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Mechanistic Study of a Switch in the Regioselectivity of Hydroheteroarylation of Styrene Catalyzed by Bimetallic Ni–Al through C–H Activation

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Abstract: We previously reported a highly efficient protocol for bimetallic Ni–Al-catalyzed hydroheteroarylation of styrene with benzimidazole based on C–H bond activation. We have now delineated the mechanism of this process, providing a rationale for an observed switch in regioselectivity in the presence of the Lewis acid, $AlMe_3$. The present mechanistic study gives insights for the rational development of catalysts that exhibit required linear/branched selectivity.

Introduction

Transition-metal-mediated C–H bond activation and functionalization has garnered significant interest in the past decade. The ability to circumvent additional steps associated with prefunctionalized coupling partners renders the synthetic strategy appealing for a myriad of applications.[1] From the perspective of synthetic and catalytic utility, judiciously controlling C–H bond functionalization for site selectivity would be highly desirable. Recently, several research groups have reported the use of specific directing groups on the substrates or alteration of the structural morphology of metal-bound ligands to facilitate the desired regioselectivity.[2] However, because of the requirement of tedious synthetic manipulations for the installation of directing groups, these strategies are inherently limited.

Lewis-acid-assisted transition metal catalysis has slowly caught the interest of the synthetic community for its cooperative effect of enhancing the rate and controlling the selectivity of the respective transition metal catalyst.[3] For example, the groups of Hartwig[3a] and Nolan[3b] have reported that Lewis acids such as $AlCl_3$ and BEt_3 accelerate palladium-mediated reductive elimination reactions. Knochel reported the direct palladium-catalyzed arylation of methyl-substituted pyridine promoted by $ZnCl_2$, $Sc(OTf)_3$, and $BF_3{\cdot}OEt_2$ with excellent regioselectivity.[3c] Similarly, our group,[4] as well as those of Nakao and Hiyama[5] and Kanai,[6] have observed the beneficial effect of added $AlMe_3$ in promoting nickel-mediated C–H bond activation of heteroarenes. More recently, we reported a switch in the regioselectivity for C–H functionalization of benzimidazole derivatives with styrene and allylbenzene to afford either linear or branched products when using $AlMe_3$.[7] In this work, we present a detailed mechanistic investigation of this branched/linear regioselectivity with regard to the synergistic interaction between Ni and Al bimetallic catalysts bearing amino-NHC (nitrogen heterocyclic carbene) ligand **1a**.

Results and Discussion

Hydroheteroarylation of styrenes by C–H bond activation of benzimidazole

Our group has previously reported the direct amino-NHC nickel-catalyzed hydroheteroarylation of styrene with benzimidazole by C–H bond activation, as summarized in Table 1.[7a] High selectivity in favor of the branched product with good yield was observed with various styrene substrates. Interestingly, addition of $AlMe_3$ to the reaction mixture resulted in complete reversal of the site selectivity in favor of the linear product (anti-Markovnikov). Moreover, electronic modulation of the styrene component did not seem to perturb the linear selectivity. For instance, complete linear regioselectivity and excellent

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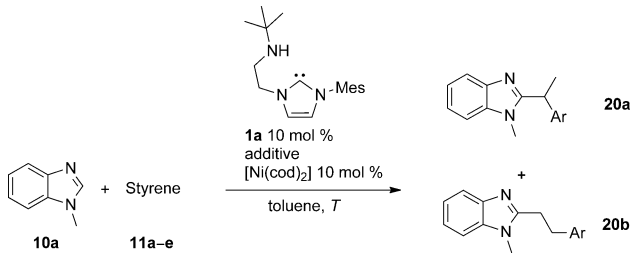
Table 1. Scope of the reaction in terms of various styrenes with benzimidazole: branched and linear selectivities in the absence and presence of $AlMe_3$.[a]



Entry	Styrene	Without $AlMe_3$, $T=150\,^{\circ}C$ Yield [%]	Selectivity B/L	10 mol% $AlMe_3$, $T=100\,^{\circ}C$ Yield [%]	Selectivity B/L
1	11a	70	100:0	85	0:100
2	11b	50	100:0	88	0:100
3	11c	69	100:0	96	0:100
4	11d	67	100:0	93	0:100
5	11e	97	100:0	90	4:96
6	11f	72	100:0	66	55:45

[a] The reactions were carried out using **10a** (0.50 mmol) and styrene (0.75 mmol) and products were determined by ^1H NMR analysis with isolated yields based on **10a** as the limiting reagent. 10 mol% of $[Ni(cod)_2]$, $AlMe_3$, and NHC ligand **1a**.

the resulting reaction profiles are shown in Figure 1. The formation of linear product **20ab** in the presence of $AlMe_3$ (diamonds) reached completion (90% yield) within 150 min, whereas the reaction without $AlMe_3$ (circles) was still in the induction period at this time. Clearly, the presence of $AlMe_3$ had a remarkable impact on the reaction rate. Close inspection of the ^1H NMR spectra for the stoichiometric reaction of $AlMe_3$ with **1a** revealed the generation of an Al–benzimidazole adduct (**3**), and the methyl signal of benzimidazole was shifted upfield from $\delta=2.61$ to 2.20 ppm. Furthermore, the identity of **3** was confirmed by a single-crystal X-ray study, which revealed that $AlMe_3$ was datively coordinated to the benzimidazole nitrogen (Figure 2).[7a,8] Thus, we postulated that coordination of the Lewis acid to benzimidazole would increase the acidity of the C2–H bond, resulting in the observed higher activity. It is imperative to mention the recent advances in the use of Lewis acid additives to enhance reaction rates; for example, the groups of Hartwig, Nolan, and Knochel have employed the Lewis acids $AlCl_3$ and BEt_3 for reductive elimination reactions mediated by palladium.[3]

To understand the nature of the C–H bond cleavage process in the present (amino-NHC) nickel-catalyzed hydroarylation reaction, we first performed a series of competition experiments with various benzimidazole derivatives. Our findings revealed that neutral benzimidazole **10a** was functionalized only 0.93 times that of its electron-rich counterpart **10i** [Eq. (1)], thus suggesting that an electrophilic aro-

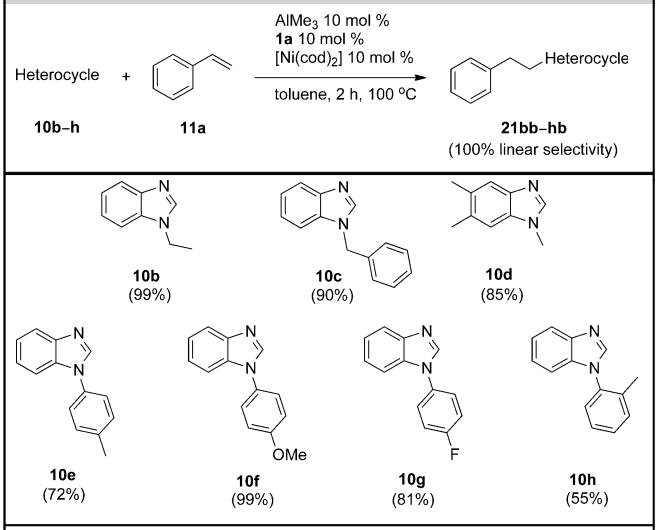
yield were observed for 4-methylstyrene (**11b**), 4-methoxystyrene (**11c**), 4-fluorostyrene (**11d**), and 4-phenylstyrene (**11e**) derivatives. An exception to this trend was found with 2-vinylnaphthalene (**11f**), for which no chemical bias for site selectivity was observed, resulting in a product distribution of equal amounts of the linear and branched isomers. The lack of selectivity with **11f** was attributed to more effective π-conjugated stabilization due to the naphthalene ring.

As illustrated in Table 2, catalytic C–H bond activation promoted by the Al-Ni bimetallic system is also conceivable with other benzimidazole derivatives. High levels of linear selectivity and good yields were consistently obtained with various benzimidazoles.

Mechanistic studies on the C–H bond activation

The accelerating effect of $AlMe_3$ on Ni-mediated C–H bond activation of benzimidazole is clearly evident from the fact that the yields of reactions in the presence of $AlMe_3$ (85–96%, Table 1) are generally higher than those in the absence of Lewis acid additives (50–70%, Table 1). To delineate the role of $AlMe_3$ in promoting the reaction, product conversions in the presence and absence of $AlMe_3$ were monitored as a function of time by sampling small aliquots of the reaction mixtures;

Table 2. Scope of the reaction in terms of various heterocycles in the presence of $AlMe_3$ as an additive.[a]



[a] The reactions were carried out using **10** (0.50 mmol) and styrene (0.75 mmol) and products were determined by ^1H NMR analysis with isolated yields based on **10** as the limiting reagent. 10 mol% $[Ni(cod)_2]$, $AlMe_3$, and NHC ligand **1a**.

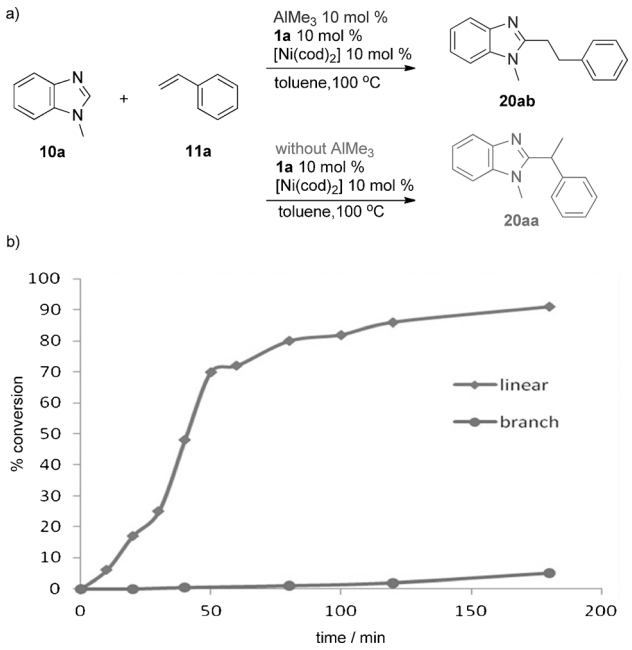


Figure 1. The reaction rate profile for the reaction of **10a** and **11a** in the presence (diamonds) and absence of $AlMe_3$ (circles).

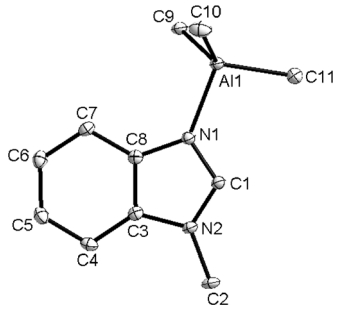
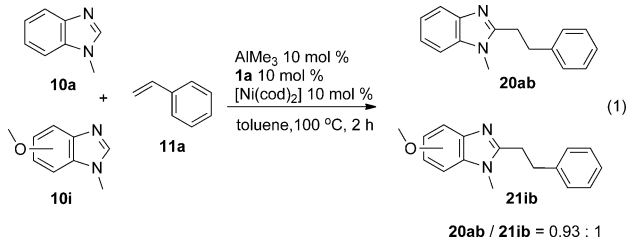


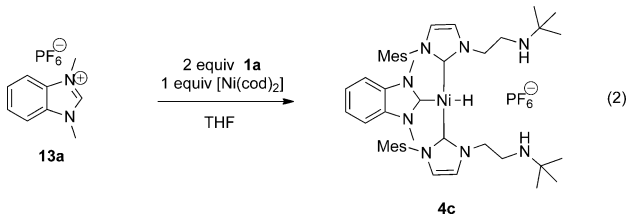
Figure 2. The molecular structure of Al–benzimidazole adduct **3**.[7a]

matic C–H bond activation pathway is less likely to be operative in the Ni–Al bimetallic system.[9]



Subsequently, we examined the C–H bond activation process by employing benzimidazole isotopically labeled at C2, [D_1]-**10a**. Intermolecular competition in the presence of $AlMe_3$ resulted in a kinetic isotope effect (KIE) of $k_H/k_D \approx 3.56$, diagnostic of C–H bond breaking in an oxidative addition mechanism, most probably as a reversible rate-limiting step. A positive KIE of 4.61 was also observed for the reaction performed in the absence of $AlMe_3$. These KIE outcomes are in striking contrast to our previous C–H bond activation studies on pyridine, which displayed only a small primary KIE of 1.25,[4] highlighting the requirement of π-coordination of pyridine prior to the C–H bond breaking.

Close monitoring by ^{1}H NMR of the catalytic hydroarylation of styrene with benzimidazole **10a** mediated by the nickel-aluminum catalyst system revealed a very weak upfield signal at $\delta = -12.05$ ppm, indicating the appearance of nickel hydride as a result of C–H bond breaking by oxidative addition. Unfortunately, however, we were unable to isolate this intermediate, thus preventing us from further elucidating the identity of this species in the catalytic process. Nonetheless, the benzimidazolium salt **13a**, with its two substituents on the nitrogen atoms, should bear considerable resemblance to the Lewis pair adduct **3** and thus serve as an appropriate model compound to delineate the nature of the reaction intermediates. When [$Ni(cod)_2$] (cod = 1,5-cyclooctadiene) was treated with stoichiometric amounts of **1a** and benzimidazolium salt **13a**, an Ni–H signal appeared at $\delta = -12.92$ in the ^{1}H NMR spectrum [Eq. (2)], which could be assigned to a new nickel hydrido complex, **4c**. Unequivocal confirmation of the structure of **4c** as a nickel hydride was provided by X-ray analysis of a single crystal grown from a solution in CH_3CN/hexane at $-20\,^\circ$C (Figure 3). Complex **4c** exhibits a distorted square-planar geometry, in which the two amino-NHC moieties have a *trans* disposition to avoid any unfavorable steric interaction, thus forc-



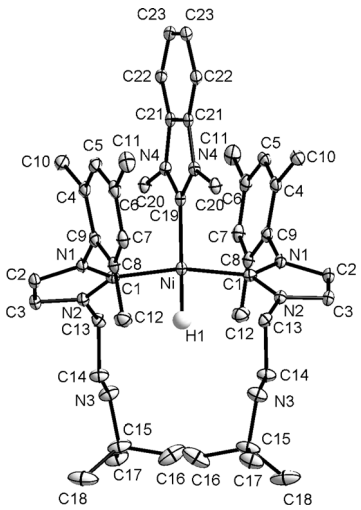


Figure 3. ORTEP representation of Ni hydrido complex **4c** with thermal ellipsoids drawn at the 30% probability level. All other hydrogen atoms, with the exception of NiH, have been omitted for clarity. Selected bond lengths (Å) and angles (deg.): Ni–C1 1.893(2), Ni–C19 1.907(3), N1–C1 1.365(3), N1–C2 1.394(3); C1-Ni-C1A 167.25(13), C1-Ni-C19 96.38(6).

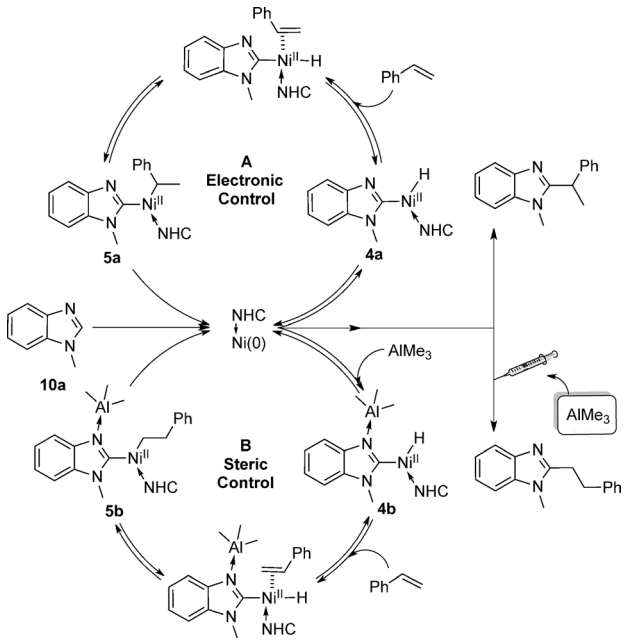


Figure 4. Proposed mechanism for C–H bond activation in the hydroheteroarylation of styrene.

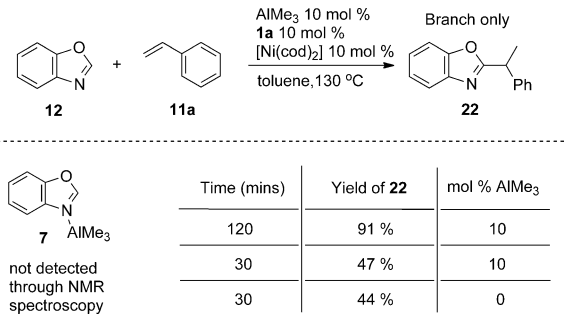
ing the hydride and benzimidazole into a mutually *trans* arrangement. This isolated solid-state structure provided further evidence in support of an oxidative addition mechanism for C–H bond breaking. A similar Ni hydride complex has been reported by Cavell's group for Ni-mediated C–H activation/alkene insertion to produce a linear 2-alkyl imidazolium salt.[10]

Based on our experimental observations, we were able to confirm our previously proposed mechanistic pathway, as illustrated in Figure 4.[7a] The C–H bond functionalization in hydroarylation proceeds through the following mechanistic steps: (1) concerted oxidative addition of the C–H bond to generate intermediate Ni–H species **4**, (2) facile coordination of styrene to the metal followed by migratory insertion to yield Ni alkyl species **5**, and (3) reductive elimination of **5a** (pathway A) under electronic control and **5b** (pathway B) under steric control to afford branched and linear products, respectively.

Mechanistic implications of branched/linear selectivity

In the proposed mechanism, the selectivity for the branched product is dictated by electronic preference for the π-benzylnickel species **5a**, a feature that is well documented.[5f,11] As a consequence, the catalytic cycle "A" under electronic control is manifested in formation of the Markovnikov product. On the other hand, we believe that $AlMe_3$ plays a critical role in favoring selectivity for the linear product. Based on the isolation of the Al–benzimidazole adduct (**3**) (see above), we postulate that the dormant reaction pathway "B" is activated, thus avoiding steric repulsion at the Ni center in **4b**. In our previous studies on Ni-mediated C–H bond activation of pyridine, we found that $AlMe_3$ not only activates the C–H bond towards functionalization, but also invokes a steric environment promoting *para* selectivity.[4] Attempts to isolate and characterize the intermediate resembling complex **4b** bearing adduct **3** have thus far not been fruitful. We therefore undertook a series of indirect experiments to confirm our hypothesis of steric-based linear selectivity induced by $AlMe_3$ as a chemical switch.

It is interesting to note that the catalytic reaction of benzoxazole (**12**) under similar conditions with 10 mol% $AlMe_3$ furnished solely the branched product in good yield (91%) and failed to produce any detectable amount of the linear isomer. ^1H NMR spectroscopy revealed no such Lewis acid adduct (**7**) for benzoxazole. Moreover, we also observed that the extent of the reaction after 30 min was not significantly different in either the presence (47%) or absence (44%) of $AlMe_3$ (Scheme 1). This negative result highlights the importance of interaction between the Lewis acid and the heterocycle for promoting both linear selectivity and high reaction rate.



Time (mins)	Yield of **22**	mol % $AlMe_3$
120	91 %	10
30	47 %	10
30	44 %	0

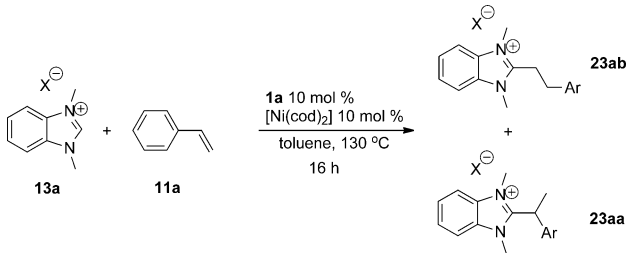
Scheme 1. Reaction of **12** and **11a**.

Steric influence on linear selectivity

At this stage, our focus was to understand the influence of steric variations of the heteroaromatic substrates on selectivity. Again, variation of the substituents on the nitrogen atoms of the benzimidazolium salt was considered to provide a useful molecular model for elucidating the steric effects of both $AlMe_3$ and the side arm of the imidazole on the selectivity of the reaction. Initial efforts were focused on optimizing the range of benzimidazolium salts with different counter anions (Table 3). The best optimized yield (69%) with a high linear selectivity of 4:1 for **13a**·PF_6^- was achieved under conditions similar to those used previously.

Under the optimized conditions, the substrate scope in terms of benzimidazolium salts with PF_6^- as counterion in the hydroheteroarylation of styrene was probed, and the results are summarized in Table 4. The 1,3-dimethyl benzimidazolium salt **13a** performed quite well, giving a moderate yield (69%) with a linear/branched selectivity of 8:2 (entry 1). $AlMe_3$ is not required to induce linear selectivity in this catalytic reaction. Replacing the methyl groups with larger pendants such as ethyl (**13b**, entry 2; **13f**, entry 6) and isopropyl (**13c**, entry 3) increased the linear/branched selectivity to 8.5:1.5 and 9:1. Benzyl derivative **13d** gave complete linear selectivity with a yield of 68% (entry 4). Unfortunately, a more sterically encumbered benzimidazolium salt (**13g**, entry 7) bearing two isopropyl side arms failed to react, thus representing the upper

Table 3. Screening process.[a]



Entry	Anion X^-	L/B	Yield [%]
1	BF_4^-	7:3	28
2	I^-	–	0
3	PF_6^-	4:1	69

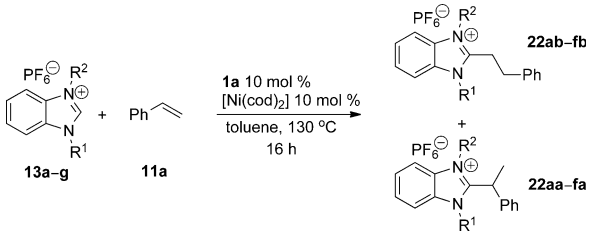
[a] The reactions were carried out using **13a** (0.5 mmol) and **11a** (0.75 mmol) and products were determined by ^{1}H NMR analysis. 10 mol% [Ni(cod)$_2$] and 10 mol% NHC ligand **1a**.

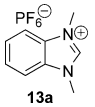
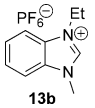
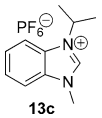
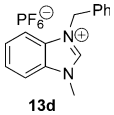
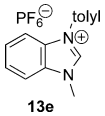
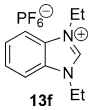
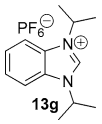
limiting case for steric control of this reaction.[12] Surprisingly, the linear/branched selectivity decreased to 7:3 for the 1-methyl-3-(*p*-tolyl)benzimidazolium salt (**13e**), even though the steric bulk of tolyl (**13e**) is clearly larger than that of methyl (**13a**). This outcome may seem counterintuitive to conventional wisdom about steric effects. It should be borne in mind, however, that simplified steric demand concepts offer only a snapshot of a molecule without considering the level of flexibility exhibited in different parts of the molecular framework. Considering the anisotropic steric nature of the mesityl groups, we believe that they may freely rotate in a certain direction to minimize steric repulsion with the nickel complex, thus leading to a less sterically encumbered environment within the complex and favoring branched selectivity.

Nevertheless, the experimental outcomes illustrated in Table 4 are indicative of a high correlation between steric demand and linear selectivity. More importantly, two substituents or side arms on the heteroarene in the vicinity of the C–H activation site are required to ensure high linear selectivity; this is further validated by observations on benzimidazole **10j** bearing a pyridinyl group. We speculated that the pyridine moiety in **10j** could compete with the imidazole nitrogen centers for the incoming Lewis acid, thus reducing the efficacy of $AlMe_3$ as a second steric control site for promoting high linear selectivity. As expected, the linear/branched selectivity decreased dramatically to only 33:16 when the reaction was performed under similar conditions in the presence of 10 mol% $AlMe_3$ (Scheme 2). In fact, a ten-fold increase in the amount of $AlMe_3$ (100 mol%) was required to obtain high linear selectivity. This outcome with **10j** again demonstrates that a single pendant substituent on the benzimidazole is insufficient to ensure a high linear/branched selectivity.

Next, we monitored reactions with a range of NHC ligands in the hope of understanding their effect on selectivity. The results of the C–H bond activation of benzimidazolium salt **13a** using different NHC ligands are summarized in Figure 5. The amino-NHC framework **1a** (L/B = 4:1) appeared to be a more effective scaffold than IMes (L/B = 51:49) for exerting a high

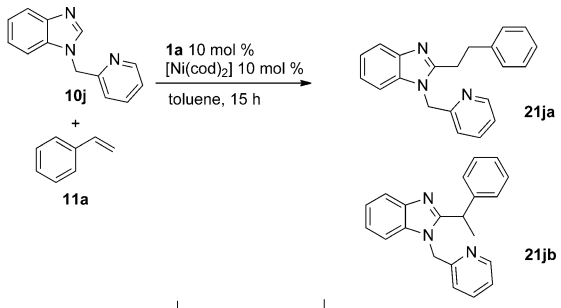
Table 4. Hydroheteroarylations of styrene with various benzimidazolium salts.[a]



Entry	**13**	L/B	Yield [%]
1	 **13a**	8:2	69
2	 **13b**	8.5:1.5	97
3	 **13c**	9:1	99
4	 **13d**	10:0	68
5	 **13e**	7:3	54
6	 **13f**	9:1	99
7	 **13g**	--	no reaction

[a] The reactions were carried out using **13** (0.5 mmol) and styrene (0.75 mmol) and product yields were determined by ^{1}H NMR analysis. 10 mol% [Ni(cod)$_2$], $AlMe_3$, and NHC ligand **1a**.

linear selectivity in the reaction. Unfortunately, no reactivity was observed when IPr was employed as a ligand under similar reaction conditions, further reflecting the steric limitations of the Ni system. For a more in-depth understanding of the steric properties of the NHC ligands around the nickel center, the percent buried volumes (%V_{bur}) of both **1a** and IMes were calculated using the SambVca method developed by Cavallo and co-workers.[13] In this method, the %V_{bur} value indicates the portion of a sphere around the metal occupied by the ligand. For this study, we considered complex **4c** and compared it with the previously reported **4d** used by Cavell's group as a benchmark ligand. The buried volume of the amino-NHC ligand **1a** (28.1%) was apparently smaller than that of IMes (32.1%). However, the reaction of **1a** gave higher linear selectivity than that with the IMes ligand, which would appear to be at variance with steric control of the linear/branched selec-



% mol $AlMe_3$	21ja	21jb
0	0 %	23 %
10	33 %	16 %
100	69 %	13 %

Scheme 2. Reaction of **10j** and **11a**.

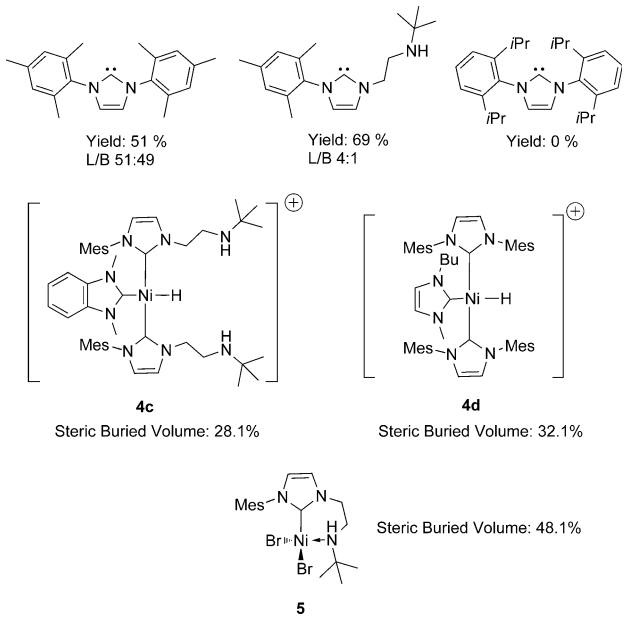


Figure 5. Dependence of reaction selectivity on NHC ligand.

tivity. This apparent anomaly may be rationalized by considering that, unlike typical monodentate Arduengo NHC ligands such as IMes, **1a** has a bidentate framework bearing a free dangling *tert*-butylamine arm, which may fleetingly coordinate to the metal center in a rapid manner. Overall, this intermittent coordination behavior with the metal would be likely to increase the average steric demand in complexes and thus favor linear product formation. In support of this rationale, we calculated the steric buried volume based on a known bidentate structure from our previous work, the amino-NHC nickel(II) complex **5**.[14] Indeed, a bidentate feature in amino-NHCs generates a large buried volume of 48.1%, thus making a compelling case for sterically controlled selectivity. Furthermore, the theoretical findings on cobalt-mediated hydroarylation of styrenes by Fu's group further support our observation of ligand-controlled regioselectivity based on steric effects.[15]

Conclusions

In summary, without resorting to functional group manipulations on the substrate or ligand, we have disclosed a new mode of chemically regioselective switching for C–H bond functionalization of benzimidazole derivatives. The catalytic method involves a cooperative interaction between Ni and Al to create a steric environment for obtaining the linear product. Omission of the $AlMe_3$ co-catalyst switches the reaction towards branched selectivity. Equally importantly, $AlMe_3$ has a remarkable impact on the rate of the reaction. Based on a molecular model of a benzimidazolium salt, we have successfully isolated Ni hydride intermediate **4c** involved in the C–H transformation. The key feature that ensures high linear over branched selectivity in the hydroheteroarylation of styrene is the presence of two substituents or side arms on the heteroarene components in the vicinity of the C–H activation site. We anticipate that further detailed studies of this bimetallic catalysis may facilitate its possible wider application in C–H bond activation.

Experimental Section

Synthesis of Ni-hydrido complex (4c)

A solution of amino-NHC (1.43 g, 5.0 mmol) in THF (35.0 mL) was added to a solution of $[Ni(cod)_2]$ (0.69 g, 2.5 mmol) in THF (35.0 mL) at room temperature. After stirring for 1 h, the orange solution was added dropwise to a vial containing 1,3-dimethyl-benzimidazolium hexafluorophosphate (0.70 g, 2.4 mmol) and the mixture was stirred for 3 d at room temperature. The resulting mixture was filtered and the collected solid was washed with hexanes. The crude solid was further purified by recrystallization from acetonitrile/hexanes (80:20, v/v) to give complex **4c** (1.47 g, 66%) as colorless crystals. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 7.31$ (s, 2H), 7.28–7.25 (m, 2H), 7.22–7.19 (m, 2H), 6.81 (br, 6H), 4.36 (t, $J = 6.2$ Hz, 4H), 3.04 (q, $J = 6.7$ Hz, 4H), 2.85 (s, 6H), 2.33 (s, 6H), 1.45 (br, 12H), 1.07 (s, 20H), −12.92 ppm (s, 1H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 200.5, 183.7, 140.3, 137.1, 137.0, 135.8, 130.2, 123.8, 123.6, 122.9, 110.6, 53.2, 51.3, 43.1, 33.6, 29.7, 21.5, 17.6 ppm; HR-MS (ESI): calcd for $[C_{45}H_{65}N_8Ni]^+$: 775.4686; found: 775.4689.

General procedure for nickel-mediated hydroheteroarylation of styrene

Styrene **11a** (0.75 mmol) was added to a solution of $[Ni(cod)_2]$ (14 mg, 0.05 mmol), amino-NHC (**1a**; 14 mg, 0.05 mmol), and the requisite benzimidazolium salt derivative **13[x]** (0.5 mmol) in toluene. After sealing the reaction vessel, it was removed from the glovebox and the solution was heated at 130 °C for 16 h. The resulting mixture was filtered through Celite, which was then washed with acetone. The combined filtrate and washings were concentrated in vacuo to afford the crude product, which was further purified by flash chromatography eluting with ethyl acetate/acetone.

Crystallography

Details of the crystal structure determination are given in the Supporting Information. CCDC-988238 (**4c**) contains the supplementary crystallographic data for this paper. These data can obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: alkenes · C–H bond activation · homogeneous catalysis · nickel · regioselectivity

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