Olefination

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Catalytic Intermolecular Tail-to-Tail Hydroalkenylation of Styrenes with α Olefins: Regioselective Migratory Insertion Controlled by a Nickel/N-Heterocyclic Carbene**

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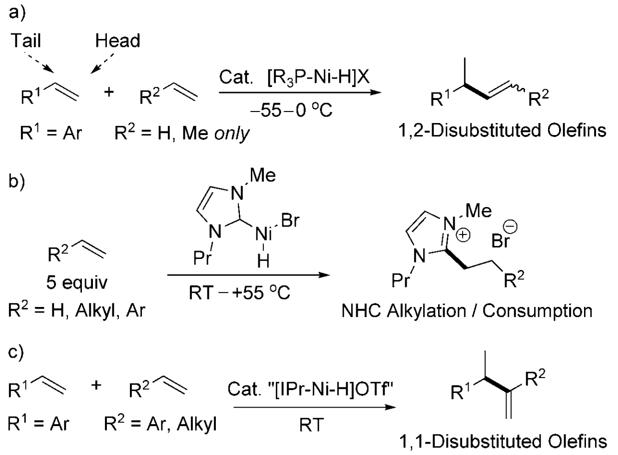
New syntheses of alkenes are important in organic chemistry. Particularly attractive are those methods that use a chemical feedstock such as ethylene, α-olefins, and styrenes as one of the components.[1] Major advances in this area include catalytic olefin cross-metathesis and hydrovinylation, which join two different alkenes together to provide internal olefins and α olefins, respectively.[2–4] Although more functionalized conjugate carbonyls and dienes are used as one of the partners,[5,6] the direct addition of monoenes to these systems is also an important advance in the field.[7,8] Recently, some of these alkene coupling technologies have been developed to achieve the asymmetric synthesis of biologically important molecules, with ibuprofen being a representative example.[6e,9] Nevertheless, all of the above methods are either characterized by head-to-head (h-h) or tail-to-head (t-h) C–C bond formation or use ethylene as one of the components; tail-to-tail (t-t) hetero-hydroalkenylation should provide branched terminal 1,1-disubstituted alkenes, but such products are observed only in small amounts, or in intramolecular cases wherein the geometric constraints of ring closure play a substantial role. Also, although phosphorus-based nickel(II) hydride complexes (Scheme 1 a) have been shown to achieve good selectivity and turnover numbers by exploiting various monodentate P ligands, hemilabile ligands, and counter ions,[10] successful cases of using long-chain α olefins as intermolecular hetero-hydroalkenylation substrates are not reported; as such substrates only isomerize into internal olefins.[3g,11] N-heterocyclic carbene (NHC) nickel(II) hydride complexes ({(NHC)NiH}) have been rarely studied for this purpose, possibly because alkyl reductive elimination of NHCs can be a very effective process (Scheme 1 b), wherein the alkene hydrometalation is the first step, similar to that of a typical {PNiH}-catalyzed (P = P ligand) hydrovinylation. We surmised that {(NHC)NiH}-catalyzed hetero-hydroalkenylation may be possible by using NHCs having different structural characteristics relative to those that undergo reductive eliminations under optimized reaction conditions.[12] The change in the regioselective outcome of the nickel(0)-catalyzed silyltriflate/alkene/aldehyde coupling that resulted from replacement of the P ligand with NHC encouraged us to test {(NHC)NiH} for t-t hydroalkenylation.[13,14]



Scheme 1. Distinct ligand effect upon nickel hydride mediated hydroalkenylation. a) $[(R_3P)NiH]X$-catalyzed t-h hydroalkenylation. If R^2 is a long-chain alkyl group isomerized starting material is observed. X = OTf or halide. b) {(NHC)NiH}-catalyzed reaction lead to NHC-alkyl reductive elimination. c) [(IPr)NiH]OTf-catalyzed t-t hydroalkenylation described herein. Tf = trifluoromethanesulfonyl.

Herein we describe the first highly selective intermolecular t-t hetero-hydroalkenylation of several types of vinylarenes with unactivated α olefins to selectively yield branched 1,1-disubstituted alkenes with limited isomerization, which is in contrast to the observations from previous work (Scheme 1 c). This reaction is also the first NiH-catalyzed hydroalkenylation that is not constrained to the use of ethylene/propene[3g] as one of the reaction partners for the styrene substrates; the more-common and structurally diverse α olefins that were unable to undergo the hydroalkenylation with vinylarenes under previous reaction conditions,[3] are now viable substrates for providing a variety of alkenes directly from a chemical feedstock in a single operation.[15] The closest precedent to the transformation that we report herein appears to be the cobalt-catalyzed 1,4-hydrovinylation and nickel-catalyzed conjugate addition using α olefins and P ligands reported by Hilt et al. and Jamison and co-workers, repectively; both methods yielded 1,1-disubstituted olefins in very high selectivity.[5a,6a,b] An oxidative cyclization-like strategy involving a metallacycle was proposed to account for the h-t regioselectivity achieved within those systems, yielding vari-

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ous linear heterocoupling products, which are in contrast to the t-t branched products described below that are obtained from migratory insertion reactions controlled by NHC.

Initally, 1-octene and styrene were selected as substrates and reacted in the presence of a catalytic amount of in situ generated [(IPr)NiH]OTf (IPr = 1,3-bis(2,6-di-isopropylphenyl) imidazol-2-ylidene), which was obtained by modifying a procedure reported by Jamison and co-workers (that is, [(IPr)NiP(OPh)$_3$]-mediated silyltrilflate/alkene/aldehyde coupling via an oxanickellacycle intermediate with P(OPh)$_3$ removed), in toluene.[13a] The same catalyst can apparently be generated from combining IPr and [{(allyl)NiBr}$_2$], the product of which undergoes anion exchange in a manner analogous to the {PNiH} catalyst generation protocol.[16] The Jamison procedure was chosen because of its technical simplicity (RT generation from a commercial source, no precatalyst preparation) and because it avoided the use of the coordinating halide anion, which may have an adverse effect on catalytic activity.[10,13a]

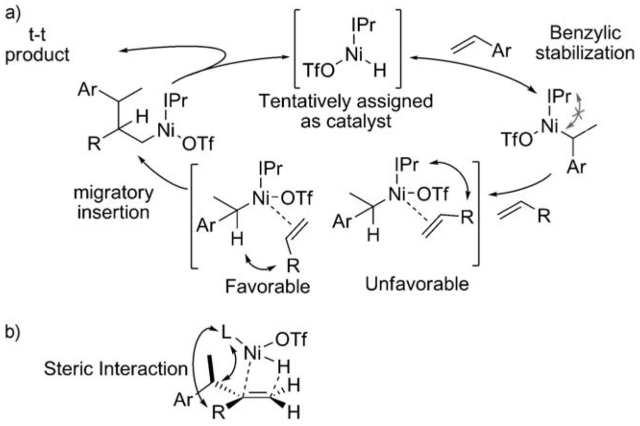
Although these modifications are simple, we found that unconventional t-t hetero-hydroalkenylation of styrene and 1-octene can be achieved at room temperature and under atmospheric pressure (Table 1, entry 1). Commonly employed alkyl aluminum halide additives or co-catalysts used in related systems were found to be unnecessary. A minor product observed for the reaction reported herein is the homo t-t 1,1-disubstituted alkene product from the styrene. Other reported systems for styrene dimerization generally favor either the t-h or h-h product as well as polymerization.[5c,17] The use of a slightly smaller IMes (IMes = 1,3-di(2,4,6-trimethyl-pheny-l)imidazolin-2-ylidene) ligand also gave the hetero product, but a fall in the hetero/homo selectivity was observed (90 %, 80:20). Ethereal solvents such as THF can also be used in this reaction, giving similar yield and selectivity (96 %, 88:12). In light of these interesting observations, we decided to study the scope of the reaction. We found that scaling up the reactions did not diminish the high yield, and that the t-t product was generally observed in all cases examined. The systems tolerate electron-rich and electron-deficient styrenes bearing substituents such as alkyl and ether groups, as well as OAc and F (entries 2–5, 13–16). Relatively labile functionalities, such as AcO and benzylic chloride, remain intact under the standard conditions (entries 4, 6, 15). 2-Vinylnaphthalene was also found to be a possible substrate (entry 7). In addition to straight-chain 1-octene and α/β-branched α olefins, substrates with a high tendency to yield stable conjugate alkenes by isomerization also underwent reaction to give the corresponding products in good yield and selectivity (entries 8–11).

A possible rationale for the formation of a product with a high t-t selectivity and scope for new substrates is depicted in Scheme 2. This proposal is largely based on the results from the most well-studied styrene–ethylene hydrovinylation using P-based NiH catalysts[3] and the results obtained herein. The [(IPr)NiH]OTf that was presumably generated in situ could preferentially add to the vinylarene to form an electronically more stable benzylic nickel complex in a fashion similar to that of the typical {PNiH}-catalyzed vinylarene hydrovinylation. It is thought that the less sterically demanding α olefin preferentially coordinated to the metal center in a way that minimized the steric repulsion with the ligand. A selective migratory insertion then occurred forming a new C–C bond between the two of the reacting alkenes, thus providing the high hetero/homo and t-t/t-h selectivity observed. Finally, a formal *syn*-β-hydride elimination step regenerates the catalyst.

Table 1: Scope of catalytic t-t hydroalkenylation.

Entry[a]	R^1	R^2	Yield [%][b]	Hetero/Homo Product
Hetero-hydroalkenylation				
1	Ph	*n*-hexyl	82[c]	64:36
	Ph	*n*-hexyl	95	90:10
	Ph	*n*-hexyl	80[d]	47:53
	Ph	*n*-hexyl	91[e]	86:14
2	*p*-MeC$_6$H$_4$	*n*-hexyl	93	86:14
3	*p*-OMeC$_6$H$_4$	*n*-hexyl	90	88:12
4	*p*-OAcC$_6$H$_4$	*n*-hexyl	92	89:11
5	*p*-FC$_6$H$_4$	*n*-hexyl	92	84:16
6	*p*-CH$_2$Cl(C$_6$H$_4$)	*n*-hexyl	37[f,g]	90:10
7	2-Napthyl	*n*-hexyl	68[g]	94:6
8	Ph	cyclohexyl	72	53:47
	Ph	cyclohexyl	70[g,h]	69:31
9	Ph	*i*Bu	90	87:13
10	Ph	CH$_2$Ph	81	87:13
11	Ph	(CH$_2$)$_2$Ph	92	95:5
Homo-hydroalkenylation				
12	Ph	–	90	–
13	*p*-MeC$_6$H$_4$	–	95	–
14	*p*-OMeC$_6$H$_4$	–	94	–
15	*p*-OAcC$_6$H$_4$	–	45[g]	–
16	*p*-FC$_6$H$_4$	–	35	–

[a] See Scheme 1 c and the Experimental Section for procedures. Reaction conditions: "[(IPr)NiH]OTf" (5 mol %); for hetero-hydroalkenylation vinylarene/α olefin = 1:3, and 2 mmol vinylarene for homo-hydroalkenylation; toluene (2 mL). Yield and ratio were determined by GC analysis using C$_6$(CH$_3$)$_6$ as a standard, homo product refers to vinylarene t-t dimer. A limited amount of other regioisomers and other olefin isomers can be detected by GC analysis; see the Supporting Information. [b] Based on vinylarene, sum of hetero- and homo t-t products. [c,d] Yield based on 1-octene, styrene/1-octene = 1:1 and 3:1, respectively. [e] A 2.5-fold scale. [f] No homo dimer was observed by GC analysis; potentially a result of thermal decomposition. Homo dimer can be observed in the NMR spectra of both the crude reaction mixture and the isolated product. [g] Determined by NMR analysis of the crude reaction mixture. [h] Slow addition of styrene over 5 h at 35 °C.

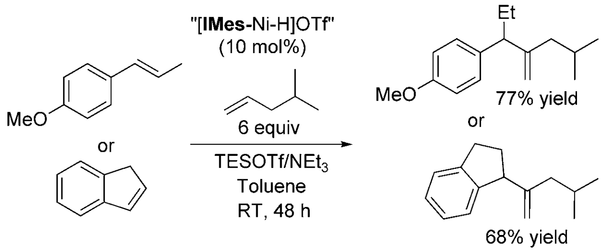


Scheme 2. a) Proposed mechanism. The poor orbital overlap (gray arrow) slows NHC-alkyl reductive elimination. The size of the *n*-nexyl group is less than the Ph group, so hetero-hydroalkenylation is more favorable. b) Alkene stability. When L is larger than a P ligand (e.g., IPr) then isomerization is less likely because the hydrometalation step is more difficult.

The 1,1-disubstituted alkene products obtained are quite reactive towards isomerization to the thermodynamically more stable internal or conjugate olefins. Remarkably, only limited isomerization and no significant product oligomerization were observed. We surmise that the above observations and the successful use of long-chain α olefins can both be explained by the steric effect of the IPr ligand. It should be emphasized that the recent alkene isomerization study using various {PMH} (M = Pd,Ni) complexes by RajanBabu and co-workers inspired us to select a bulky NHC ligand (IPr) to minimize the potential alkene isomerization. The study showed that alkene isomerization (i.e., hydrometalation and β-hydride elimination steps involved) is sensitive to the steric environment of the substrates and the P ligand employed. Certain 1,1-disubstituted olefin isomerizations were found to be difficult even when the sterically less hindered PPh_3 was used under more forcing conditions.[11,13e] In this sense, our products are expected not to isomerize into internal alkenes when using IPr as a ligand.[12d] Similarly, this hypothesis may also account for the success of using long-chain α olefins, which is in contrast to using them with the {PNiH} catalysis.

Notably, removing the P additives (e.g., PPh_3, $P(OPh)_3$) and the careful selection of the NHC are necessary to promote hydroalkenylation over the elimination processes observed by Cavell and co-workers, and Jamison and co-workers, respectively.[12a–c,13a] P ligands were used as accelerators for NHC-alkyl or H-X eliminations from [(NHC)Ni(H or alkyl)]X complexes. Hypothetical criteria for an effective NHC-alkyl elimination have been proposed, and the key step involves orbital mixing between the hydrometallated alkene and the NHC. We selected a bulky IPr ligand and avoided P ligands accordingly, with the intention to hinder the possible orbital mixing step and thus the eliminations; as a result catalytic hydroalkenylation occured. Several additional experiments were carried out to elucidate the factors that may account for the dramatic changes in behavior (e.g., P additives, temperature, and solvent; see the Supporting Information), and the results support our belief that the choice of NHC is most responsible for the observed behaviors, and that the avoidance of PPh_3 helps in terms of hydroalkenylation efficiency. It has also been reported that without $P(OPh)_3$ as an additive, a higher stability of [(IPr)-NiH]OTf towards bases was observed as compared with that of a P analogue. This stability may explain the high functional group compatibility observed herein.[13a–c]

Finally, vinylarenes having additional substituents at the β-position were also found to be good substrates under the optimized reaction conditions (Scheme 3).[3g,18] Initial attempts using IPr were not successful, however, with the operative mechanism in mind, a slightly smaller NHC (IMes) and a sterically more demanding α olefin were tested. This combination leads to a longer life time for the benzylic Ni species and slower isomerization of the α-olefin. Reasonable yields were observed, with ≤ 1 % homo vinylarene dimers, as determined by GC analysis.



Scheme 3. Anethole and indene t-t hetero-hydroalkenylation with an α olefin. TES = triethylsilyl.

In summary, a simple, highly regioselective and catalytic intermolecular t-t hetero-hydroalkenylation of two readily available types of monoene was achieved. The products may be useful for the synthesis of more highly substituted products for metathesis and other conventional olefin functionalization technologies.[19] Notably, the t-t hetero-hydroalkenylation currently works only when vinylarenes are used as one of the components with monoenes, and simple aliphatic internal alkenes are not compatible substrates.[20] The distinct ligand effect observed may also facilitate developments in NiH/alkyl and {(NHC)Ni} chemistry. Our current efforts include investigating other potential substrates, evaluating the identity of the active catalyst, and searching for simpler catalyst generation methods. In gaining some mechanistic insights, a reaction with a higher turnover and better atom efficiency can be developed.

Experimental Section

Catalyst generation: $[Ni(cod)_2]$ and IPr (0.05 mmol, 5 mol% each) were added to an oven-dried test tube equipped with a stir bar in a glove box. After sealing the test tube with a septum, it was removed from the glove box and connected to a N_2 line. The mixture was dissolved in 2 mL of degassed toluene and stirred at RT for 1 h. 1-octene (10 mol%), NEt_3 (0.3 mmol), *para*-anisaldehyde (5 mol%), and TESOTf (10 mol%) were then added sequentially and the resulting reaction mixture was stirred for 15 mins at RT.

Hetero-hydroalkenylation (t-t): The α olefin (3.0 mmol) and vinylarene (1.0 mmol) or amount indicated in Table 1) were added to the above-described mixture at RT. After stirring the reaction mixture for 24 h, the mixture was diluted with 4 mL *n*-hexane, and then stirred for 30 min (open to the air). The reaction mixture was then filtered through a short plug of silica gel and rinsed with 75 mL 20% ethyl acetate/*n*-hexane. The solvent was removed from the filtrate, and the resulting residue was purified by flash column chromatography on silica gel (see the Supporting Information) to afford the products. For β-substituted vinylarenes (Scheme 3), [Ni-(cod)$_2$] and IMes (0.05 mmol, 10 mol% each) were used, and an additional 3 equivalents of the α olefin was added after 1 d.

Vinylarene homo-hydroalkenylation (t-t): The above procedure described above was used, wherein the vinylarene (1 mmol) was used instead of the 3 mmol of α-olefin.

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