Synergistic Effects of Hemilabile Coordination and Counterions in Homogeneous Catalysis: New Tunable Monophosphine Ligands for Hydrovinylation Reactions
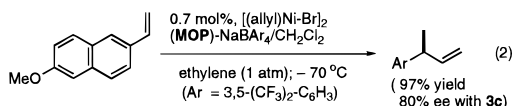
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Heterodimerization of olefins is a reaction of enormous synthetic potential, since it has been demonstrated that excellent yields and selectivities can be achieved under exceptionally mild conditions in many cases.[1,2] For example, we have recently shown that using catalysts derived from [(allyl)Ni(Br)]₂ and a tertiary phosphine in combination with a silver salt, a nearly quantitative hydrovinylation of vinylarenes can be achieved (eq 1). In our

$$
\text{Ar} \xrightarrow[\substack{\text{CH}_2\text{Cl}_2,\ -56\ ^\circ\text{C},\ 2\text{h}}]{\substack{\text{ethylene (1 atm.)}\\ 0.35\ \text{mol\%}\ [(\text{allyl})\text{Ni-Br}]_2\\ \text{Ph}_3\text{P/AgOTf}}} \underset{\textbf{1}\ (90\text{-}99\ \%)}{\text{Ar}} + \underset{\textbf{2}\ (0\ \%)}{\text{Ar}} \quad (1)
$$

initial efforts to find a broadly applicable asymmetric version of this reaction,[2] we considered the requirement of a coordination site for ethylene on the putative cationic Ni intermediates, and chose *(R)*-2-diphenylphosphino-2′-alkoxy-1,1′-binaphthyl (MOP),[3] in which the 2′-methoxy group would play the role of a 'hemilabile' ligand[4] (eq 2). With the fortuitous choice of this

$$
\text{MeO} \xrightarrow[\substack{\text{ethylene (1 atm.)};\ -70\ ^\circ\text{C}\\ (\text{Ar} = 3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)}]{\substack{0.7\ \text{mol\%},\ [(\text{allyl})\text{Ni-Br}]_2\\ (\textbf{MOP})\text{-NaBAr}_4/\text{CH}_2\text{Cl}_2}} \text{Ar} \underset{\substack{(\ 97\%\ \text{yield}\\ 80\%\ \text{ee with}\ \textbf{3c})}}{} \quad (2)
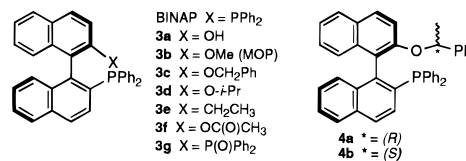$$

ligand, we also realized that counterions played a key role in the success of this reaction. For example, we found that AgOTf, which gave in many cases isolated yields >95% with Ph₃P as a ligand, gave low yields in the hydrovinylation reactions using the MOP ligands. In sharp contrast, the use of Na⁺ B[(3,5-(CF₃)₂C₆H₃)]₄⁻ (NaBARF) in conjunction with MOP fully restored the activity of the catalyst (eq 2).[5] Since this original discovery, we have sought to clarify the role of hemilabile chelation and of the effect of various counterions on the efficiency and selectivity of the Ni-and Pd-catalysts for this reaction. With this goal, variation of the 2′ substituent of the MOP ligand was studied. In addition, we synthesized a new class of "tunable" hemilabile 1-aryl-2,5-

Table 1. Ligand Substituent Effects on Hydrovinylation of 2-Methoxy-6-vinylnaphthalene[a]

entry	ligand	group X in **3**	yield (%)	%ee	remarks
1	(R)-BINAP	Ph₂Ph	0		
2	**3b** (MOP)	OCH₃	>98	62	
3	**3c**	OCH₂Ph	97	73	−55 °C
			87	73	AgNTF₂
4	**3c**	OCH₂Ph	93	80	at −70 °C
5	**3d**	O-*i*-Pr	69	70	
6	**3e**	CH₂CH₃	12	<3	
7	**3f**	OC(O)CH₃	0		
8	**3g**	P(O)Ph₂	0		
9	**4a**	OC(H)(Ph)(CH₃)	96	71	(R,R)
10	**4b**	OC(H)(Ph)(CH₃)	79	65	(R,S)

[a] See eq 2 for typical procedure.[6] Isolated yield; ee determined by HPLC.

dialkylphospholanes which were found to be exceptionally good ligands for the exacting hydrovinylation reaction, *if and only if the appropriate counterions are used.* The results of these studies are reported in this paper.

BINAP X = PPh₂
3a X = OH
3b X = OMe (MOP)
3c X = OCH₂Ph
3d X = O-*i*-Pr
3e X = CH₂CH₃
3f X = OC(O)CH₃
3g X = P(O)Ph₂

4a * = (R)
4b * = (S)

The results of hydrovinylation using the 2′-modified MOP ligands are shown in Table 1.[6] Replacement of the −OMe group of MOP with a OCH₂Ph (**3c**) resulted in an isolated yield of 97% (73% ee) for the hydrovinylation of 2-methoxy-6-vinylnaphthalene (MVN) at −55 °C. The 2′-isopropoxy derivative **3d** gave lower conversions (69%) with little change in the selectivity (70% ee) as compared to **3c**. The ligand with an the *(R)*-phenethyl side chain, **4a**, prepared by the Mitsunobu reaction of **3a**, gave an excellent reaction (96% isolated yield, 71% ee) in the hydrovinylation of MVN, whereas the use of the ligand, **4b** (*(S)*-phenethyl side chain), under otherwise identical conditions resulted in only a moderate yield (entries 9 and 10). The first clear indication of the role of hemilabile chelation came from the hydrovinylation experiments using the ligand **3e**, in which the alkoxy group of MOP was replaced by an ethyl group. Under the standard conditions (eq 2) using the BARF as the counterion, the corresponding Ni-complex gave only 17 and 12% conversion in the hydrovinylation of styrene and MVN, respectively. Most strikingly, the ee of the isolated product was nearly zero in both cases! If the hemilabile ligation is important, one should expect different reactivities from ligands with varying donor properties.[4b,c] Accordingly, the allyl(Ni)-complexes of 2′-acetoxy (**3f**) and the 2′-diphenylphosphinoxy (**3g**)[7] analogues of MOP failed to produce any hydrovinylation products from styrene and MVN under the standard conditions (entries 7 and 8). Phosphineoxide is known to be a strongly coordinating group,[4c] and it is not surprising that ethylene is unable to displace this group from the Ni coordination sphere. Also, carbonyl groups are known to be better hemilabile ligands than ether oxygens.[8a]

Next we turned our attention to 1-aryl-2,5-dialkylphospholanes, a ligand scaffolding that appears to hold great potential in asymmetric catalysis.[9] A series of simple phospholane derivatives

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

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(5) (a) For the use of Ar₄B⁻ in olefin dimerization reactions, see: DiRenzo, G. M.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 8, 6225. (b) For reviews on weakly coordinating anions, see: Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405; Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(6) See Supporting Information for details.

(7) As with other chelating phosphines, BINAP gave no reaction. The monophenoxy BINAP ligand **3g** was prepared by a low-temperature oxidation of BINAP with Davis' oxaziridine (H. Park, unpublished results). Davis, F. A.; Chen, B. C. *Chem. Rev.* **1992**, *92*, 919.
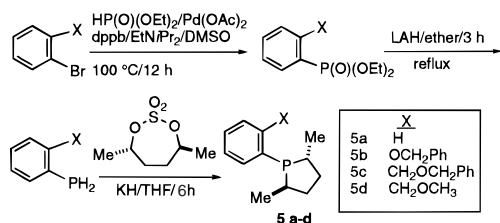
Scheme 1. Synthesis of 1-Aryl-2,5-dialkylphospholanes

**Table 2.** Effect of Counterions on the Hydrovinylation of Styrene Using "Hemilabile" Ligands[a]

		yield of product (%)		
entry	additive	**5a**	**5c**	remarks
1	AgOTf	94	<4	37%ee (S) with **5a**
2	AgClO$_4$	95	<2	29% isom. with **5a**
3	AgNTf$_2$	<2	48	47%ee (S), 9% isom. with **5c**
4	AgSbF$_6$	<2	94	48%ee (S) with **5c**
5	NaBAr$_4$[b]	<2	97	50%ee (S) with **5c**

[a] For reaction conditions see Supporting Information. [b] Ar = 3,5-(CF$_3$)$_2$−C$_6$H$_3$; ee determined by HPLC.

5a−d, prepared according to Scheme 1,[6] were tested as ligands in the Ni-catalyzed asymmetric hydrovinylation reactions. Our initial investigations started with ligands **5a**, and a close analogue, **5b**, with a potential hemilabile group at the ortho-position. While we found that **5a** to be an excellent ligand for the Ni-catalyzed hydrovinylation of vinylarenes, especially with OTf as the counterion (vide infra Table 2), **5b** led to significant isomerization of the initially formed product **1** (to **2**) under the standard reaction conditions (eq 2) even at −55 °C. One of the principal differences between **5b** and the ligand **3b**, we conjectured, was the placement of the hemilabile alkoxy group with respect to the phosphorus. In **5b** it is on the β carbon and in **3b** it is on the δ carbon, resulting in 5- vs 7-membered Ni-chelate intermediates in the respective cases. To probe the effect of the relative positioning of the hemilabile group, the *o*-benzyloxymethyl analogue **5c** was prepared, and most gratifyingly, this ligand proved to be one of the best for highly selective hydrovinylation reactions.

The results of hydrovinylation of styrene using **5a** and **5c** are shown in Table 2. For the simple phospholane ligand **5a**, *with no possibility of hemilabile coordination*, the reaction did not proceed unless a weakly coordinating anions such a OTf is used (entries 1 and 2). Incidentally, ClO$_4^-$ was also acceptable, except that significant isomerization of the primary product was observed. Additives such as AgBF$_4$, NaBPh$_4$, AgNTf$_2$, AgSbF$_6$, and NaBARF gave practically *no reaction* under the standard conditions (entries 3−5). In sharp contrast, when ligand **5c** (or **5d**) with the *o*-alkoxymethylphenyl substituent were used, best results were obtained with noncoordinating counteranions BARF and SbF$_6^-$ (entries 4 and 5). Not surprisingly, AgOTf, AgClO$_4$, AgBF$_4$, and NaBPh$_4$ were found to be ineffective in these cases.[10]

Some indication of the effect of counterions on the relative stability/reactivity of the 1,5-phospholane complexes can be obtained by a variable temperature ^{31}P and ^{1}H NMR study of the (allyl)Ni[**P**]X (**P** = **5a**, **5c**, X = Br, OTf, SbF$_6$ and BARF).[6] The proton spectra between 27 and −70 °C are broad and generally unintelligible. At 27 °C, the catalytically *inactive* complex (allyl)-Ni[**5a**](Br), shows two peaks (1:1) in the ^{31}P spectrum at δ 43.10 and 42.08, characteristic of the square planar *endo-* and *exo-* diastereomers shown below. There are no changes in the spectrum

Diastereomers of ((allyl)[Ni][**5a**](Br)
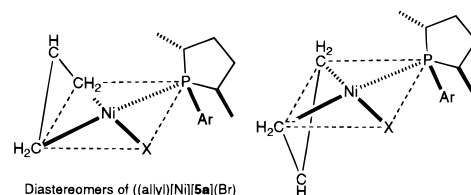
as the solution is cooled to −70 °C, except for small changes in chemical shifts (<1 ppm). The catalytically active triflate complex ((allyl)Ni[**5a**](OTf)) shows the same peaks (at 27 °C, δ 43.89 and 43.31), but the peaks in both ^{31}P and ^{1}H NMR are considerably broadened at temperatures below −20 °C. Upon cooling the complex new peaks begin to appear, and at −70 °C, a complex spectrum consisting of at least eight lines is obtained.[6,11,12] As compared to the stable neutral bromide complex, (allyl)Ni[**5a**](Br), partial decomposition of the triflate complex, (allyl)Ni[**5a**](OTf), can be observed in the NMR tube after several hours. A similar behavior is observed for the SbF$_6$ and BARF complexes. In particular, the (allyl)Ni[**5a**](BARF) undergoes rapid decomposition even at room temperature as it is being prepared, showing a multitude of broad peaks (δ 43.73, 43.03, 42.34, and 41.06) at 0 °C. The temperature-dependent changes of all complexes except that of the BARF complex are completely reversible, which leads to one to suspect that in the *absence of hemilabile ligation, the highly dissociated* BARF-complex is very unstable (vide infra). In sharp contrast, the (allyl)Ni[**5c**](BARF), is a remarkably stable species showing no sign of decomposition upon storage at room temperature for several days.[6] It exhibits ^{1}H NMR spectrum between temperatures 27 and −70 °C, indicative of highly fluxional behavior. The room temperature ^{31}P NMR spectrum consists of a broad singlet at δ 23.63, which remains unchanged even at −70 °C, except for some line broadening and minor changes in the chemical shift. Similar behavior (^{31}P NMR δ 23.71) is seen for the other *active* complex (allyl)Ni[**5c**](SbF$_6$). The neutral, catalytically *inactive* complex (allyl)Ni[**5c**](Br), on the other hand shows two sharp peaks in the ^{31}P NMR (at 0 °C 37.04 and 36.44, ratio ~3:2) at temperatures between 0 and −40 °C, suggesting stable *exo-* and *endo-*isomers similar to (allyl)Ni[**5a**](Br). As expected[8b] hemilabile coordination of an ether oxygen results in an upfield shift of the ^{31}P signal (Δδ = ~12 ppm). The corresponding (allyl)Ni[**5c**](OTf) [major ^{31}P δ = 31.3] was found to undergo rapid decomposition in the NMR tube. One plausible explanation why the triflate salt (allyl)-Ni[**5c**](OTf) is catalytically inactive might be that with the hemilabile oxygen and a coordinating counterion there is little chance of ethylene incorporation to initiate the reaction. Also, in the absence of an internal hemilabile ligand, catalysts with highly dissociated counterions (BARF, SbF$_6$) appear to have only transient existence, which might explain why there is no reactions when they are involved. Studies to clarify such mechanistic details are underway.

Supporting Information Available: Experimental procedures for the synthesis of ligands **3f**, **3g**, **4a**, **4b**, **5a−c**, their ^{1}H, ^{13}C, and ^{31}P NMR spectra, procedures for their use in hydrovinylation reactions. Selected variable-temperature ^{1}H and ^{31}P NMR spectra of complexes of the general structure (allyl)Ni(ligand)(counterion) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Triflate ion is known to coordinate to nickel in a bidentate fashion at low temperature. Pörshke, K.-R.; Krause, J.; Haack, K.-J.; Nickel, T.; Proft, B. *Proceedings of the Ninth International Symposium on Homogeneous Catalysis, Jerusalem, 1994*; p 55. In addition, at −70 °C, some restricted rotation around the P−Ni bond can also be expected.[11a]