VIP N-Heterocyclic Carbenes Very Important Paper

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Catalytic Asymmetric Hydroalkenylation of Vinylarenes: Electronic Effects of Substrates and Chiral N-Heterocyclic Carbene Ligands**

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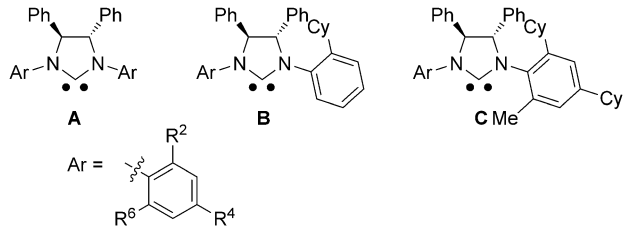
Abstract: *An asymmetric tail-to-tail cross-hydroalkenylation of vinylarenes with terminal olefins was achieved by catalysis with NiH complexes bearing chiral N-heterocyclic carbenes (NHCs). The reaction provides branched gem-disubstituted olefins with high enantioselectivity (up to 94% ee) and chemoselectivity (cross/homo product ratio: up to 99:1). Electronic effects of the substituents on the vinylarenes and on the N-aryl groups of the NHC ligands, but not a π,π-stacking mechanism, assist the steric effect and influence the outcome of the cross-hydroalkenylation.*

The transition-metal-catalyzed cross-hydroalkenylation is an atom-economical method for the synthesis of substituted olefins,[1] and has undergone an incredible growth over the past decade, accompanied by the development of important new concepts to solve challenging problems.[2,3] Recently, we have reported the tail-to-tail (t-t) hydroalkenylation of vinylarenes, catalyzed by in situ generated $[IPr\text{-}NiH]^+$ (Scheme 1).[4] Such processes directly employ simple olefins and vinylarenes, and give an assortment of unsymmetrical branched *gem*-disubstituted olefins.[5]

As part of our continued efforts to discover new applications for N-heterocyclic carbenes (NHCs) in transition-metal catalysis, we became interested in identifying chiral NHC ligands to promote an asymmetric version of the hydroalkenylation reaction. We began our investigation with C_2-symmetric NHC ligands **A1**–**A4** (Figure 1), which were derived from (1*S*,2*S*)-1,2-diphenyl-1,2-ethanediamine.[6,7] While both [1,3-bis(2,6-di-*iso*-propylphenyl)]-imidazolidin-2-ylidene (SIPr) and imidazol-2-ylidene (IPr) were effective ligands in the racemic tail-to-tail cross-hydroalkenylation,[7] the use of the corresponding NHC ligand *rac*-**A1** led to a significant drop in reactivity (Table 1, entry 1).[8] We suspected the vicinal Ph groups to have an unfavorable steric effect, by pushing the N-aryl groups with their bulky isopropyl substituents in *ortho* position too close to the reaction center, thereby increasing the activation energy for the coordination of the substrate and lowering the reactivity. Further studies showed that both the size and the number of N-aryl *ortho* substituents played very important roles in determining the reactivity and selectivity of the hydroalkenylation (Table 1, entries 2–4). A higher reactivity could be achieved by using NHC ligands with less than four N-aryl *ortho* substituents. The cross-product (*S*)-**3aa** was obtained in 21% yield and with 73% *ee* by using the C_2-symmetric NHC **A4** with two cyclohexyl substituents in *ortho* positon (one on each of the two N-aryl groups),[9] and the reaction also gave the cross-product **4aa**,[10] a tail-to-head isomer of **3aa**, in 47% yield. The success of NHCs of general structures **B** and **C** (Figure 1, **B1**–**B5** and **C1**–**C3**) with their various N-aryl substituents was limited (Table 1, entries 5–12).[6] The best balance of *ee* value, reactivity, and selectivity was achieved with **B2**, the C_1-symmetric structure of which is closely related to that of the C_2-symmetric NHC **A4** (Table 1, entry 6).

Inspired by the electronic effects of NHC ligands on Ru-catalyzed olefin metathesis, we were also interested in the

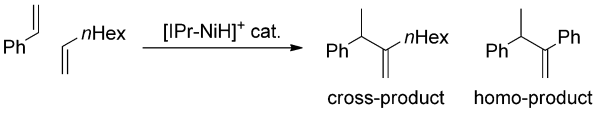


	R^2	R^6	R^4
A1	*i*Pr	*i*Pr	H
A2	Me	Me	H
A3	Me	Cy	Cy
A4	Cy	H	H

	R^2	R^6	R^4
B1	Me	Me	H
B2	Me	Cy	Cy
B3	Et	Cy	Cy
B4	Me	*t*Bu	*t*Bu
B5	*i*Pr	*i*Pr	*i*Pr

	R^2	R^6	R^4
C1	Ph	H	H
C2	9-Phen	H	H
C3	L-menthyl	H	H
C4	Cy	H	OMe
C5	Cy	H	F

Figure 1. Structures of NHC ligands. Cy = cyclohexyl, 9-Phen = 9-phenanthracenyl.



Scheme 1. Catalytic tail-to-tail hydroalkenylation. $[IPr\text{-}NiH]^+$ catalyst generated in situ from $[Ni(cod)_2]$, IPr, 1-octene, *p*-anisaldehyde, $TESOTf/NEt_3$, in toluene, under N_2 atmosphere, at RT, for 24 h. cod = 1,5-cyclooctadiene, TES = triethylsilyl.

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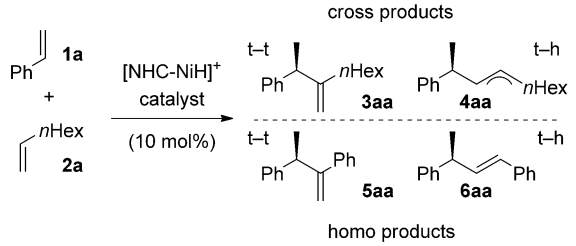
Table 1: Screening of chiral NHC ligands for the asymmetric cross-hydroalkenylation of styrene (**1a**) with 1-octene (**2a**).[a]



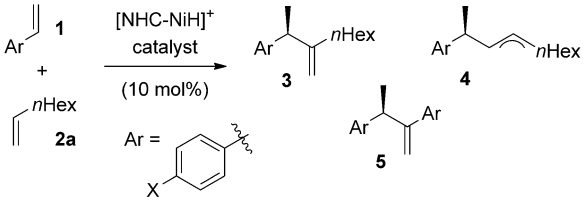
Entry	NHC	*ee* [%][b]	Yield [%][c]		
		3aa	**3aa**	**4aa**	**5aa**
1	*rac*-**A1**	–	5	< 5	< 5
2	**A2**	26	76	< 5	9[d]
3	**A3**	13	11	< 5	1
4	**A4**	73	21	47	1
5	**B1**	63	67	24	5[e]
6	**B2**	73	82	11	3
7	**B3**	69	77	12	3
8	**B4**	58	43	5	6
9	**B5**	15	43	10	< 5
10	**C1**	60	55	15	4
11	**C2**	72	11	< 5	< 5
12	**C3**	73	84	< 5	< 5
13	**C4**	69	80	14	3
14	**C5**	75	81	7	3

[a] Catalyzed by in situ generated presumed NHC-Ni hydride complex. See Experimental Section for preparation procedure and separation of **3aa.** Product **4aa** was obtained as an inseparable mixture of internal olefins, and product **6aa** was not obtained with any of the examined catalysts. [b] Determined by HPLC analysis of the corresponding epoxides. [c] Determined by ^{1}H NMR spectroscopy. [d] 46% *ee*. [e] 76% *ee*.

electronic effects of our catalysts on the hydroalkenylation.[11,12] We thus prepared NHC ligands with activating substituents at the N-aryl group (**C4** and **C5**) and investigated their influence on the reaction. Unlike in related studies with Ru catalysts, the electronic nature of the N-aryl substituents had no significant effect on the catalytic activity and yield of the hydroalkenylation (Table 1, compare entry 6 with entries 13 and 14).[13] A slight change in the *ee* values of the products as a function of the NHC N-aryl substituents prompted us to investigate the electronic effect of the vinylarene substituent on the *ee* values (Table 2). Interestingly, the asymmetric induction ability of the NHC N-aryl substituents and the vinylarene substituents has until now not been studied systematically.

First, we examined *para*-substituted vinylarenes with different electronic properties. Typical NHC ligands, such as **B1** or **B2**, lack π-conjugation at their heterocyclic core and are generally considered to have a strong σ-donating character with limited π-accepting ability compared to phosphorus-based ligands.[14] Therefore, the lengths of the NHC–Ni bond and the N–aryl bonds (and thus the steric effect of the NHC ligand on the hydroalkenylation) are not expected to change significantly with substrates that have different electronic properties.[15] However, the *ee* values of products **3** increased

Table 2: Influence of NHC ligands with different electronic properties and of substituents X of vinylarenes **1** on the hydroalkenylation.



Entry	NHC	X	*ee* [%][a]	Yield [%][b]		
			3	**3**	**4**	**5**
1	**B2**	F	60	73	8	1
2	**B2**	H	73	82	11	3
3	**B2**	OMe	77	80	16	2
4[c]	**B1**	F	38	65	23	5
5[c]	**B1**	OMe	73	69	15	8
6	**C4**	F	51	77	10	1
7	**C4**	H	69	80	14	3
8	**C5**	H	75	81	7	3
9	**C5**	OMe	82	84	13	2

[a] Determined by HPLC analysis of the corresponding epoxides. [b] Determined by GC analysis. [c] Yield determined by ^{1}H NMR spectroscopy.

gradually from X = F to X = OMe in a given NHC carboskeleton (Table 2, entries 1–5). This tendency is interesting, as it defies typical explanations that are entirely based on the *trans* influence,[16] which would normally predict the opposite tendency (i.e. gradual increase of the *ee* value from X = OMe to X = F). Our results thus suggest that the π character of the NHC–Ni^{II} bond might be more pronounced than we would normally expect from a first-row transition metal in a high oxidation state. Alternatively, π-face electron donation, as observed in NHC-Ru^{II} complexes,[11] might be operative in our NHC-Ni^{II} complexes. It should be noted that the *trans* coordination of electron-deficient substrates might not lenghten the NHC–Ni^{II} bond (or move the chiral steric element on the NHC further away from the metal center) any more than the pure σ-interaction of an electron-rich substrate.

Second, vinylarenes and NHCs with different electronic properties (Table 2, entries 6–9) were employed for a systematic study. This study showed that the above-described changes in *ee* values were not a direct result of a) π–π-stacking or attractive electrostatic interactions between the NHC N-aryl groups and the vinylarene, or b) steric effects between the F and OMe groups. The best *ee* values were obtained with an OMe group at *para* position of the vinylarene and an F substituent at the NHC N-aryl group (Table 2, entry 9). Exchanging the position of these two electronic activators, that is, having the F group at *para* position of the vinylarene and an OMe substituent on the NHC N-aryl group, resulted in the worst *ee* value (Table 2, entry 6 vs. entry 9, more than 30% difference in *ee* values).

Further analysis of the results showed that the electronic effects of both the NHC N-aryl group and the vinylarene might be synergistic. This can be deduced from the extend

with which the *ee* value increased with the introduction of both electronic activators in the favorable combination (Table 2, entry 2 vs. entry 9). This increase is higher than the sum of the increases, when only one of the electronic activators was present (entries 3 and 8). Moreover, this tendency can also be observed with the unfavorable combinations (Table 2, compare entries 1, 2, 6, and 7).

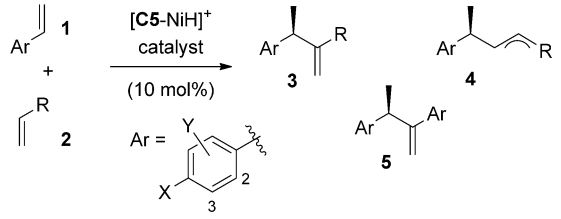
Overall, a comparison of the results in Table 1 (entries 6, 13, and 14) and Table 2 shows that the coordination of an external π-*system*, such as a vinylarene, could effectively change the asymmetric induction ability of an NHC–Ni complex at a high oxidation state. The synergistic effect we observed is remarkable, especially with regard to a) the effect of electronic changes on the asymmetric induction ability of the NHC ligand, and b) in an asymmetric Ni-catalyzed hydrocyanation with bis-1,2-diarylphosphinites, only an aryl group with a *para*-OMe substituent had an effect on the *ee* value of the product, whereas an aryl group with a *para*-F substituent had no effect.[17] The π-face electron donation and related effects of NHC substituents, such as their impact on bond lengths and back bonding, and the inductive and resonance effects of NHCs have been known for years.[11,12] Yet, new synthetic strategies based on the influence of the electronic properties of the substrate on the *ee* value of the product have not been reported until now, probably because those products and NHCs that were used were not chiral, and the alkenes used in those pioneering studies had similar electronic properties.[11,12] At this stage of our investigation, we can only attribute our overall observations to the changing electron density at the Ni center, however, the exact origin of the observed synergistic effect still needs to be investigated.

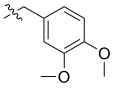
We should also note that there is no clear correlation between the discussed electronic effects and the ratio, in which cross- and homo-products are formed (Table 2, entries 6–9). We attribute the significant improvement of the stereoselectivity of the hydroalkenylation (from former 9:1 with IPr, to a range of 96:4 to 99:1 with NHCs) to the increased steric demand at the reaction center during vinylarene insertion. The improved ratio of cross- to homo-products is presumably a result of increased steric repulsions between the vicinal Ph group and the N-aryl *ortho* substituents.[18]

With the above-described observations in mind, we next studied the scope of the hydroalkenylation of various vinylarenes with **C5** as the ligand (Table 3). We were pleased to achieve high yields, as well as good chemo- and regioselectivities in most cases. The *ee* values improved with the use of sterically more demanding terminal olefins. The system accepted vinylarenes with substituents in *para*, *ortho*, and *meta* position (Table 3, entries 1–4). Apart from vinylanisoles, a thioanisole and a bulky vinylarene were also compatible substrates for this reaction (Table 3, entries 5 and 6). The scope of the terminal olefin was studied by using 4-*tert*-butoxy-styrene (Table 3, entries 7–12). Steric effects resulted in *ee* values up to 94% when we used allylbenzene instead of 1-octene or related non-aromatic vinylalkanes, including cycloalkyl or acyclic alkyl compounds.

Based on prior results of asymmetric reactions that were catalyzed by P-Ni^{II} and NHC-Ni^{II} complexes,[2] and an experiment that supported the presence of NiH (aldehyde reduction by an in situ generated [SIPr-NiH]OTf),[19] we formulated a tentative working hypothesis to explain the major stereochemical outcome of the hydroalkenylation with steric effects (Figure 2). An analysis of the results obtained with a series of closely related NHCs (**A3**, **A4**, and **B2** in Table 1) showed that the N-aryl *ortho*-Me substituent might play an important role with regard to reactivity and regioselectivity. It should be noted that the theoretical investigation

Table 3: Scope and selectivity of the hydroalkenylation using **C5** as the ligand to generate the presumed [**C5**-NiH]$^+$ catalyst.



Entry	X, Y	R	*ee*[a] [%] **3**	Yield[b] [%] **3**	Ratio[b] **3:4**	**3:5**
1	OMe, H	Bn	89	87	93:7	96:4
2	H, 3-OMe	Bn	86	81	89:11	95:5
3	H, 2-OMe	Bn	88[c]	57	85:15	87:13
4	OMe, 3-OMe	Bn	90	87	91:9	96:4
5	SMe, H	Bn	86	70	91:9	95:5
6	*t*Bu, H	Bn	85[c]	75	90:10	90:10
7	O*t*Bu, H	*n*Hex	84[c]	81	86:14	96:4
8	O*t*Bu, H	*i*Bu	86	82	89:11	96:4
9	O*t*Bu, H		86	75	88:12	93:7
10	O*t*Bu, H		89	79	89:11	95:5
11	O*t*Bu, H	Bn	94	85	92:8	96:4
12	O*t*Bu, H		93	87	93:7	96:4

[a] Determined by HPLC analysis. [b] Determined by GC analysis. [c] Determined by HPLC analysis of the corresponding epoxides or diols after epoxidation or dihydroxylation, respectively.

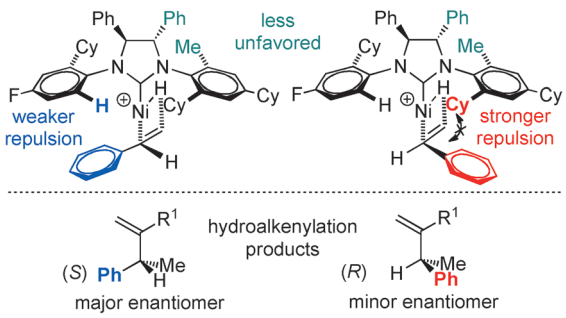


Figure 2. Tentative transition-state models for the hydroalkenylation in order to explain the observed stereochemical outcome when **C5** is used as the ligand.

of the P-Ni^{II}-catalyzed hydrovinylation of styrene suggested an alternative β-hydrogen transfer mechanism,[20] and without taking the above-discussed electronic properties into account, our steric model alone cannot explain the large differences observed with different vinylarenes.

In summary, a catalytic asymmetric intermolecular tail-to-tail hydroalkenylation of vinylarenes with terminal olefins offers a direct way to chiral unsymmetrical *gem*-disubstituted olefins from electron-rich monoenes. The result showed that the asymmetric induction ability of the NHC-Ni complex is tunable by the electronic properties of the NHC N-aryl substituents and those of external π-systems, such as vinylarenes. The obtained information might also be of general use in the development of asymmetric NHC/transition-metal catalysis and the asymmetric co-dimerization of other olefins.

Experimental Section

Typical procedure of the catalyst preparation: In a glove box, [Ni(cod)$_2$] (0.05 mmol, 10 mol%) and NHC (10 mol%) were added to an oven-dried test tube equipped with a stir bar. The tube was sealed with a septum, taken out of the glove box, and connected to an N_2 line. The mixture was dissolved in dried degassed toluene (2 mL) and stirred at room temperature for 1 h. 1-Octene (15 mol%), NEt_3 (60 mol%), *p*-anisaldehyde (10 mol%), and TESOTf (22 mol%) were then added sequentially and stirred at room temperature for 5 h.

Standard hydroalkenylation: The vinylarene (0.5 mmol) and the terminal alkene (1.5 mmol) were added to the solution containing the in situ prepared "NHC-NiH" catalyst. The reaction mixture was stirred at room temperature for 40 h. After the addition of *n*-hexane (4 mL), the solution was stirred for 30 min under air. The reaction mixture was then filtered through a short plug of silica gel and rinsed with diethyl ether (75 mL). The solvents were removed under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel to afford the hydroalkenylation products.

Keywords: asymmetric catalysis · hydroalkenylation · N-heterocyclic carbenes · nickel · olefins

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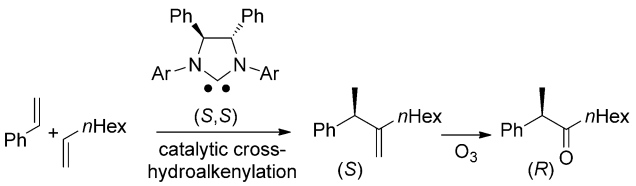

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