene substrates has been reported. Y.Yokoyama, Y.Terada, and H.Kawashima, *Bull. Chem. Soc. Jpn.*, **1991**, *64*, 2563.

11 The standard experimental procedure adopted was as follows. A Schlenk tube was charged with $[Rh(COD)Cl]_2$ (1mol%) and phosphine (2mol%), evacuated and flushed with nitrogen (3 times). THF was added followed by a solution of di-(2-propenyl)-dimethylsilane (1 equivalent) in THF. The resultant yellow solution was then stirred at -78°C for 10 minutes and then catecholborane (2 equivalents) added. After a further 30 minutes at -78°C, the reaction was warmed to -25°C and stirred at this temperature for 5 days. Ethanol was then added followed by 3M NaOH and 30% aq H_2O_2 and the reaction stirred at room temperature for 6 hours. After dilution with 1M NaOH, and extraction with ether, the combined organic layers were washed with 1M NaOH, water and brine, dried (K_2CO_3) and concentrated. The resultant crude silyldiol was dissolved in dichloromethane and treated at 0°C with 4-bromobenzoylchloride, triethylamine, and dimethylaminopyridine for 5 hours. After addition of water, the reaction mixture was extracted with ether and the combined organic layers washed with water and brine, dried ($MgSO_4$) and concentrated. The crude product was then purified by flash column chromatography and the diastereoisomeric ratio determined by nmr spectroscopy using the chiral shift reagent $[Pr(hfc)_3]$. In all cases examined this value was not altered during the chromatography process.

12 In the double asymmetric hydrogenation of diketones reported by Kawano *et al* (ref. 3) only 1,3-diketones afforded high yields and selectivities. This was attributed to the ability of these substrates to chelate the transition metal catalyst.

13 D.Männig and H.Nöth, *Angew.Chem.Int.Ed.Engl.*, **1985**, *24*, 878; It should be noted that this mechanism was proposed for a catalyst system derived from Wilkinson's catalyst, $Rh(PPh_3)_3Cl$.

14 We are attempting to isolate and characterise these intermediate complexes.

15 E.G.Thaler, K.Folting, and K.G.Caulton, *J.Am.Chem. Soc.*, **1990**, *112*, 2664.

16 Cationic rhodium complexes with diphenylphosphinopentane have been shown to exhibit a *trans* biphosphine arrangement. J.M.Brown, P.A.Chaloner, A.G.Kent, B.A.Murrer, P.N.Nicholson, D.Parker, and P.J.Sidebottom, *J.Orgmet.Chem.*, **1981**, *216*, 263.

17 A similar result could be obtained through monohydroboration of this symmetrical substrate. However, to date, efforts to efficiently isolate products corresponding to the hydroboration of only one of the two vinyl units have not been successful. This is attributed to the relative instability of the vinylsilane to the oxidation conditions.

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