

Nickel-catalyzed coupling reactions of alkenes*

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Abstract: Several reactions of simple, unactivated alkenes with electrophiles under Ni(0) catalysis are discussed. The coupling of olefins with aldehydes and silyl triflates provides allylic or homoallylic alcohol derivatives, depending on the supporting ligands and, to a lesser extent, the substrates employed. Reaction of alkenes with isocyanates yields *N*-alkyl acrylamides. In these methods, alkenes act as the functional equivalents of alkenyl- and allylmetal reagents.

Keywords: nickel; alkenes; allenes; alkynes; aldehydes; isocyanates.

INTRODUCTION: FROM ALKYNES TO ALLENES TO ALKENES

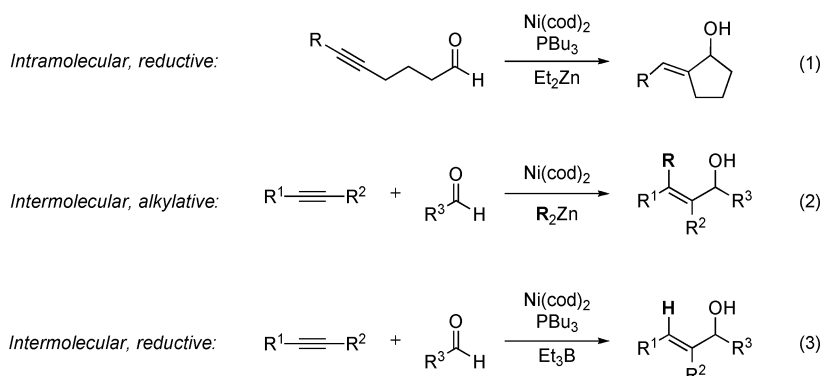
Catalytic reactions that effect selective C–C bond formation allow for the rapid assembly of highly functionalized molecules from simple precursors. Aliphatic terminal alkenes (alpha olefins), industrially produced on a megaton scale each year, are highly desirable precursors for such transformations due to their low cost and functional group compatibility [1]. As part of our program directed toward developing C–C bond-forming reactions of simple, ideally commercial, starting materials, we became very interested in transition-metal-catalyzed alkene–aldehyde coupling processes. For these hypothesized methodologies to come to fruition, however, we were required to build on lessons learned from the development of coupling reactions of alkynes and allenes in our laboratory and others.

The Ni-catalyzed coupling of alkynes and aldehydes to form allylic alcohols was first described in 1997 by Montgomery (Scheme 1, eqs. 1–2) [2]. In the presence of a phosphine ligand and diethyl zinc, alkynals underwent reductive cyclization. In the absence of ligand, alkylative cyclization occurred, with a carbon substituent installed from the organozinc reagent. At the same time, Montgomery reported a three-component alkylative coupling of alkyne, aldehyde, and organozinc; however, intermolecular reductive coupling was not observed, even in the presence of phosphine.

In 2000, our laboratory reported the first catalytic method for intermolecular reductive coupling of alkynes and aldehydes, utilizing a Ni(0) catalyst, tributylphosphine, and triethylborane as the stoichiometric reducing agent (Scheme 1, eq. 3) [3]. Di- or trisubstituted allylic alcohols can be obtained with high regioselectivity from terminal or internal alkynes, respectively, and aromatic or aliphatic aldehydes.

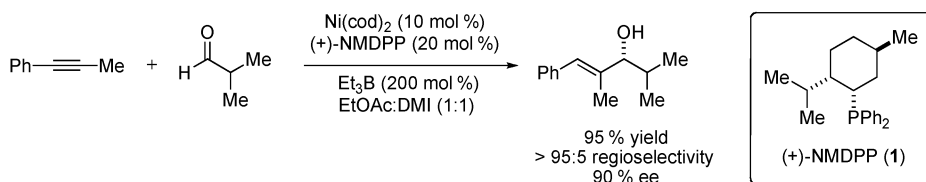
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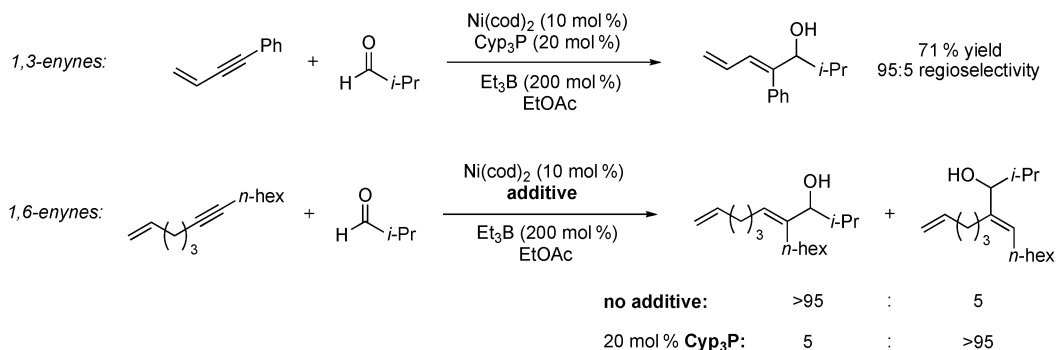
Scheme 1 Alkyne–aldehyde reductive couplings.

An enantioselective variant of this reaction using the chiral monophosphine ligand neomenthylidiphenylphosphine (NMDPP, **1**) emerged from our laboratory in 2003 (Scheme 2) [4]. In conjunction with ozonolysis, the alkyne–aldehyde reductive coupling is also useful in the preparation of α -hydroxyketones in high enantiopurity (up to 96 % ee). Recently, Montgomery has successfully applied a chiral *N*-heterocyclic carbene (NHC) ligand to the Ni(0)-catalyzed coupling of alkynes, aldehydes, and triethylsilane to give silyl-protected allylic alcohols (up to 85 % ee) [5].



Scheme 2 Enantioselective, Ni(0)-catalyzed reductive coupling of alkynes and aldehydes.

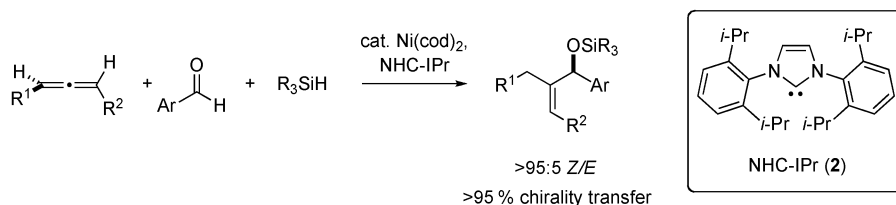
In the course of these investigations of alkynes, it was found that 1,3- and 1,6-enynes reacted with very high degrees of regioselectivity, the result of an alkene directing effect (Scheme 3) [6]. Intriguingly, in the case of 1,6-enynes, not only does the tethered alkene lead to a high degree of regioselectivity, but the sense of regioselectivity can also be switched by the presence (or absence) of a catalytic amount of a phosphine ligand.



Scheme 3 Regioselectivity in the reductive coupling of enynes and aldehydes.

In addition to their reactions with aldehydes, alkynes were shown to undergo catalytic reductive coupling reactions with epoxides [7] and imines [8]. These and other studies on the Ni(0)-catalyzed coupling reactions of alkynes have been further detailed in several recent reviews [9].

Like alkynes, allenes contain a carbon with sp -hybridization. However, until 2005, transition-metal-mediated multicomponent coupling reactions of unactivated allenes with aldehydes were known to occur only at the sp^2 -hybridized carbons, affording homoallylic alcohols [10]. We then reported a rare example of intermolecular addition of an electrophile to the central, sp -hybridized, and ostensibly least nucleophilic carbon of an unactivated allene (Scheme 4) [11]. Not only did this reaction afford *Z*-allylic alcohol derivatives with high regioselectivity, it also allowed for the preparation of highly enantioenriched products via efficient chirality transfer from axially chiral allenes. A key finding in this work was the superiority of silanes to triethylborane and other Lewis acidic reducing agents.



Scheme 4 Enantioselective and regioselective Ni-catalyzed coupling of allenes, aldehydes, and silanes.

Conceptually, we reasoned, the reductive coupling reactions we had developed of alkynes and allenes with aldehydes could be replaced with *non-reductive* coupling between an alkene and aldehyde. This had potential to eliminate compatibility issues introduced by sometimes-harsh reducing agents. Not only are numerous olefins commercially available, synthetic methods abound for their preparation. However, we had already incorporated alkene units into intermolecular reductive coupling reactions: 1,3- and 1,6-enynes underwent reductive coupling at the alkyne only. Could we find another way to access what seemed to be the lower intrinsic reactivity of alkenes?

NICKEL-CATALYZED COUPLING REACTIONS OF ALKENES

When we began our work with alkenes, several intramolecular alkene–aldehyde coupling processes had been reported, including the titanium-catalyzed reductive cyclization of enals and enones [12]. Ogoshi described a Ni-promoted reductive cyclization of enals, but this process was stoichiometric in Ni [13]. Later on, several examples of catalytic, intramolecular alkene–ketone coupling reactions were reported [14]. Despite this progress, transition-metal-catalyzed *intermolecular* reactions (reductive or otherwise) of this type remained elusive.

Historically, the most direct method for intermolecular coupling of unactivated alkenes and aldehydes to form homoallylic alcohol products is the carbonyl-ene reaction [15]. Typically, the alkenes employed in intermolecular carbonyl-ene reactions are 1,1-disubstituted and trisubstituted olefins. Electron-deficient enophiles such as glyoxylates are generally more efficient than simple aromatic or aliphatic aldehydes. Consequently, we wished to develop a reaction with features not amenable to existing carbonyl-ene methodology: first, the ability to transform less activated alkenes; second, enhanced and complementary electrophile scope; and third, the option to produce allylic alcohols in addition to homoallylic products.

Intermolecular coupling of alkenes, aldehydes, and silyl triflates

Pivotal to our work was Ogoshi's observation that a Lewis acid, such as a silyl triflate, facilitated the formation of an oxanickellacycle through cyclization of an α,ω -enal [13]. We proposed that if the intermolecular coupling of an alkene and aldehyde occurred, the Ni–alkyl bond could undergo a β -hydride elimination, followed by the removal of triflic acid from Ni to regenerate the Ni catalyst.

Our investigations began with the simplest alkene, ethylene, and benzaldehyde. After examining a variety of phosphorous-based ligands, we found that we were able to achieve catalysis of intermolecular alkene–aldehyde coupling when Ni(cod)₂, tris-(*o*-methoxyphenyl)-phosphine [(*o*-anisyl)₃P], triethylamine, and triethylsilyl triflate (Et₃SiOTf) were used [16,17].

Under 1 atm of ethylene, a variety of aromatic aldehydes undergo efficient coupling to yield the silyl ether of an allylic alcohol (Table 1). Different phosphines, such as dicyclohexylphenylphosphine and triphenylphosphine, give lower yields under the same reaction conditions. Other common silyl triflates can be used in the coupling reaction, providing orthogonal protection of the hydroxyl group when necessary (**3f**, **3g**).

Table 1 Ni-catalyzed coupling of ethylene, aldehydes, and silyl triflates.

$\text{H}_2\text{C}=\text{CH}_2 + \text{R}-\text{CHO} \xrightarrow[\text{Et}_3\text{N, Toluene, rt}]{\text{Ni(cod)}_2, \text{Ligand, R}_3\text{SiOTf}} \text{R}-\text{CH}(\text{OSiEt}_3)-\text{CH}=\text{CH}_2$									
entry	R (aldehyde)	R ₃ SiOTf	product	isolated yield (%)	entry	R (aldehyde)	R ₃ SiOTf	product	isolated yield (%)
1	Ph	Et ₃ SiOTf	3a	82 (65) ^b	8		Et ₃ SiOTf	3h	80
2	<i>p</i> -tolyl	Et ₃ SiOTf	3b	88 (65) ^b	9	2-furyl	Et ₃ SiOTf	3i	38
3	<i>o</i> -tolyl	Et ₃ SiOTf	3c	93 (64) ^b	10 ^f		Et ₃ SiOTf	3j	25
4	<i>p</i> -anisyl	Et ₃ SiOTf	3d	95 (65) ^c	11 ^f		Et ₃ SiOTf	3k	34
5	2-naphthyl	Et ₃ SiOTf	3e	95 (83) ^b	12	piv	Et ₃ SiOTf	3l	70
6	2-naphthyl	Me ₃ SiOTf	3f	60	13		Et ₃ SiOTf	3m	81 (40) ^{c, d}
7	2-naphthyl	<i>t</i> -BuMe ₂ SiOTf	3g	67	14	cyclohexyl	Et ₃ SiOTf	3n	25 ^d (34) ^{d, e}

^aStandard procedure: Ni(cod)₂ (20 mol %) and (*o*-anisyl)₃P (40 mol %) were dissolved in 2.5 mL toluene under argon. Ethylene (balloon, 1 atm) was substituted for argon. Triethylamine (600 mol %), the aldehyde (100 mol %, 0.5 mmol), and silyl triflate (175 mol %) were added. The reaction was stirred for 6–18 h at 23 °C.

^b(*o*-anisyl)₃P was replaced by Cy₂PhP.

^c(*o*-anisyl)₃P was replaced by Ph₃P.

^dYield determined by ¹H NMR using DMF as a standard.

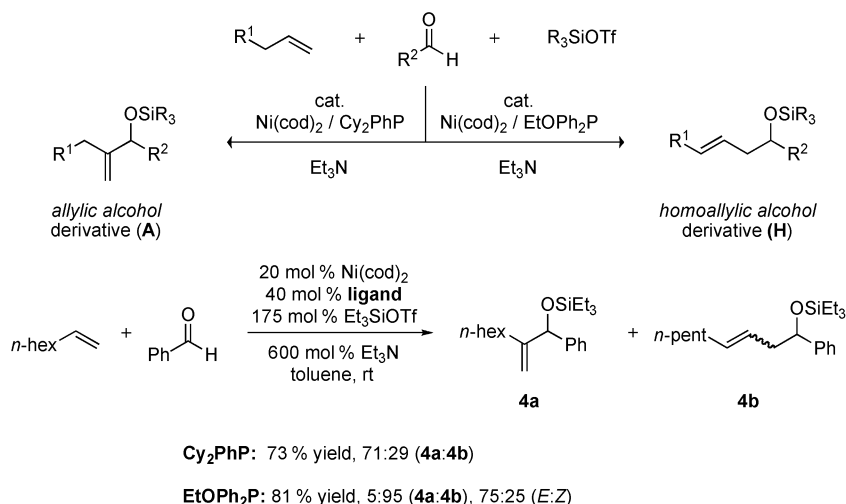
^eConducted under 2 atm of ethylene.

^fStirred at room temperature for 30 h.

Notably, sterically encumbered tertiary aliphatic aldehydes such as pivaldehydes (**3l**) and 2,2-dimethyl-3-oxo-propionic acid methyl ester (**3m**) couple with ethylene in good yield. Several hetero-aromatic aldehydes (**3h**, **3i**) are also tolerated, even in the presence of electrophilic silyl triflates. A competing (but unsurprising) side reaction occurs in coupling reactions with enolizable aldehydes, which react rapidly with the silyl triflate and triethylamine to form alkenyl silyl ethers. The coupling of ethylene with cyclohexanecarboxaldehyde (**3n**) is fast enough, however, that a significant amount of coupling product is observed and can be isolated.

Electron-rich aromatic aldehydes are more efficient substrates than their electron-poor counterparts. Aldehydes with electron-donating *para*-substituents (Me and OMe) react in some of the highest yields observed for the coupling reaction. Electron-withdrawing *para*-substituents (CF₃, CO₂Me) suffer from incomplete conversion, even after extended reaction time. In these and only these cases, side products resulting from a pinacol coupling are observed.

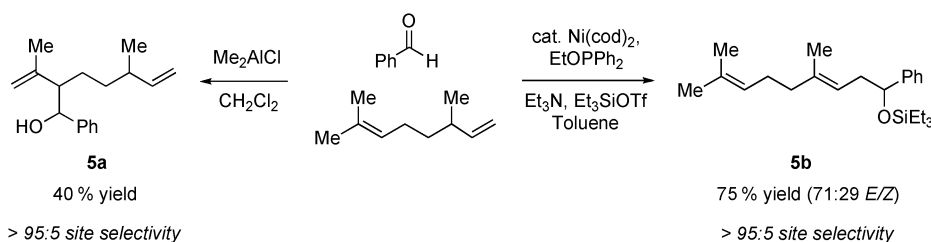
The encouraging results obtained with ethylene prompted us to examine the scope of the reaction with respect to other alkenes. Alpha olefins such as 1-octene can afford more than one possible product depending on where the new C–C bond is formed. Two distinct types of coupling product are typically observed: a 1,1-disubstituted allylic alcohol product (**A**) and a homoallylic alcohol product (**H**). By varying the phosphine ligand, one coupling product may be favored over the other (Scheme 5).



Scheme 5 Ni-catalyzed coupling of alpha olefins, aldehydes, and silyl triflates leads to two types of product.

The ratio of coupling products appears to be determined by a combined effect of the electron-donating ability and the cone angle of the phosphine ligands. Excellent H:A selectivity (95:5) can be achieved by using a less electron-rich phosphine with small cone angle, such as (EtO)Ph₂P [18]. Modest selectivity favoring the A product can be obtained by using an electron-rich phosphine with a large cone angle, such as Cy₂PhP. The nature of the alkene may play a role as well, as bulkier alkene substituents appear to increase the H:A ratio.

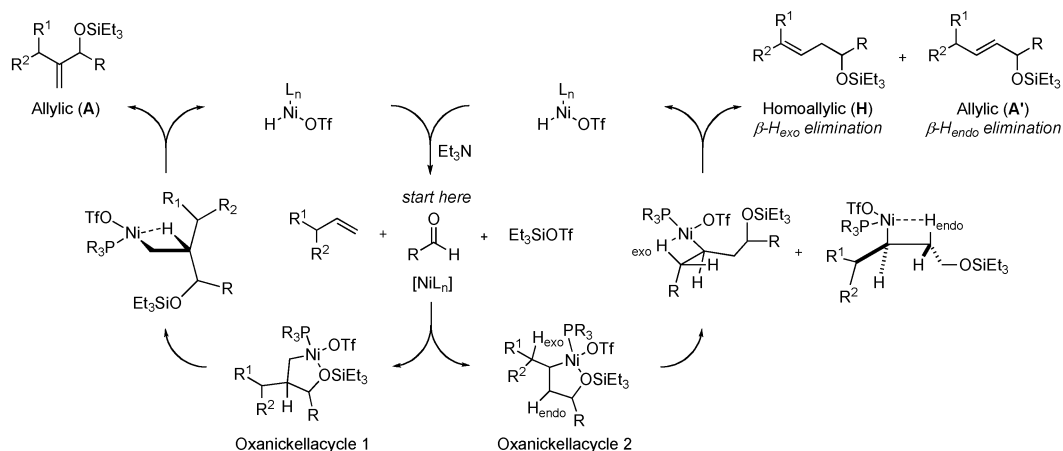
While the reaction conditions favoring the homoallylic product amount to a carbonyl-ene-type process, we do not believe that a Lewis acid-catalyzed carbonyl-ene reaction mechanism is operating here. In the coupling of β-citronellene and benzaldehyde, the Ni(0)-phosphine system selectively reacts with the monosubstituted olefin, whereas a classical Lewis acid reacts at the more nucleophilic trisubstituted double bond (Scheme 6). Further supporting the idea that the Ni-catalyzed coupling of alkenes, aldehydes, and silyl triflates does not involve a carbonyl-ene reaction mechanism is the obser-



Scheme 6 Coupling of β -citronellene and benzaldehyde reveals a distinct reactivity pattern in the Ni-catalyzed reaction relative to a traditional Lewis acid-catalyzed carbonyl-ene reaction.

vation that ethylene, with no allylic hydrogen, also participates in this coupling reaction using the same Ni(0)-phosphine catalyst.

Instead, we propose that the alkene–aldehyde coupling commences with the formation of an oxanickellacycle from a Ni(0) complex (Scheme 7). The regioselectivity of oxanickellacycle assembly determines the product distribution (H:A ratio). A syn β -hydride elimination would afford the coupling product and a Ni–hydride species, analogous to a Heck reaction [19]. Base-promoted reductive elimination of the Ni–hydride intermediate could regenerate the Ni(0) catalyst. A base-mediated β -elimination of the oxanickellacycle via an E2-like mechanism cannot be completely ruled out. However, we believe that the observation of isomerization and dimerization (hydrovinylation) of the starting olefins suggests the presence of a Ni–hydride species, likely formed by a β -hydride elimination.



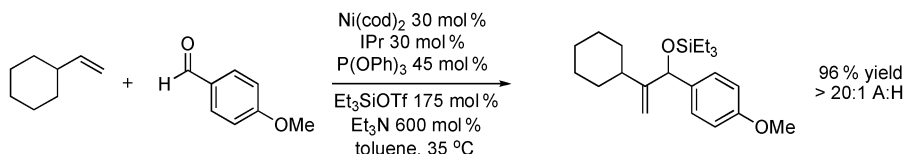
Scheme 7 Proposed mechanism for Ni-catalyzed coupling of alkenes, aldehydes, and silyl triflate.

While we had attained greater than 95:5 H:A selectivity in the alkene–aldehyde coupling, a general method for high A:H selectivity remained elusive. However, we recently were able to remedy that deficiency by exploiting a synergistic relationship between a strong σ donor and a strong π acceptor [20]. In preliminary investigations of NHC ligands in these transformations, we found that IPr (**2**) was highly selective for the allylic product, even when a branched alkene was used. However, the reaction did not appear to proceed catalytically. Additionally, side products resulting from hydrosilylation of the aldehyde (reduction) and hydrovinylation were formed in significant quantities [21].

We suspected that both the formation of side products and lack of catalysis might be caused by the fact that the electron-rich ligand retards formal reductive elimination of triflic acid to regenerate a Ni(0) species. Stalling the catalytic cycle results in accumulation of a [Ni(NHC)H](OTf) species, which

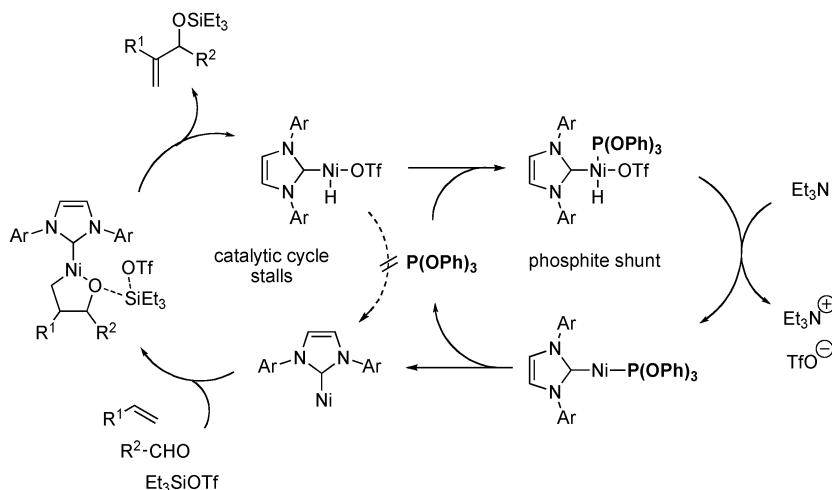
is responsible for the side reactions. We examined a variety of additives reported to accelerate reductive elimination or stabilize Ni catalysts, including electron-poor olefins [22] and electron-withdrawing phosphines [23]. These provided slight catalytic activity, but had significant flaws in terms of competing reaction of added alkene or erosion of the A:H ratio with electron-poor phosphines. However, very electron-deficient phosphite ligands proved to be highly effective additives.

Triphenylphosphite in particular not only rendered the reaction catalytic, but also suppressed formation of the homoallylic product and dramatically reduced hydrosilylation and hydrovinylation (Scheme 8). Both IPr and $(\text{PhO})_3\text{P}$ were necessary for catalysis: when IPr is absent, no product is observed; when phosphine is absent, no turnover is observed. Unlike other phosphorus-based additives, $(\text{PhO})_3\text{P}$ did not diminish the A:H selectivity, perhaps because it cannot promote the reaction on its own. Remarkably, donor (IPr) and acceptor (phosphite) do not interfere with each other.



Scheme 8 High selectivity for the allylic product in dual IPr/ $(\text{PhO})_3\text{P}$ system.

This dual NHC/phosphite system resulted in an impressive A:H selectivity of greater than 20:1 in all cases examined. Additionally, more alkene substrates were suitable, including styrenes and relatively encumbered α -branched alkenes. Both the selectivity and the broader substrate scope may be related to the sterically demanding and highly σ -donating nature of IPr. The ligand orients the alkene substituents away from the Ni center, and also is expected to accelerate the oxidative coupling. We propose that the phosphite additive promotes reductive elimination by reducing the electron density at a coordinatively unsaturated Ni center, rescuing the catalytic cycle by a shunt mechanism (Scheme 9).



Scheme 9 Proposed mechanism for coupling of alkenes and aldehydes catalyzed by $[\text{Ni(IPr)\{P(OPh)}_3}]$.

Unlike the related transition-metal-catalyzed reductive coupling reactions developed by our group and others, the Ni-catalyzed coupling of alkenes, aldehydes, and silyl triflates in its various forms is not an overall reductive process. In theory, the coupling of alkene and aldehyde does not necessitate a third

component to form the allylic or homoallylic alcohol derivatives. However, both alkenes and aldehydes are generally unreactive toward each other, meaning that activation of one or both of the components is necessary. The Lewis acidic nature of silyl triflate apparently provides sufficient activation of the electrophile for the Ni catalyst to promote the coupling reaction.

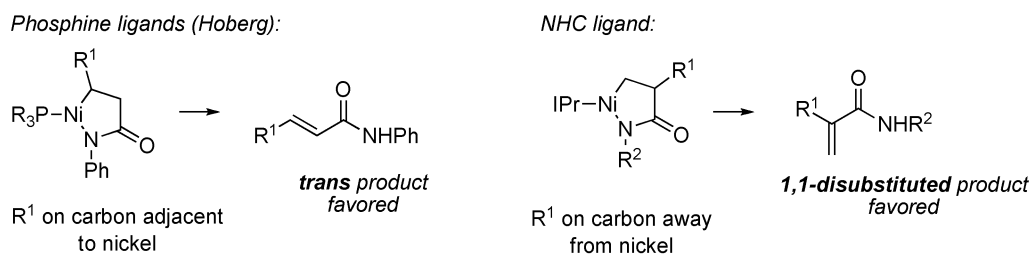
The Ni-catalyzed reaction we have described offers an alternative to both alkenylmetal reagents [when Cy_2PhP or $\text{IPr}/(\text{PhO})_3\text{P}$ are used] or allylmetal reagents [when $(\text{EtO})\text{Ph}_2\text{P}$ is used]. The substitution of alkenes for these organometallic species should offer considerable advantages in ease of preparation and functional group compatibility.

Intermolecular coupling of alkenes and isocyanates

Following our initial work with aldehydes, we became interested in expanding the scope of electrophiles with which simple alkenes could be coupled. Our attention was drawn to pioneering studies by Hoberg, who reported the stoichiometric and catalytic coupling reactions of phenyl isocyanate and ethylene on Ni(0) with trialkyl phosphine ligands, yielding *N*-phenylacrylamide [24–25]. A variety of other olefins, both activated and unactivated, have been reported to react with phenyl isocyanate with Ni(0) and phosphine ligands; the major product is the *trans*-disubstituted α,β -unsaturated amide [26]. Only in two cases is a 1,1-disubstituted acrylamide observed (as a minor product, in 3 and 13 % yield).

Hoberg proposed that the reaction proceeds via an azanickelacyclopentanone intermediate, which then undergoes β -hydrogen elimination. Presumably, in order to obtain 1,2-disubstituted α,β -unsaturated amides, the alkene substituent would be on the carbon adjacent to Ni in the relevant nickellacycle. We felt that, as in the coupling of alkenes with aldehydes, a bulky NHC ligand might result in the formation of the alternative nickellacycle, in which the olefin substituent is pointed away from the metal center.

Indeed, in the presence of catalytic Ni(0) and the NHC ligand IPr, C–C bond formation was observed to form selectively at the 2-position of the olefin, yielding *N*-alkylated acrylamides [27]. The NHC ligand gives products with the opposite sense of regioselectivity compared to those obtained when phosphine ligands are used (Scheme 10). We found that excellent conversion could be obtained upon heating. The scope of the reaction appears to be limited to bulky, electron-rich alkyl isocyanates; a common side reaction is oligomerization of the isocyanate, which may be catalyzed by free NHC ligands in solution [28].



Scheme 10 Proposed regioselectivity of nickellacycle formation in the catalytic coupling reaction of alkenes and isocyanates.

While unbranched α -olefins have a fairly modest preference for carboxamidation at the 2-position of the olefin, alkenes with branching at the allylic or homoallylic position proceed with very good selectivity (Table 2). A third, homoallylic product is formed from allylbenzene in which the double bond has moved into conjugation with the aromatic ring, but this is not observed in other cases. Again, the reaction appears to be selective for monosubstituted olefins. Low conversion is observed in the cases

of 1,1-disubstituted, *cis*-, and *trans*-olefins. Esters and silyl-protected alcohols, and in some cases even ketones, are tolerated under the reaction conditions.

Table 2 Scope and selectivity in Ni-catalyzed coupling of alkenes and isocyanates.

entry ^a	R ₁	R ₂	R ₃	product(s)	yield a ; b ; c (%) ^b
1	<i>n</i> -hexyl	Cy	-	6a , 6b	79; 14; 0
2	<i>n</i> -hexyl	<i>t</i> -Bu	-	7a , 7b	74; 17; 0
3		<i>t</i> -Bu	-	8a	91; 0; 0
4 ^c		Cy	-	9a , 9b	74; 5; 0
5 ^c	PhCH ₂	Cy	Ph	10a , 10b , 10c	65; 8; 22
6 ^c	PhCH ₂	<i>t</i> -Bu	Ph	11a , 11b , 11c	83; 1 ^d ; 5 ^d
7 ^c		Cy	-	12a	86; 0; 0
8		Cy	-	13a , 13b	74; 13; 0
9		<i>t</i> -Bu	-	14a , 14b	70; 2; 0
10		<i>t</i> -Bu	-	15a , 15b	65; 9; 0

^aStandard conditions: Reactions were run with 0.5 mmol of 1-octene, 1.0 mmol of isocyanate, 0.05 mmol of Ni(cod)₂, and 0.05 mmol of IPr in 0.5 mL toluene under Ar(g) in a sealed tube at 60 °C for 18–24 h.

^bIsolated yields.

^cReaction was run using 2 mL of toluene.

^dIsolated as a mixture of **10b** and **10c**, with relative ratios determined by ¹H NMR.

The alkene–isocyanate coupling is unique among the systems we have examined thus far in that it does not require a third component to proceed. However, as in our work with aldehydes, what are ostensibly the least activated alkenes react. The NHC ligand seems to play an important role in favoring reaction at the more substituted position of the alkene. In this reaction, we again can utilize a simple alkene as the functional equivalent of a 2-alkenylmetal reagent.

CONCLUSIONS

We have described several new reactions of simple alkenes catalyzed by Ni(0). An NHC ligand allows us for the first time to selectively produce 1,1-disubstituted acrylamides in the coupling of alkenes and isocyanates. In the intermolecular reaction of alkenes, aldehydes, and silyl triflates, we have the ability to produce either allylic or homoallylic alcohol derivatives with excellent selectivity by judicious choice of supporting ligands. We have studied the attributes of ligand and substrate that tend to favor one product over the other, and we have documented a notable case of synergy between two distinct ligand types. In these reactions, simple alkenes are conceptual, and indeed practical, surrogates for alkenyl- and allyl-metal reagents.

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