The Hydrovinylation Reaction: A New Highly Selective Protocol Amenable to Asymmetric Catalysis

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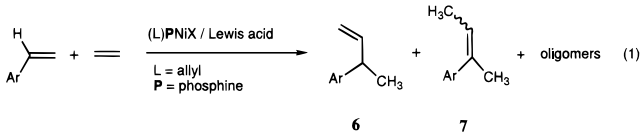
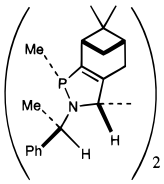
Carbon−carbon bond forming reaction is arguably the most important type of bond construction in organic chemistry; yet, paucity of methods for the stereoselective incorporation of abundantly available carbon feedstocks such as CO, CO_2, HCN, or simple olefins to prochiral substrates is one of the major limitations in this area.[1] One potentially important class of such reactions is the cationic $[Ni-H]^+$-catalyzed olefin dimerization reaction.[2,3] There had been only limited success in finding an enantioselective variation of this reaction partly because of the competing oligomerization of starting olefins and isomerization of the primary products (eq 1). In this paper we report our initial





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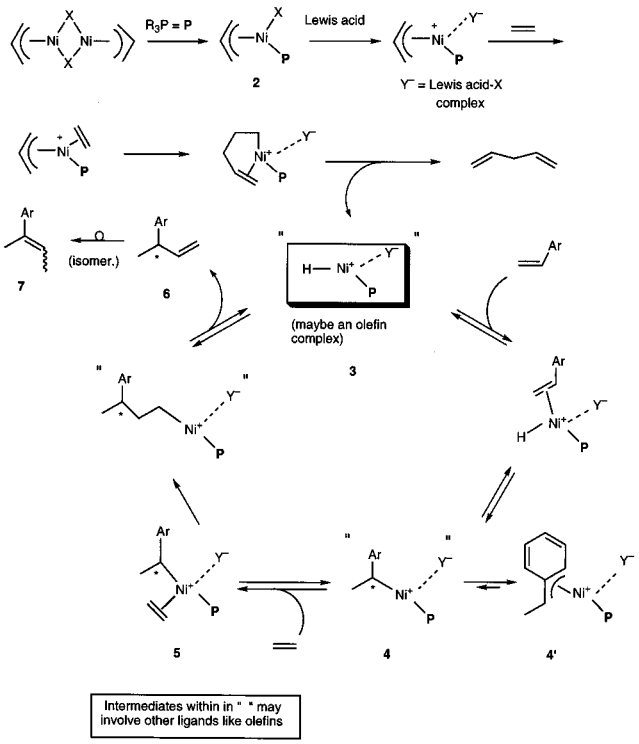
findings on a new and versatile protocol for the heterodimerization of vinyl arenes and ethylene. We further demonstrate that high enantioselectivity for this reaction can be achieved by using *a chiral phosphine with an appropriately placed hemilabile coordinating group*. To the best of our knowledge, such a control element has not been exploited in asymmetric catalysis.

The hydrovinylation reaction has a long history[2−9] and, as early as 1988, Wilke cited unpublished results of an asymmetric hydrovinylation of styrene in the presence of allyl nickel halide,

Scheme 1. Mechanism of Hydrovinylation



$EtAlCl_2$ and an esoteric azaphospholene ligand (**1**).[2] Subsequent work directed at simplifying the ligand structure[7] has shown that the original system is narrow in scope and is possibly of limited value for the development of a broadly applicable hydrovinylation reaction. More recent procedures are complicated by the need for higher pressures (15−25 bar) of ethylene[8] or incompatibility with substrates which have Lewis basic centers.[9] Selectivities of rhodium,[4] ruthenium[5] and palladium[6] catalyzed codimerization of styrene and ethylene are also poor.

In search of hydrovinylation conditions amenable to asymmetric catalysis, we decided to concentrate our efforts on improving the synthesis of the cationic nickel hydride complex and the associated counterion (Scheme 1, **3**), which could act as the catalyst in the reaction. This species is formed by the Lewis acid-assisted dissociation of the Ni−X bond from the 16-electron phosphine complex **2**, coordination of ethylene, coupling of the allyl and vinyl moieties, and subsequent β-hydride elimination. Insertion of the vinyl arene to the Ni−H gives a benzylic complex (**4**) which can be stabilized as an η-3 intermediate (**4′**). The coordinatively unsaturated **4** can react with ethylene (and possibly *not another vinyl arene*, if the phosphine is sufficiently bulky) to give **5**, which can undergo an insertion followed by β-hydride elimination, completing the catalytic cycle. The problems encountered in the previous attempts could be traced to two factors: (a) the poor reactivity of the substrates carrying a heteroatom could result from the reaction of the Lewis acid (for example, Et_2AlCl) with these Lewis basic centers; (b) the isomerization of the initially formed 3-aryl-1-butene (**6**) to 2-aryl-2-butene (**7**) is presumably mediated by the nickel hydride. We reasoned that the scope and selectivity of hydrovinylation could be significantly increased by eliminating the troublesome Lewis acid through the use of weakly coordinat-

(1) For a topical, highly readable article dealing with the new challenges facing synthetic organic chemistry, see: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. For lead references to highly catalytic asymmetric C−C bond-forming reactions using feedstock carbon sources, see: (hydroformylation) Agbossou, F.; Carpentier, J.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485. Nozaki, K.; Sakai, N.; Nanno, T.; Higashijima, T.; Mano, S.; Horiuchi, T.; Takaya, H. *J. Am. Chem. Soc.* **1997**, *119*, 4413. (hydrocyanation) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869. (use of olefins) Mortreux, A. In *Metal Promoted Selectivity in Organic Synthesis*; Noels, A. F., Graziani, M., Hubert, A. J., Eds.; Catalysis by Metal Complexes, Vol. 12; Kluwer Academic: Dordrecht, The Netherlands, 1991; p 47.

(2) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185. Wilke, G.; Monkiewicz, J.; Kuhn, H. U.S. Patent No. 4,912,274, 1990. Jolly, P. W.; Wilke, G. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 2, p 1024.

(3) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235.

(4) For the first report of codimerization of ethylene (1000 atm) and styrene using Rh(III), see: Alderson, T.; Jenner, E. L.; Lindsey, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 5638.

(5) Umezaki, H.; Fujiwara, Y.; Sawara, K.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2230.

(6) (a) Britovsek, G. J. P.; Keim, W.; Mecking, S.; Sainz, D.; Wagner, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1632. (b) Drent, E. U.S. Patent No. 5,227,561, 1993. (c) Unpublished results from this laboratory.

(7) Angermund, K.; Eckerle, A.; Lutz, F. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50b*, 488.

(8) Ceder, R.; Muller, G.; Ordinas, J. I. *J. Mol. Catal.* **1994**, *92*, 127. For an earlier version of this reaction, see: Kawata, N.; Maruya, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3217.

(9) Monteiro, A. L.; Seferin, M.; Dupont, J.; Souza, R. F. *Tetrahedron Lett.* **1996**, *37*, 1157.

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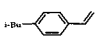
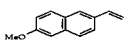
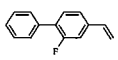
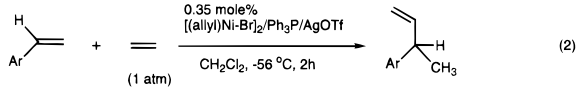
Table 1. Hydrovinylation of Vinylarenes

Entry	Substrate	% Yield[a]	Conditions[b]
1	styrene	>95 (99+)	(i)
2	3-methylstyrene	>95 (98)	(i)
3	4-methoxystyrene	>95 (98)	(i)
4	4-chlorostyrene	81 (89)	(i)
5	4-bromostyrene	>95 (98)	(i)
6	2-vinylnaphthalene	(99+)	(i)
7		(90) (97)	(i) with 0.5 mole% cat. (ii)
8		> 90 (99+) >97 (99+)	(i) with 1.4 mole% cat. (iii)
9		(88)	(i)

[a] In brackets are the yields estimated by gas chromatography. [b] See the text: (i) [(allyl)NiBr]$_2$, (0.35 mol %)/Ph_3P/AgOTf/CH_2Cl_2/−55 °C/2 h; (ii) [(allyl)NiBr]$_2$, (0.70 mol %)/(*R*)-MOP (**8a**)/$Ar'_4B^-Na^+$/CH_2Cl_2/−56 °C/2 h; (iii) [(allyl)NiBr]$_2$, (0.70 mol %)/(*R*)-MOP−OBn (**8b**)/$Ar'_4B^-Na^+$/CH_2Cl_2/−56 °C/2 h.

ing counteranions such as triflate or tetraaryl borate (Ar_4B^-).[10] Furthermore, it should be possible to prevent the isomerization of the initially formed terminal olefin (e.g., **6** → **7**) by manipulation of the phosphine ligand, **P** and/or the metal.

After an extensive scouting program, we have found that most of the our expectations have been borne out. The hydrovinylation of various vinylarenes proceeds with *unprecedented* chemical yield and selectivity when a combination of allylnickel bromide dimer, a weakly coordinating counterion such as triflate (OTf^-) or Ar_4B^- and a monophosphine is employed as the precatalyst (eq 2 and Table 1). Typically the reaction is carried out at −56



(2)

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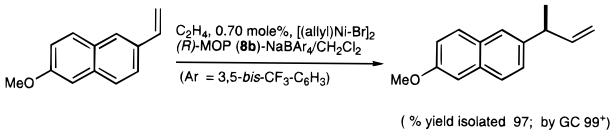
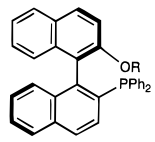
°C in methylene chloride as solvent under 1 atm of ethylene pressure using 0.007 equiv of the catalyst.[11] Under these conditions, no oligomerization of either the vinyl arene or ethylene is detected. In sharp contrast to the previously reported Lewis acid-mediated reactions,[9] vinylarenes with Lewis basic centers such as oxygen, chlorine, and bromine undergo the reaction with remarkable ease (entries 3−5 and 8). 4-Isobutylstyrene, 3-fluoro-4-phenylstyrene, and 2-methoxy-6-vinylnaphthalene (entries 7, 8, 9), all potential precursors for important antiinflammatory agents, gave excellent yields of the expected hydrovinylation products. Hydrovinylation product of 4-bromostyrene (entry 5) is another potentially important precursor that could be transformed into a variety of useful intermediates via organometallic cross-coupling reactions. As expected,[8] the use of a number of *chelating* phosphines, aminophosphines, and 1,2-bis-diarylphosphinites gave no product under otherwise identical conditions.[6c,12] Preliminary experiments indicate that olefins with strongly electron-withdrawing substituents on the aromatic nucleus (for example, 3,5-bis-(trifluoromethyl)styrene, 2-vinylpyidine) are poor substrates for this reaction. Methyl substitution at the α- or β-carbons of styrene also leads to poor yields (21 and 49%, respectively).

The new reaction protocol is easily adapted for an asymmetric reaction. Considering the intermediacy of several cationic nickel species in this reaction, we decided that a monophosphine that also carrries a hemilabile group[6a,13] might have an advantage, since such a ligand can stabilize these intermediates by internal coordination. Our choice for this purpose was Hayashi's 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MOP) ligand (**8a**),[14] which carries, in addition to the phosphine, a methoxy group that could now serve as the ancillary ligand. Most gratifyingly, in the initial attempts using the (*R*)-MOP as the ligand, 2-methoxy-6-vinylnaphthalene (MVN) and 4-isobutylstyrene gave nearly quantitative yields of the products (*S*-isomers) in 62 and 40% enantiomeric excess (ee),[11] respectively (eq 3). In addition, we

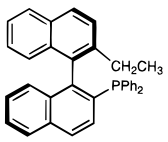


(3)

(% yield isolated 97; by GC 99+)



8a R = CH_3
8b R = CH_2Ph



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also discovered that with the MOP ligands, tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate anion (TFPB)[15] gave a substantially improved catalyst vis-á-vis the corresponding triflate (entries 7 and 8). A minor modification in the ligand structure (use of $-OCH_2Ph$, **8b**, instead of −OMe) improves the ee for MVN to 80% when the reaction is carried out at −70 °C. *These weakly coordinating O-alkyl groups of the ligand appear to be crucial for the success of the reaction since yield and enantioselectivity for the ligand with an ethyl group (**9**) in place of the methoxy group are only 13 and 3% ee, respectively.*

Further work in this area will involve optimization of the initial results by electronic and steric tuning of the MOP ligands and identification of other chiral ligand systems with hemilabile groups. Such studies and extensions to other heterodimerizations involving dienes and other monolefins are in progress.

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Supporting Information Available: Details of experimental procedures and spectroscopic, GC, and HPLC data of products (8 pages). See any current masthead page for ordering and Internet access instructions.

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(10) For the use of Ar_4B^- in related reactions, see: DiRenzo, G. M.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 6225.

(11) See the Supporting Information for detailed experimental procedures and identification of the configuration of the products.

(12) These include 1,3-bis(diphenylphosphino)propane (DPPP), 2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl (BINAP), (2,2-dimethyl-1,3-dioxolane-4,5-diylbismethylene)bisdiphenylphosphine (DIOP), *N*-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM).

(13) (a) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658. (b) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.

(14) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945.

(15) Brookhart, M.; Grant, B.; Volpe, A. *Organometallics* **1992**, *11*, 3920.