Hydrovinylation and Related Reactions: New Protocols and Control Elements in Search of Greater Synthetic Efficiency and Selectivity

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Abstract: New protocols for highly selective and nearly quantitative heterodimerization of ethylene or propylene with various functionalized vinylarenes are described. Under these conditions, which are compatible with a wide variety of functional groups, cylization of 1,6-dienes and hydrovinylation of norbornenes can also be accomplished. Also presented are possible strategies for stereochemical control, including a crucial role for hemilabile ligands in enantioselective catalysis.

Keywords: asymmetric catalysis · C–C coupling · cyclizations · hydrovinylations · ligand effects · nickel · palladium

Introduction

In this era of heightened environmental awareness and the ever-increasing demand for higher efficiency from chemical processes, one of the major challenges facing organic synthesis is the selective incorporation of abundantly available carbon, hydrogen, oxygen, and nitrogen sources into other common substrates. In this context, enantioselective carbon–carbon bond-forming reactions that use carbon feedstock materials, such as CO and HCN, and simple olefins, such as ethylene and propene, is an important goal.[1] One potentially important class of such reactions is the [Ni^{+}–H]-catalyzed olefin oligomerization reaction, which forms the basis of the Dimersol technology (propylene dimerization)[2] and the Shell Higher Olefin Process (SHOP).[3] The astonishingly high turnover frequency (625 000 [propylene] $[Ni]^{-1} h^{-1}$) observed for $[\eta^3$-(allyl)$Ni(PR_3)]^{+}[RAlX_3]^{-}$ in the catalytic dimerization of propene makes this system among the most active of the homogeneous catalysts, and, predictably, applications in fine chemical synthesis have been eagerly sought ever since the initial discovery. An important such application is the heterodimerization of simple olefins, of which the hydrovinylation reaction (addition of ethylene) is a prototypical example.

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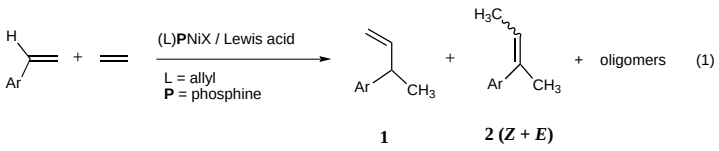
Discussion

Heterodimerizations with ethylene: The hydrovinylation reaction has a long history. Since the first report of a high-pressure (1000 atm) ethylene/styrene codimerization in the presence of $RhCl_3$,[4] the use of various metals such as Ru,[5] Co,[6] Pd,[7] and Ni[8–11] has been investigated, even though Pd and Ni are the most studied metals. Hydrovinylation of vinylarenes has attracted the most attention, since the product 3-aryl-1-butenes are potential intermediates for widely used 2-arylpropionic acids.[12] Styrene serves as a prototypical test case for this reaction. Almost invariably, the reaction is complicated by isomerization of the initially formed 3-aryl-1-butene (**1**) to a mixture of the *Z*- and *E*-2-aryl-2-butenes (**2**) and oligomerization of the starting olefins [Eq. (1)]. The best



1 **2 (*Z* + *E*)** (1)

results obtained prior to our current work are compiled in Table 1. Careful examination of the published work reveals that except for the Wilke system, which uses the azaphospholene ligand $\mathbf{P_1}$ (entries 4 and 5, Table 1), no other catalyst gives satisfactory yield and selectivity in this potentially important reaction. Subsequent work[10e] directed at simplifying the structure of the esoteric azaphospholene $\mathbf{P_1}$ has shown that this ligand has a narrow scope, and is possibly of limited value for the development of a broadly applicable hydrovinylation reaction.

All the available evidence points to a mechanism involving a cationic nickel hydride associated with a weakly coordinated counter ion (**4**, Scheme 1). This species is formed by the Lewis-acid-assisted dissociation of the Ni–X bond from the 16-electron phosphine complex **3**, coordination of ethylene, coupling of the allyl and vinyl moieties, and subsequent β-hydride elimination. Insertion of the vinylarene to the Ni–H

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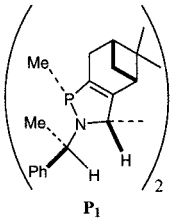
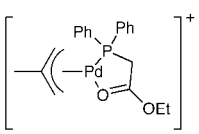
Table 1. Hydrovinylation of vinylarenes. Best practices prior to the current work.

	Catalyst	Reaction conditions	Yield [%] for 3-Ph-1-butene (1)	Selectivity[a]	Remarks	Ref.
1	$[(Ph_3P)_2Ni(mesityl)Br]$	styrene/Ni = 17, BF_3, OEt_2, 0 °C, 15 min, < 1 atm C_2H_4, CH_2Cl_2	67	91 %	9 % isomers and styrene dimer	8a
2	$[\{PhCH_2)_3P\}_2Ni(mesityl)(CH_3CN)]^+[BF_4]^-$	styrene/Ni = 500 – 1000, 25 °C, 1 h, 15 atm C_2H_4, THF	96	97 %	poor yield with α-Me-styrene; tolerant to Cl, OMe groups exotherm at the end of reaction	8b
3	$[Ni(CH_3CN)_6][BF_4]_2$, Ph_3P, $EtAlCl_2$	styrene/Ni = 400, 25 °C, 30 min, 10 atm C_2H_4, CH_2Cl_2	90	90 %	not tolerant to Lewis basic groups (Cl, OMe) on arene	9
4	$[\{\eta^3$-(allyl)NiCl$\}_2]$, **P_1**, $Et_3Al_2Cl_4$	styrene/Ni = 1948, − 72 °C, 3.25 h, 1 atm C_2H_4, CH_2Cl_2	97	?	93 % ee (*R*) for styrene 85 – 95 % *ee* for various vinylarenes; limited to **P_1** as ligand	10b
5	$[Ni(OAc)_2]$, **P_1**, $AgBF_4$	styrene/Ni = 685, − 30 °C, 80 min, 1 atm C_2H_4, CH_2Cl_2	46	?	75 % *ee* (*R*) for styrene; limited to **P_1** as ligand	10b
6	$[\eta^3$-$(C_4H_7)Pd$–**P_2**$]^+[BF_4]^-$	a) styrene/Pd = 400, 25 °C, 30 atm C_2H_4, CH_2Cl_2, 1 h	41	92	8 % isom.	7d
		b) same, 3 h	100	9	91 % isom.	
7	$[(Ally)Pd$**P_3**$]^+[SbF_6]^-$	styrene/Pd = 500 – 1000, 10 °C, 15 min, 10 atm C_2H_4, CH_2Cl_2	66	94	86 % *ee* (*S*). For Pd, SbF_6 better than OTf as a counter ion	7e

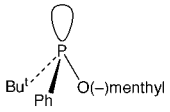
[a] for 3-Ph-1-butene (**1**)



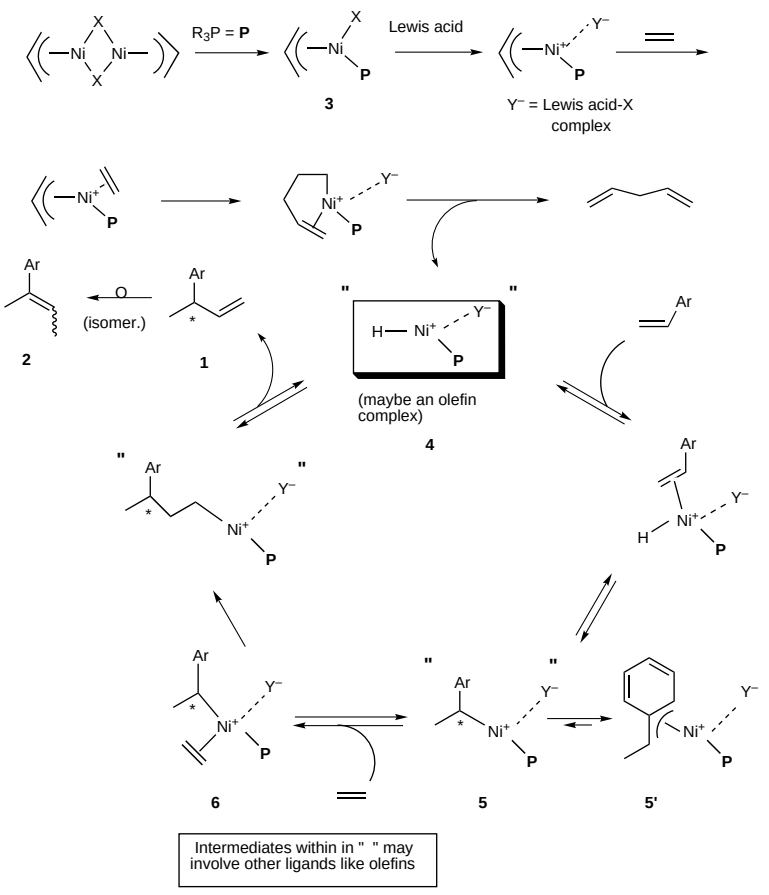
P_1



(η^3-(C_4H_7)-Pd^+-**P_2**)



P_3



Scheme 1. Mechanism of hydrovinylation.

bond gives a benzylic complex **5**, which can be stabilized as an η^3 intermediate **5′**. The coordinately unsaturated **5** can react with ethylene (and possibly *not another vinylarene*, if the phosphine is sufficiently bulky) to give **6**, which can undergo an insertion followed by β-hydride elimination; this completes the catalytic cycle. Some of the limitations 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 (**1**) to 2-aryl-2-butene(s) (**2**) could be mediated by a very reactive nickel (or palladium) hydride. The isomerization reaction appears to be a major drawback, especially for the Pd-mediated reaction.[7] We reasoned that the scope and selectivity of hydrovinylation could be significantly increased by eliminating the troublesome Lewis acid, and using in its place a weakly coordinating counter anion, such as OTf,[13] or a noncoordinating counter anion, such as tetraarylborate (Ar_4B^-),[14] in conjunction with a hemilabile group on the phosphine.[15] Further it should be possible to prevent the isomerization of the initially formed terminal olefin (e.g., **1**→**2**) by manipulation of the phosphine ligand, **P**, and/or the metal.

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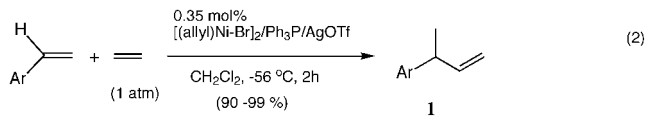
After an extensive scouting program in which we systematically varied the ligand and the counter ion, a new protocol was arrived at. The hydrovinylation of various vinylarenes proceeds with *unprecedented* chemical yield and selectivity when a combination of allylnickel bromide dimer and a weakly coordinating counter ion such as triflate (OTf^-) is employed as the precatalyst [Eq. (2) and Table 2]. Alternatively, $Na^+Ar_4B^-$(Ar = 3,5-$(CF_3)_2C_6H_3$) along with a monophosphine that carries a hemilabile ligand can also be employed [vide infra, Eq. (4)]. Typically the reaction is carried out at $-56\,^\circ C$ in methylene chloride as the solvent under 1 atmosphere of ethylene pressure with 0.007 equivalents of the catalyst. Under these conditions no oligomerization of either the vinylarene or ethylene is detected. In sharp contrast



(2)

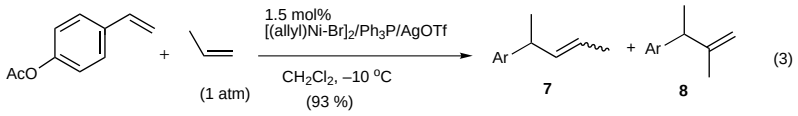
Table 2. Hydrovinylation of vinylarenes.[11]

	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	6-MeO-2-vinyl-naphthalene	(90)	i), 0.5 mol % catalyst
		(97)	ii)
8	4-*i*-Bu-styrene	> 90 (99+)	i), 1.4 mol % catalyst
		> 97 (99+)	iii)
9	3-F-4-Ph-styrene	(88)	i)

[a] In brackets are the yields estimated by gas chromatography. [b] 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(**12a**)/$Ar'_4B^-Na^+$/CH_2Cl_2/ – 56 °C/2h; iii) [(allyl)-NiBr]$_2$, (0.70 mol %)/*(R)*-MOP-OBn(**12b**)/$Ar'_4B^-Na^+$/CH_2Cl_2/ – 56 °C/2 h

to the previously reported Lewis-acid-mediated reactions, vinylarenes with Lewis basic centers such as oxygen, chlorine, and bromine undergo the reaction with remarkable ease (entries 3, 4, 5, and 7; Table 2). 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. The hydrovinylation product of 4-bromostyrene (entry 5) is another potentially important precursor that could be transformed into a variety of useful intermediates through organometallic cross-coupling reactions. As expected, the use of a number of *chelating* phosphines, aminophosphines, and 1,2-*bis*-diarylphosphinites gave no product under otherwise identical conditions.[16] Preliminary experiments indicate that olefins with strongly electron-withdrawing substituents on the aromatic nucleus (for example, 3,5-di-trifluoromethylstyrene, 2-vinylpyridine) are poor substrates for this reaction. Methyl substitution at the α- or β-carbon atoms of styrene also leads to poor yields (21 and 49 %, respectively) under these conditions.

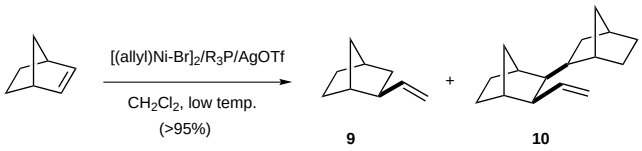
Heterodimerization with other olefins: Unlike heterodimerization reactions of ethylene, a synthetically useful heterodimerization reaction that uses propene[7a,b, 17] was not developed until recently. We find[18] that propene reacts with styrene and substituted styrenes under conditions slightly modified from what was previously described for ethylene[11] and gives excellent yields of the expected products. An example of a substrate with a Lewis-basic acetoxy group is shown in Equation (3). The reaction with propene proceeds at higher temperature (-15^o to $10\,^\circ C$ vs. $-56\,^\circ C$ for ethylene), especially in the case of the more electron-deficient styrene derivatives. As expected, a mixture of regioisomeric products



(3)

(**7** and **8**) are formed in which addition of propene-C_1 to the benzylic position predominates.

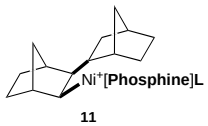
We find that the protocol using [(allyl)NiBr]$_2$/phosphine/AgOTf [Eq. (2) and (3)] works equally well for the hydrovinylation of norbornene, the course of the reaction being dependent on the phosphine that is employed.[19] Tricyclohexylphosphine gives the expected 1:1 adduct (**9**), whereas triphenylphosphine gives a 2:1 adduct (**10**) between norbornene and ethylene (Scheme 2). This is presumably related to



Phosphine	Cone angle	Temp.	9	10
[cyhex]$_3$P	180^0	-70 °C	100	0
Ph_3P	145^0	-55 °C	1	97

Scheme 2. Ligand control: hydrovinylation of norbornene.

the cone angles of the two phosphines and the relative reactivities of the two olefins. It is conceivable that norbornene is more reactive than ethylene and thus undergoes a fast initial dimerization when a less crowded phosphine (Ph_3P) is used. The initially formed σ-nickel complex **11** cannot undergo β-hydride elimination, for stereoelectronic reasons, and hence reacts with another olefin (ethylene) giving finally the 2:1 adduct **10**. With a bulky phosphine, only addition to ethylene is feasible giving the 1:1 adduct.

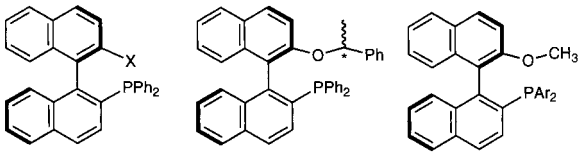


11

Asymmetric catalysis of the hydrovinylation reaction: Heterodimerization reactions of 1,3-cyclooctadiene with ethylene was one of the first examples of an asymmetric carbon–car-

bon bond-forming reaction ever reported, even though the selectivity was unacceptably low.[20] Under similar conditions, norbornadiene gave up to 49% yield (77.5% *ee*) of (+)-vinylnorbornene. These reactions appear to be plagued by isomerization and other side reactions. The details of the reaction conditions for this and many other hydrovinylations remain largely unpublished except in dissertations and reviews.[10d] The best procedures for asymmetric hydrovinylations of vinylarenes (Table 1, entry 4),[10b] cyclopentadiene,[10b] and norbornene[10b] use Wilke's azaphospholene **P$_1$** (Table 1) with $[(allyl)NiCl]_2$ and $Et_3Al_2Cl_3$ (or Et_2AlCl). Unfortunately, the azaphospholene **P$_1$** is a very special ligand and, as noted earlier, attempts to modify its structure have not been successful.[10e] A (−)-menthol-derived *P*-chiral phosphinite **P$_3$** (Table 1, entry 7)[7e] could represent an important class of ligands for Pd-catalyzed hydrovinylation of vinylarenes if the selectivity and yield can be improved. The only other hydrovinylation substrate for which good enantioselectivity has been observed is 1,3-cyclohexadiene.[21]

Having failed to carry out the reaction with chelating phosphines,[16] we turned our attention to monophosphines. Considering the requirement of an open coordination site for ethylene in this reaction, we decided that a monophosphine that also carried a hemilabile group[15] might have an advantage, since such a group can stabilize the putative cationic intermediates by internal coordination. In addition, this coordination might lead to better diastereoselective discrimination at the key Ni–H addition to the prochiral faces of the olefin during the early stages of the reaction (Scheme 1). Our initial choice for this purpose was Hayashi's 2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl (MOP) ligand (**12a**),[22] which carries, in addition to the tertiary



12a X = OCH_3
12b X = OCH_2Ph
12c X= CH_2CH_3
12d X = $OC(O)CH_3$
12e X = $P(O)Ph_2$

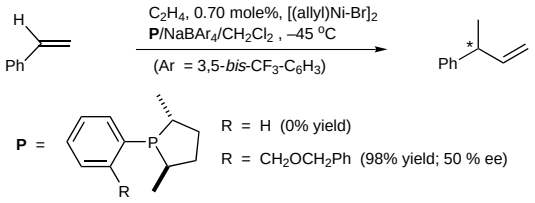
13a * = (R)
13b * = (S)

12a Ar = Ph
14a Ar = 3,5-$(Me)_2$-C_6H_3
15a Ar = 3,5-$(CF_3)_2$-C_6H_3

phosphine, a methoxy group that could now serve as an ancillary ligand. After a disappointing start with AgOTf as the promoter, which gave practically no reaction, we recognized that with *(R)*-MOP as the ligand, tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate anion (TFPB)[14, 23] gave a substantially improved catalyst vis-á-vis the corresponding triflate.

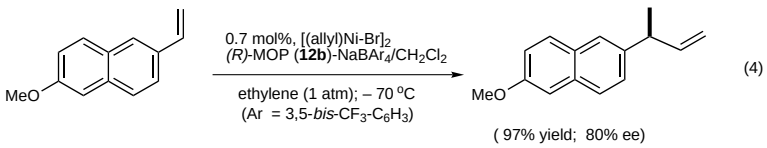
2-Methoxy-6-vinylnaphthalene (MVN) and 4-*iso*-butylstyrene gave nearly quantitative yields of the products in 62% and 40% *ee* (*S* isomers), respectively, [Eq. (4)].[11] In addition, we also discovered that a minor modification in the ligand structure (**12b**), with the use of $-OCH_2Ph$ instead of $-OMe$, improved the *ee* for MVN to 80% when the reaction was carried out at $-70\,^{\circ}C$. 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 ethyl group (**12c**) in place of the methoxy group are only 13% and 3% *ee*, respectively. Further support for the hemilabile coordination comes from the different reactivities of the two diastereomers of ligands **13a** and **13b**. The former gave a nearly quantitative yield (>99%) of the product in 71% *ee*, whereas the latter gave 79% yield and 65% *ee* under otherwise identical conditions. Substitution at the 2′-position with coordinating groups such as acetoxy (**12d**) and diphenylphosphenoxy (**12e**) also totally inhibit the reaction at low temperature. Finally the electronic effect of the ligand on the hydrovinylation selectivity was examined with the ligands **12a**, **14a**, and **15a**. Ligand electronic effects appear to have no effect on this reaction;[24] in each case the chemical yield and *ee* were almost identical (94 ± 2% and 63 ± 1%, respectively).

Since the original discovery of the importance of the hemilabile ligand for high enantioselectivity, we have recognized that such effects are equally important in a number of other monophosphines that promote the hydrovinylation reaction.[25] An example is shown in Scheme 3.



Scheme 3. Effect of hemilabile ligation in asymmetric hydrovinylation.

Intramolecular reactions: Synthesis of carbocyclic and heterocyclic compounds: The dimerization reaction can be applied for the synthesis of cyclic compounds if the reaction is carried out in an intramolecular fashion. In this context, the Pd-catalyzed cyclization of eneynes, which in principle could involve a $[L_nPd–H]^+$ intermediate, is a well-known reaction.[26] However, relatively little attention has been paid to the corresponding cyclization of α,ω-dienes with late transition metal catalysts.[27] Except for a few isolated reports,[28] Pd- and Ni-catalyzed reactions have not been explored for the synthesis of carbocyclic compounds until recently. An early example is shown in Equation (5).[28d] We find that the conditions developed for the hydrovinylation of vinylarenes can be applied for the efficient cyclization of α,ω dienes [Eq. (6) and (7)].[29] The availability of starting materials and the diminished Lewis acidity of these metals (vis-à-vis early transition metals[27]) should make this process especially attractive for substrates that contain heteroatoms. As illustrated in Equations (8) and (9), with unsymmetrical dienes there is also the possibility of very good regiochemical control. Enantioselective synthesis of alkylidenecyclopentanes is currently under investigation in our laboratories.



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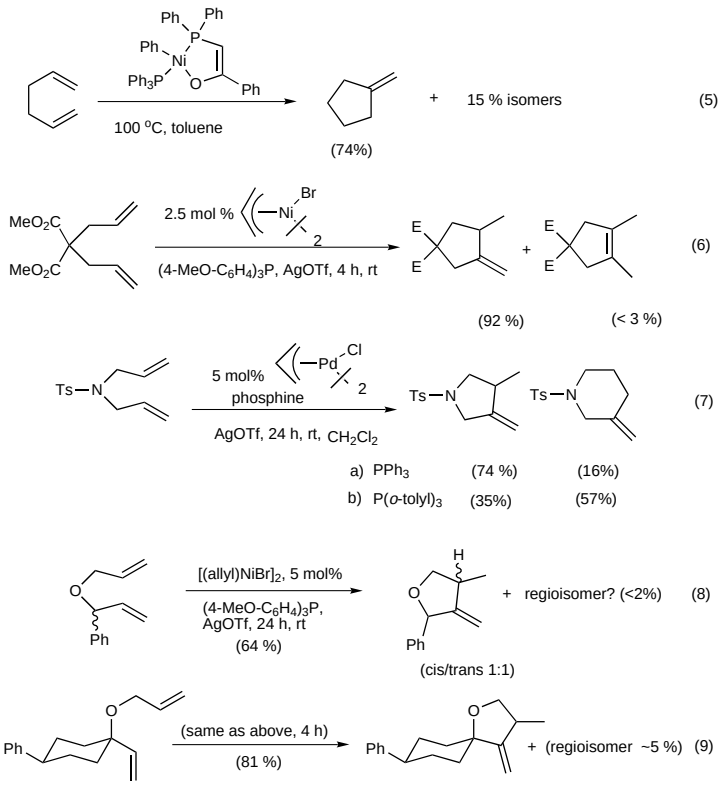

Future Prospects

The heterodimerization reaction of olefins appears to have great potential as a carbon–carbon bond-forming reaction. Anecdotal evidence from the literature and our own recent results suggest that various combinations of ethylene and propylene with vinylarenes, strained olefins, and α,β-unsaturated carbonyl compounds[8c, 30] are suitable starting materials for this reaction. The reaction is highly catalytic with respect to the metal and proceeds under conditions that are remarkably tolerant of a wide spectrum of common functional groups. Exceptional control of chemo- and stereoselectivity based on the properties of the coordinated ligand has been demonstrated. The results of these studies could be further exploited with a number of widely different, tunable ligand systems that have been discovered recently. With the on-going synthetic and mechanistic studies in several laboratories, we anticipate the scope and limitations of both the inter- and intramolecular versions of the reaction to expand considerably in the near future.

Acknowledgment

We acknowledge the financial assistance by the US National Science Foundation (CHE-9706766), US Environmental Protection Agency (R826120-01-0), and the Petroleum Research Fund of the American Chemical Society.

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