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Intramolecular Aminocyanation of Alkenes via N–CN Bond Cleavage**

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Abstract

A metal-free, Lewis acid-promoted intramolecular aminocyanation of alkenes was developed. $B(C_6F_5)_3$ activates N-sulfonyl cyanamides, leading to formal cleavage of the N–CN bonds in conjunction with vicinal addition of sulfonamide and nitrile groups across an alkene. This method enables atom-economical access to indolines and tetrahydroquinolines in excellent yields, and provides a complementary strategy for regioselective alkene difunctionalizations with sulfonamide and nitrile groups. Labeling experiments with ^{13}C suggest a fully intramolecular cyclization pattern due to lack of label scrambling in double crossover experiments. Catalysis with Lewis acid is realized and the reaction can be conducted under air.

Keywords

Bond Activation; Lewis Acid; Mechanism; Aminocyanation; Alkene

Alkene addition reactions are a hallmark of organic chemistry, yet significant problems remain unsolved.^[1] Recent successes include forming new C–N bonds in conjunction with vicinal C–C,^[2,3] C–O,^[4] C–N,^[5] C–H,^[6] or C–X^[7] bonds. These alkene aminofunctionalization reactions represent a unique strategy for the synthesis of valuable nitrogen-containing heterocycles. Despite significant developments, the established aminofunctionalization methods typically rely upon an exogenous electrophile (e.g., aryl halides) or nucleophile (e.g., halides, amines, carboxylates) to furnish the subsequent C–C or C–heteroatom bonds vicinal to the nitrogen (Scheme 1).^[8] To our knowledge, a direct intramolecular addition approach to aminocyanation is unexplored.

Recently, our group^[9] and Nakao's group^[10] independently reported two metal-catalyzed oxyfunctionalization reactions of alkenes through the activation of O–CO and O–CN bonds of esters and cyanates, respectively. Though this early work was pioneering, the corresponding chemistry to install nitrogen is potentially more powerful. Due to the versatile

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synthetic utility of the cyano group^[11] and the persistent demand for methods to prepare functionalized nitriles,^[12] we envisioned that the aminocyanation of alkenes (Scheme 1) would allow straightforward access to β -aminonitriles. These compounds are versatile precursors to the biologically and pharmacologically important β -amino acids.^[13] To our surprise, the well-developed strategies for alkene aminofunctionalization^[2-7] have only recently been applied in introducing cyano groups onto the alkene double bond. In 2013, Xiong, Li, Zhang, and co-workers reported the first example of alkene aminocyanation. Their work focused on aminocyanation of styrenes in an intermolecular context and was thought to proceed via a Cu-promoted radical addition pathway using TMS-CN as the cyanide source and *N*-fluorobenzenesulfonimide as the nitrogen source.^[14]

Cyanamides (R^1R^2N-CN) are versatile one-carbon, two-nitrogen building blocks for heterocycle synthesis.^[15] These bench-stable compounds are easily prepared by reaction of the corresponding secondary or tertiary amine with BrCN (von Braun reaction).^[16] While most transformations of cyanamides occur at the cyano group, methods for cleaving the N-CN bond of cyanamides are rare, presumably due to the double bond character of N-CN bonds.^[17] Owing to this challenge, catalytic cleavage of N-CN bonds has only recently been reported.^[18,19] Notably, Falck and Wang reported a Rh-catalyzed, cyano-group transfer from an *ortho* cyanamide to an alkene of an α methyl styrene. They proposed metal mediated N-CN bond cleavage as a key step and the reaction required a relatively high catalyst loading (20 mol% of Rh).^[19] This N-CN bond activation was conceptually in accordance with our early mechanistic thinking regarding alkene aminocyanation. Nevertheless, to the best of our knowledge, intramolecular aminocyanation of alkenes – by any mechanism – has never been described. Here, we report a Lewis acid-promoted intramolecular aminocyanation of alkenes. We demonstrate the construction of 2,2-disubstituted indolines^[20] and 2,2-disubstituted tetrahydroquinolines in an atom-economical fashion. The highlight of our approach is a novel mechanism for aminocyanation of alkenes via a non-degradative rupture at the N-CN bond.

Recently, *N*-cyano-*N*-phenyl-*p*-toluene sulfonamide (NCTS) has been employed as a bench-stable and less-toxic cyanation reagent in metal-catalyzed cross-coupling^[21] and arene C-H cyanations,^[22] implying a metal-mediated N-CN cleaving process. Meanwhile, Lewis acid co-catalysts, particularly BPh₃, have proven effective at accelerating metal-catalyzed carbocyanation^[23] and oxycyanation^[10] of alkenes.

We attempted to take advantage of the electron-withdrawing tosyl group to weaken the N-CN bond of NCTS-type cyanamides while incorporating the activating effect of a Lewis acid on the cyano group. Therefore, we initiated our investigation of aminocyanation conditions by treating *N*-tosyl cyanamide **1a** with a variety of transition metal and Lewis acid additives (see the Supporting Information for details on discovery and optimization). We quickly identified that the combination of rhodium (I) complexes and boron Lewis acids were effective (Table 1, entries 1-4). As Lewis acid strength increased from BPh₃ to B(C₆F₅)₃, the yield of **2a** improved from 49 to 72% with minimal reductive de-cyanation by-product **3a** observed in entry 2.^[24] Also, the temperature required for acceptable conversion of **1a** could be decreased, with 90 °C proving optimal (entries 2-4). Dramatically, a reaction employing B(C₆F₅)₃ in the absence of added rhodium still gave **2a**

in a 90% yield (entry 5)! This observation prompted us to examine other Lewis acids to promote aminocyanation. Isoelectronic Lewis acids $\text{BF}_3 \cdot \text{OEt}_2$, AlCl_3 , and Me_2AlCl each provided product **2a**, albeit in lower yields than $\text{B}(\text{C}_6\text{F}_5)_3$ (entries 6-8). Reaction of AgOTf or $\text{Cu}(\text{OTf})_2$ with **1a** failed to produce detectable amounts of **2a**, instead gave complex mixtures (entries 9-10). $\text{Zn}(\text{OTf})_2$ or $\text{Sc}(\text{OTf})_3$ were also ineffective, returning **1a** without a detectable amount of **2a** (entries 11-12). Reaction of **1a** with SnCl_4 provided **2a** in 49% (entry 13), but also provided an insoluble black precipitate as a by-product. Interestingly, BPh_3 was an ineffective promoter, even at 150 °C (entry 14).

With the identification of suitable reaction conditions, the scope of Lewis acid-promoted intramolecular aminocyanation was investigated. Substrates bearing alkyl (Table 2, entries 1 and 2) or halo groups on the aromatic ring (entries 3-5) provided the corresponding indolines in excellent yields. It is worth noting that the presence of bromide *para* to the cyanamide moiety (entry 5) was well-tolerated, as this offers a convenient handle for further functionalization. The electronic effects of *para*-substituents on the aryl ring appeared to be inconsequential as substrates containing either electron-donating ($\text{R} = \text{Me}$, OMe , entries 1 and 7) or electron-withdrawing ($\text{R} = \text{F}$, CF_3 , entries 3 and 6) groups *para* to the cyanamide underwent the reaction in excellent yields (92%). Substitution at the alkene, either alkyl or phenyl, was tolerated and, in fact, necessary for the reaction. The ethyl- and phenyl-1,1-substituted alkenes (**1i** and **1j**, entries 8 and 9) afforded the corresponding indolines in high yields; however, allyl substrate **1n** returned only unconsumed starting material (entry 13). Substrates with internal alkenes (including trisubstituted) provided complex mixtures of products, alkene substitution remains a limitation at this time. Benzyloxymethyl-substituted alkene **1m** also failed to provide product (entry 12), which was tentatively attributed to the inductive effect of the benzyloxy group (*vide infra*).^[25] An extended alkene tether found in substrate **1k** afforded the tetrahydroquinoline **2k** in 93% yield (entry 10). Changing the protecting group at nitrogen from tosyl to nosyl in substrate **1l** provided *para*-nosyl indoline **2l** in almost quantitative yield (99%, entry 11). The relatively mild conditions for cleaving nosyl groups should allow convenient post-functionalization on the nitrogen atom.^[26] Additionally, methyl substitution ortho to the cyanamide moiety (entry 14) was tolerated, giving indoline **2o** in 90% yield.

Based on the ability of $\text{B}(\text{C}_6\text{F}_5)_3$ to promote intramolecular aminocyanation, we needed to revise our mechanistic thinking. Wang and coworkers recently reported that electrophilic cyanations of indoles^[27] is accomplished using NCTS and a Lewis acid. This provides precedence for the nucleophilic cleavage of N-CN bonds and cyano group transfer under Lewis acid conditions. In aminocyanation, however, both groups are transferred to the alkene. We hypothesized that the N_{CN} lone pair of cyanamide **1a** initially coordinated to $\text{B}(\text{C}_6\text{F}_5)_3$ affording adduct **I-1** (Scheme 2).^[28] This set the stage for an intramolecular nucleophilic attack of the alkene, but the mode of attack was unclear.

We considered a mechanism involving N-CN cleavage via aziridinium ion formation (path A, Scheme 2) and a non-fragmenting pathway involving nucleophilic attack of the alkene at the central cyanamide carbon (path B, Scheme 2). Aziridinium ion formation via $\text{B}(\text{C}_6\text{F}_5)_3$ -promoted loss of cyanide was attractive due to the remarkable “anion abstracting properties of this special boron compound”.^[29, 30] The hypothesis involving nucleophilic attack of the

alkene at the central cyanamide carbon was attractive since this is the typical site of nucleophile attack on cyanamides.^[31] These hypotheses were tested by a double-crossover experiment (Scheme 2). A mixture of **1d** and the ¹³C-labeled cyanamide **1a** (**1a-¹³CN**) afforded only the non-crossover products **2d** and **2a-¹³CN**. The lack of crossover in the experiment indicated that alkene aminocyanation proceeds in a fashion that is inconsistent with the aziridinium ion hypothesis (Path A).^[32]

The crossover experiments ruled out path A. We note that the success of cyanamides bearing more nucleophilic alkenes (such as **1i** and **1j**) and the failure of cyanamides bearing less nucleophilic alkenes (**1m** and **1n**) is consistent with rate-limiting alkene attack. The mechanism by which intermediate **I-3** converts to product is not yet clear. In principle, formation of the new C-N_{Ts} bond could occur either before or after rupture of the N_{Ts}-CN bond. Intriguingly, instead of giving the corresponding four-membered benzazetidine,^[33] the reaction of *o*-isopropenyl-substituted cyanamide **1o** led to alkenyl nitrile **2o** in quantitative yield (Scheme 2, bottom).^[34] These results show that the type of cyano group transfer developed by Wang and Falck does not require added rhodium. Future work will explore the mechanistic consequence of this observation for aminocyanation.

Our mechanistic hypothesis suggested that B(C₆F₅)₃ might act as a catalyst. To test this hypothesis, **1a** was treated with 20 mol % B(C₆F₅)₃ in toluene and heated at 90 °C for an extended time (48 h). We were pleased to find that **2a** was formed in 91% yield. These results indicate that the coordination of B(C₆F₅)₃ to the product is not so strong as to preclude turnover. Due to the relatively high cost of commercial B(C₆F₅)₃, cost-saving by catalysis may be achieved at the expense of reaction time. After a successful small-scale reaction of **1c** with 20 mol % B(C₆F₅)₃ under nitrogen, we repeated the reaction on larger scale, heating at 100 °C for 48 h under an atmosphere of air. We obtained **2c** in 94% yield (Scheme 3).

In summary, we have developed a Lewis acid-promoted intramolecular aminocyanation of alkenes. The addition of transition metal catalysts or initiators is not required. We believe we have identified a new mechanistic pathway for aminative alkene difunctionalization via the addition of bench-stable, readily available, cyanamides. We demonstrated the aminocyanation reaction in the preparation of two important classes of nitrogen-heterocycles, indolines and tetrahydroquinolines in excellent yields. Current efforts are directed towards further elucidating the mechanism and expanding the scope, as well as developing intermolecular variants of aminocyanation. Further work will be directed towards development of a catalytic asymmetric variant of the reaction and further studies on the mechanism by probing the stereochemistry of the addition process.

Experimental Section

See the supporting information for experimental details.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Established methods for alkene carboamination **This Work**

Direct aminocyanation for the synthesis of β -aminonitriles

Scheme 1.
Carboamination of Alkenes

Scheme 2.
Mechanistic Experiments and Considerations

Scheme 3.
Catalysis with $\text{B}(\text{C}_6\text{F}_5)_3$ and Reaction Under Air

Table 1

Development of Aminocyanation Conditions

Entry	Metal ^a	Lewis acid ^b	Temp (°C)	Yield of 2a (%)
1	[Rh(C ₂ H ₄) ₂ Cl] ₂	BPh ₃ (1.2 equiv)	110	49 ^c
2	[Rh(C ₂ H ₄) ₂ Cl] ₂	B(C ₆ F ₅) ₃	110	72 ^d
3	[Rh(C ₂ H ₄) ₂ Cl] ₂	B(C ₆ F ₅) ₃	90	89 ^d
4	[Rh(C ₂ H ₄) ₂ Cl] ₂	B(C ₆ F ₅) ₃	80	71 ^d
5	-	B(C ₆ F ₅) ₃	90	90 ^d
6	-	BF ₃ •OEt ₂	90	31 ^d
7	-	AlCl ₃	90	52 ^d
8	-	Me ₂ AlCl	90	11 ^c
9	-	Ag(OSO ₂ CF ₃)	90	- ^e
10	-	Cu(OSO ₂ CF ₃) ₂	90	- ^e
11	-	Zn(OSO ₂ CF ₃) ₂	90	- ^f
12	-	Sc(OSO ₂ CF ₃) ₃	90	- ^f
13	-	SnCl ₄	90	49 ^c
14	-	BPh ₃	150	- ^f

^a 5 mol% Rh complex used.^b 1.0 equiv of Lewis acid was used unless otherwise specified.^c Determined by ¹H NMR analysis using *p*-methoxyacetophenone as the internal standard.^d Yield after column chromatography.^e No **2a** detected by NMR, complex mixture formed.^f No **2a** detected by NMR, only **1a** was detected.

Table 2

Scope of Alkene Aminocyanation^a

Entry	Substrate	Product	Yield (%) ^b
1	1b , R = Me	2b	92
2	1c , R = <i>t</i> -Bu	2c	92 ^c
3	1d , R = F	2d	>99
4	1e , R = Cl	2e	95
5	1f , R = Br	2f	96
6	1g , R = CF ₃	2g	94
7	1h , R = OMe	2h	99
8			>99
	1i	2i	
9			>99
	1j	2j	
10 ^d			93
	1k	2k	
11			99
	1l	2l	
12		– ^e	0
	1m		

Entry	Substrate	Product	Yield (%) ^b
13	1n	^e	0
14	1o	2o	90

Ts = *p*-toluenesulfonyl, Ns = *p*-nitrobenzenesulfonyl.

^a Conditions: substrate (0.1 mmol), B(C₆F₅)₃ (0.1 mmol), PhMe (0.5 mL), 90 °C, 24 h.

^b Yields after column chromatography.

^c Average of two runs.

^d Reaction time: 28 h.

^e Unconsumed starting material.