Hydrovinylation of Norbornene. Ligand-Dependent Selectivity and Asymmetric Variations
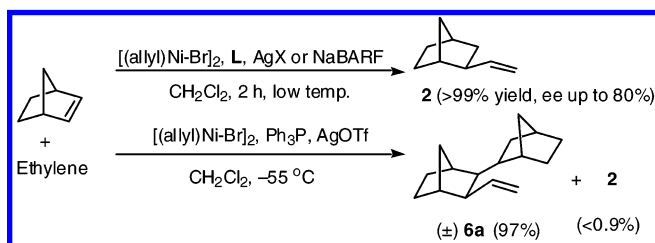
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ABSTRACT

Norbornene undergoes Ni-catalyzed (1–2 mol% allylnickel bromide/phosphine/NaBARF or AgSbF$_6$, 1 bar ethylene, −50 °C) hydrovinylation (>97% yield), giving either a 1:1 or a 2:1 (norbornene/ethylene) adduct depending on the size of the phosphine. Use of binaphthol-derived phosphoramidite ligand results in up to 80% ee for the 1:1 adduct. The course of the reaction is highly dependent on the ligand (size and configuration of the appendages) and the counteranion present.

Among asymmetric carbon−carbon bond-forming reactions, only Nozaki's Cu-catalyzed cyclopropanation[1] of styrene with ethyl diazoacetate precedes the Ni-catalyzed asymmetric hydrovinylation reaction reported by the Wilke group.[2] In one of the earliest examples of this reaction, it was found that with a catalyst system made up of π-allylnickel chloride, triethyldialuminum trichloride, and (−)-dimenthyl(2-propyl)-phosphane (4), norbornene underwent heterodimerization with ethylene to give *exo*-(+)-2-vinylnorbornane (2) along with other side-products, including 3 (*Z* + *E*) and lower oligomers (eq 1). Subsequently, (*R,R*)-azaphospholene ligand 5 was reported to give a much cleaner reaction in CH$_2$Cl$_2$ at −65 °C with up to 87% yield and 53% ee for *exo*-(−)-2-vinylnorbornane.[3] However, the lengthy synthesis and the rigorous structural requirements for high selectivity[3a] make this ligand one of limited scope. Hydrovinylation of norbornene can also be carried out under 15 bar ethylene

pressure in THF in the presence of [Ni(2,4,6-Me$_3$C$_6$H$_2$)(CH$_3$-CN)(phosphane)$_2$]BF$_4$.[4] Quantitative conversion of norbornene with up to 95% selectivity for the *exo*-2-vinylnorbornane has been reported, even though ethylene polymerization, which ensues after the depletion of norbornene, is likely to be a problem in the isolation of pure 2. Likewise, hydrovinylation using (PCy$_3$)$_2$(CO)RuHCl/HBF$_4$·OEt$_2$ gave a mixture of 2 and a poorly characterized oligomeric product in a ratio of 3:2.[5]

Recognizing the potential of this reaction for the preparation of various [2.2.1]-bicycloheptane derivatives,[6] including heteroatom analogues (eq 2), we have reinvestigated this reaction under the protocols recently developed in our laboratories for the hydrovinylation of vinylarene deriva-

(1) Nozaki, H.; Moriuti, S.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1966**, 5239.
(2) Bogdanović, B.; Henc, B.; Lösler, A.; Meister, B.; Pauling, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 954.

(3) (a) Jolly, P. W.; Wilke, G. Hydrovinylation. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 2, pp 1024−1048. (b) Wilke, G.; Monkiewicz, J.; Kuhn, H. *Preparation of Optically Active Azaphospholenes and Their Use in Catalysis for Asymmetric Codimerization of Olefins*; U.S. Patent 4912274, 1990; *Chem. Abstr.* **1991**, *114*, 43172.
(4) Muller, G.; Ordinas, J. I. *J. Mol. Catal., A: Chem.* **1997**, *125*, 97.
(5) Yi, C. S.; He, Z.; Lee, D. W. *Organometallics* **2001**, *20*, 802.

tives.[7] In this paper we report that the hydrovinylation of norbornene can be achieved in nearly *quantitative yield* with exquisite selectivity for either a 1:1 or a 1:2 (ethylene to norbornene) adduct depending on the nature of the phosphine employed.
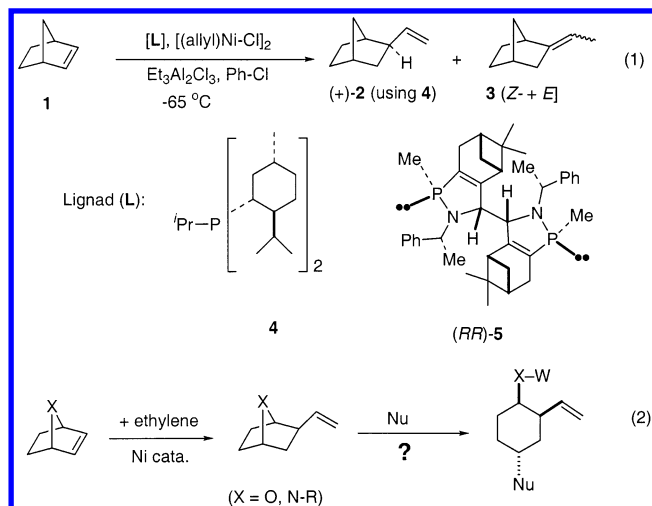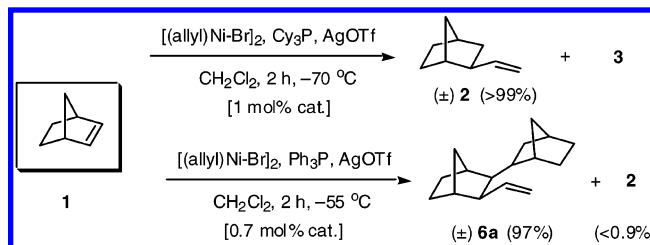

In addition, we also document the viability of a number of tunable ligands for the asymmetric hydrovinylation of norbornene, including one that gives the highest selectivity reported to date. This asymmetric-catalyzed reaction is highly dependent on the nature of the ligand and the counteranion employed. The details of these studies are reported in this paper.

Ligand-Dependent Selectivity in the Heterodimerization Reaction. Norbornene, upon treatment with ethylene in the presence of a catalyst derived from allylnickel bromide, tricyclohexylphosphine, and AgOTf, undergoes an exceptionally clean reaction to give a 1:1 heterodimer **2** (Scheme 1).[8] At −70 °C, less than 0.5% of the 2:1 adduct **6** is observed in the GC or NMR. No other oligomeric product or the isomerization product (e.g., **3**) can be detected under these conditions.

In sharp contrast, the same reaction, when carried out with triphenylphosphine as the ligand, gives almost exclusively a 2:1 adduct, **6** (Scheme 1). This reaction is best carried out at −55 °C using 0.7 mol % of the nickel catalyst. Under these conditions, less than 1% of the 1:1 heterodimer **2** is

(6) For other asymmetric transformations of norbornene, see the following. Hydrocyanation: Hodgson, M.; Parker, D.; Taylor, R. J.; Ferguson, G. *Organometallics* **1988**, *7*, 1761. Baker, M. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1292. Horiuchi, T.; Shirakawa, E.; Nozaki, K.; Takaya, H. *Tetrahedron: Asymmetry* **1997**, *8*, 57. Hydrosilylation: Hayashi, T. *Acta Chem. Scand.* **1996**, *50*, 259. Hydroalkenylation: Ozawa, F.; Kabatake, Y.; Kubo, A.; Hayashi, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1323. For hydrovinylation of norbornadiene, see ref 2 and: Pillai, S. M.; Tembe, G. L.; Ravindranathan, M. *J. Mol. Catal.* **1993**, *84*, 77.

(7) (a) Nomura, N.; Jin, J.; Park, H.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 459. (b) Nandi, M.; Jin, J.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1999**, *121*, 9899. (c) RajanBabu, T. V.; Nomura, N.; Jin, J.; Radetich, B.; Park, H.; Nandi, M. *Chem. Eu. J.* **1999**, *5*, 1963. (d) Jin, J.; RajanBabu, T. V. *Tetrahedron* **2000**, *56*, 2145. (e) Park, H.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2002**, *124*, 734. (f) RajanBabu, T. V.; Nomura, N.; Jin, J.; Nandi, M.; Park, H.; Sun, X. *J. Org. Chem.* **2003**, *68*, 8431−8446. (g) For a recent review, see RajanBabu, T. V. *Chem. Rev.* **2003**, *103*, 2845.

(8) See Supporting Information for gas chromatograms and NMR spectra of key compounds, including those of the crude products.

Scheme 1. Ligand Dependence of Hydrovinylation of Norbornene

observed. A minor component (<2%) has not been identified. As suggested by the ^{1}H and especially the ^{13}C NMR spectra, one of the two possible diastereomers of the *exo,exo*-dimer is formed in excess of 97% yield.[8] The identity of the major product as a single diastereomer was confirmed by conversion of the olefin **6** into an alcohol **7** by hydroboration and, subsequently, to the corresponding Mosher ester **8** with (*R*)-MTPA chloride (Scheme 2). Fluorine-19 (C_6D_6) NMR of

Scheme 2. Stereochemical Homogeneity of **6**
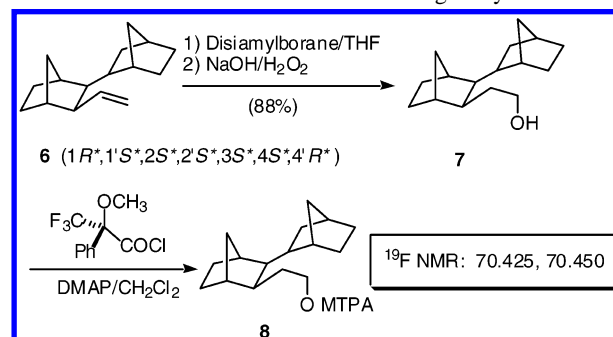
the Mosher ester shows only two peaks (δ 70.425 and 70.450) in a ratio of 1:1 in the expected range for the CF$_3$ groups, thereby confirming the homogeneity of the 2:1 adduct. These signals were also used to determine the ees of the adducts (see later). The two diastereomeric Mosher esters result from the enantiomers of **6**. The absolute configuration of the dimer, tentatively assigned as (1*R**,1′*S**, 2*S**,2′*S**,3*S**,4*S**,4′*R**)-, has not been confirmed. The choice is based on the well-known propensity of exo-addition of various reagents to norbornene[6] and the relative stabilities of the two possible *exo*-diastereomers (**6a** and **6b**) as inferred from calculations at HF/6-31G* and B3LYP/6-31G* levels (Figure 1).[9] The minor *exo,exo*-diastereomer (the unidentified component?) is approximately 6 kcal/mol less stable than the major one.

This remarkable difference in selectivity is presumably related to the relative reactivities of the two olefins and the size of the two phosphines. It is conceivable that the more reactive norbornene undergoes fast initial [**P**Ni−H]$^+$-

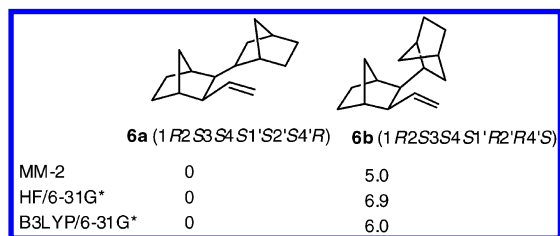(9) We thank Professor Christopher Hadad of our department for the B3LYP calculations.
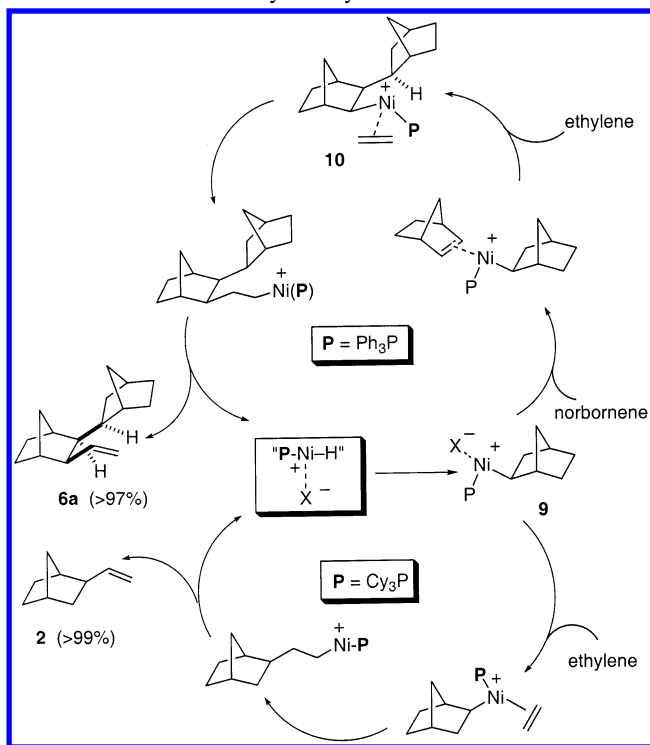
Figure 1. Calculated Relative Energies of the 2:1 Adducts **6a** and **6b**.

catalyzed dimerization[10] when a small phosphine[11] (Ph$_3$P, cone angle 145°) is used (Scheme 3). The initially formed

Scheme 3. Ligand Dependence in Norbornene Hydrovinylation

σ-complex **10**, for stereoelectronic reasons (the only H cis to Ni is at the bridgehead position), cannot undergo β-hydride elimination and hence reacts further with the smaller of the two olefins, ethylene, eventually giving the 2:1 adduct **6a**. With a bulky phosphine (e.g., tricyclohexylphosphine, cone angle 180°), the coordination sphere is too crowded to accommodate two norbornene molecules. Heterodimerization between norbornene and ethylene ensues, giving the 1:1 adduct **2**.

Asymmetric Hydrovinylation. Asymmetric heterodimerization of ethylene and other olefins is a demanding reaction

(10) For a discussion of the mechanism of hydrovinylation, see ref 7f.
(11) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) White, D.; Coville, N. J. *Adv. Organomet. Chem.* **1994**, *36*, 95.
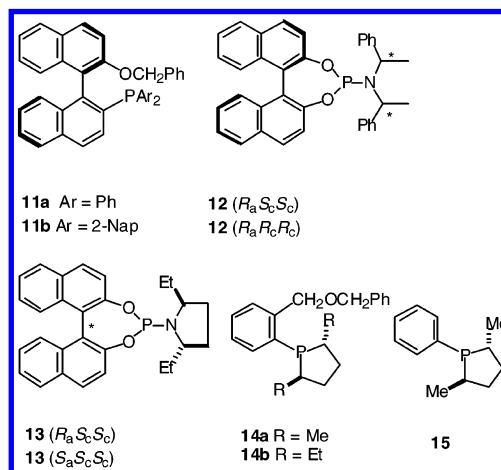
Figure 2. Ligands for Hydrovinylation of Norbornene.

where only a few ligand/metal combinations have been successful.[3a,7f] We had previously reported that nickel(II) complexes of selected triarylphosphine and phospholane ligands with an appropriately placed hemilabile group could serve as efficient catalysts for the hydrovinylation of vinylarenes.[7a−c] Leitner et al. has reported that phosphoramidites derived from binaphthol are excellent ligands for hydrovinylation of styrene derivatives.[12] We have tested several of these ligands (Figure 2, **11−15**) for asymmetric hydrovinylation of norbornene. A prototypical example of the reaction conditions is shown in eq 3 and, a summary of the results is shown in Table 1.[13] The enantiomeric excess

Table 1. Asymmetric Hydrovinylation of Norbornene[a]

| entry	ligand	additive	**2** (%)[b]	**6** (%)[b]	% ee[c]
1a	**11a**	NaBARF	69[d]	0	44
1b	**11a**	AgSbF$_6$	>99	0	50
1c	**11a**	AgNTf$_2$	>99	0	50
1d	**11b**	AgSbF$_6$	>99	0	46
2a	**12** (R_a,S_c,S_c)	NaBARF	>99	0	80
2b	**12** (R_a,S_c,S_c)	AgOTf	20[d]	0	
2c	**12** (R_a,S_c,S_c)	AgSbF$_6$	0	99	34
3	**12** (R_a,R_c,R_c)	NaBARF	<2%	0	
4a[e]	**13** (R_a,S_c,S_c)	AgSbF$_6$	0	0	
4b[e]	**13** (S_a,S_c,S_c)	NaBARF	0	0	
5a	**14a**	AgSbF$_6$	40[d]	15[d]	
5b	**14a**	NaBARF	40	60	
5c	**14b**	AgSbF$_6$	0	0	
6	**15**	AgOTf	11	88	33

[a] See eq 3 for typical procedure. Results of at least two experiments are given in each case. [b] By GC and NMR, isolated yields vary because of the volatility of **2**. [c] By NMR (see text). [d] Rest was starting material. [e] Polymers (~100%)

and the absolute configuration of the 1:1 adduct **2** were determined by conversion to known mandelic acid derivatives

(12) Franció, G.; Faraone, F.; Leitner, W. *J. Am. Chem. Soc.* **2002**, *124*, 736.

Scheme 4. Absolute Configuration of **2** and Configuration of the (*S*)-Mandelate Esters
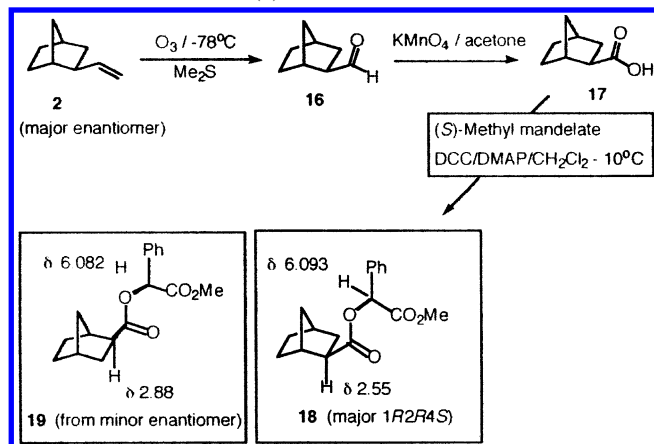
as shown in Scheme 4. Ozonolysis of **2** followed by oxidation of the resulting aldehyde (**16**) gave norbonane-2-carboxylic acid **17**, the enantiomers of which were converted into esters of (*S*)-methyl mandelate (**18** and **19**) by the standard procedure using DCC. The absolute configuration of these diastereomers had been fully established by Parker.[14] For the product **2** obtained by reaction shown in eq 3, the C2-hydrogen of the derived major methyl mandelate ester appears at δ 2.55 (reported 2.54) in the ^{1}H NMR (C_6D_6) spectrum, whereas it appears at δ 2.88 (reported 2.87) in the minor diastereomer. The benzylic hydrogens of the major and minor isomers appear at δ 6.093 (reported 6.077) and 6.082 (reported 6.061), respectively. Accordingly, the major enantiomer of the 2-vinylnorbornane can be assigned the configuration (1*R*,2*S*,4*S*). The sense of optical rotation (−) is also consistent with this assignment.[3,15] On the basis of the integral values of these signals, the enantiomeric excess for **2** was determined as 80%. The results of other hydrovinylation reactions are shown in Table 1. As expected, phosphines with large cone angles (**11a,b** and **12**) give exclusively the 1:1 adduct in nearly quantitative yield and modest enantioselectivity (entries 1, 2). Note the use of highly dissociated counteranions in these reaction.
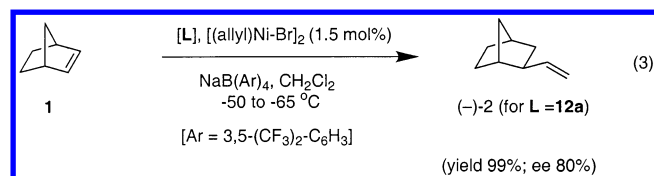
No trace of the 2:1 adduct **6** is observed under these conditions. The selectivity with the phosphoramidite ligands

(entries 2−4) depends on both the counteranion and the nature of the secondary amine appendage. Whereas the (R_a,S_c,S_c)-isomer is a good ligand (entry 2a), the corresponding (R_a,R_c,R_c)-diastereomer gives less than 2% of the product (entry 3). For the ligand (R_a,S_c,S_c)-**12**, the counteranion determines whether the 1:1 or 1:2 adduct is produced. With NaBARF, only 1:1 adduct is produced (entry 2a), whereas AgSbF$_6$ (which we have successfully used in place of NaBARF in some early hydrovinylation experiments[7e]) now gives exclusively the 2:1 adduct **6** in nearly *quantitative* yield (entry 2c)! Phosphramidites derived from (2*S*,4*S*)-diethylpyrrolidine and either (*R*)-binaphthol or (*S*)-binaphthol gave only polymeric materials (entry 4). Phospholane ligand **14a** with a benzyloxymethyl hemilabile side-chain gives a mixture of 1:1 and 1:2 adducts (entry 5). Increasing the size of the phospholane substituents (e.g., **14b**) turns off the catalytic activity. Simple 2,5-dimethylphospholane gives mostly the 2:1 adduct (entry 6). A modest enantioselectivity of 33% has been observed for this product as determined by the Mosher ester method (Scheme 2). As we have documented before,[7b] the use of AgOTf as an additive is important for ligands such as **15** with no hemilabile side-chain. Chelating ligands inhibit the reaction under the typical conditions reported here.

In conclusion, we report a remarkable ligand-dependent selectivity in the Ni-catalyzed heterodimerization of norbornene and ethylene. We also show the viability of several classes of tunable ligands for this exacting reaction, one of them giving up to 80% ee for the 1:1 *exo*-adduct. We believe that this prototypical reaction between a strained olefin and ethylene may have broader applications in the hydrovinylation of other similar substrates. Such studies are in progress.

Supporting Information Available: Full experimental details of various hydrovinylation reactions and spectroscopic and chromatographic data for characterization of compounds listed. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0356284

(13) See Supporting Information for NMR spectra from which ees were determined.

(14) Hodgson, M.; Parker, D.; Taylor, R. J.; Ferguson, G. *Organometallics* **1988**, *7*, 1761.

(15) For assignments of absolute configuration of 2-vinylnorbornenes, see: (a) Hayashi, T.; Kanehira, K.; Hioki, T.; Kumada, M. *Tetrahedron Lett.* **1981**, *22*, 137. (b) Köhler, J.; Deege, A.; Schomburg, G. *Chromatographia* **1984**, *18*, 119. See also, ref 2.