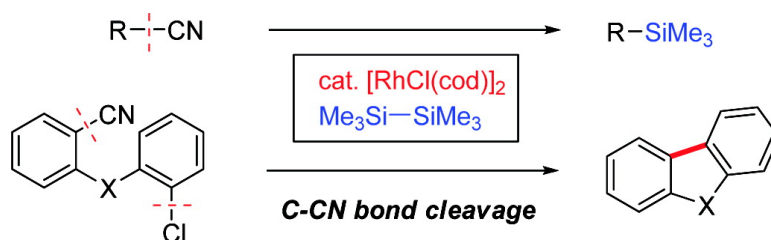


## Rhodium-Catalyzed Silylation and Intramolecular Arylation of Nitriles via the Silicon-Assisted Cleavage of Carbon#Cyano Bonds

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# Rhodium-Catalyzed Silylation and Intramolecular Arylation of Nitriles via the Silicon-Assisted Cleavage of Carbon–Cyano Bonds

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**Abstract:** A rhodium-catalyzed silylation reaction of carbon–cyano bonds using disilane has been developed. Under these catalytic conditions, carbon–cyano bonds in aryl, alkenyl, allyl, and benzyl cyanides bearing a variety of functional groups can be silylated. The observation of an enamine side product in the silylation of benzyl cyanides and related stoichiometric studies indicate that the carbon–cyano bond cleavage proceeds through the deinsertion of silyl isocyanide from  $\eta^2$ -iminoacyl complex **B**. Knowledge gained from these studies has led to the development of a new intramolecular biaryl coupling reaction in which aryl cyanides and aryl chlorides are cross-coupled.

## Introduction

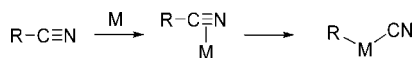
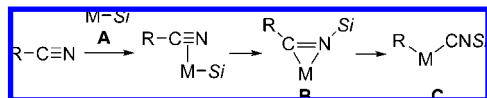
The cleavage of carbon–carbon  $\sigma$ -bonds by transition-metal complexes and their use for chemical transformation would provide a conceptually new strategy in organic synthesis. However, the inherent stability of carbon–carbon  $\sigma$ -bonds makes the development of such a process a daunting challenge. Although some success has been attained to this end, it has usually required the utilization of strained carbon–carbon bonds or chelation-assisted systems.<sup>1,2</sup> This limitation is absent in the transition-metal-mediated cleavage of carbon–carbon  $\sigma$ -bonds in nitriles, in which the strong carbon–cyano (C–CN) bond

(ca. 130 kcal/mol for Ar–CN) can be cleaved without the aid of ring strain or extra coordinating groups.<sup>3</sup> Fundamental interest in this unique process has prompted organometallic chemists to identify two discrete mechanisms for the activation of C–CN bonds. One process involves the oxidative addition to a low-valent metal center, such as Pt,<sup>4</sup> Pd,<sup>5</sup> Ni,<sup>6</sup> and others<sup>7</sup> (Scheme 1). The vast majority of reported C–CN bond cleavage reactions have occurred through this oxidative addition mechanism, and its application to catalytic processes, including isomerization,<sup>8</sup> cross-coupling,<sup>9</sup> and carbocyanation,<sup>10</sup> has also been discussed.<sup>11</sup> In 2003, Bergman and Brookhart reported an alternative mechanism in which a silyl ligand on the metal complex plays a critical role (Scheme 2, M = Rh).<sup>12–14</sup> The insertion of a cyano group into a metal–silyl bond in **A** forms the  $\eta^2$ -iminoacyl complex **B**, which undergoes the deinsertion of silyl isocyanide to afford the carbon–carbon bond cleaved complex

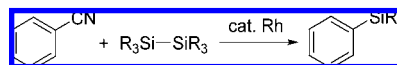
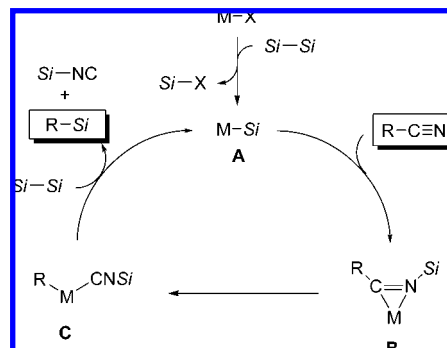
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**Scheme 1.** C–CN Bond Cleavage via Oxidative Addition**Scheme 2.** C–CN Bond Cleavage via Deinsertion of Silyl Isocyanide

C. Nakazawa subsequently reported that a silyliron complex can mediate the C–CN bond cleavage under photochemical conditions via the same mechanism (Scheme 2, M = Fe).<sup>15</sup> This iron-mediated photochemical process was further applied to the catalytic conversion of a C–CN bond into a C–H bond using hydrosilane as a reducing agent.<sup>15b,c,e</sup> Recently, Hashimoto and Tobita reported that the reaction of a ruthenium silylene complex with nitriles resulted in the formation of a ruthenium silyl isocyanide complex, as in **C** (M = Ru).<sup>16</sup> A silicon-assisted mechanism, similar to that shown in Scheme 2, has been proposed as one of the two possibilities for this ruthenium-mediated C–CN bond cleavage process. On the other hand, we recently reported that a C–CN bond can be cleaved catalytically in the presence of a rhodium complex and disilanes to form a C–Si bond (Scheme 3).<sup>17</sup> This reaction represents the first illustration that the silicon-assisted catalytic cleavage

**Scheme 3.** Rhodium-Catalyzed Silylation of Nitriles via C–CN Bond Cleavage**Scheme 4.** Mechanistic Hypothesis for the Catalytic Silylation of Nitriles

of C–CN bonds proceeds thermally. The full details of this catalysis are described herein, including reaction condition optimization, substrate scope, mechanistic aspects, and application to intramolecular arylation.

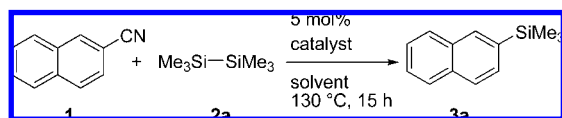
**Results and Discussion**

**Silylation of Aryl, Alkenyl, and Alkyl Cyanides.** To construct a catalytic cycle that contains a silicon-assisted C–CN bond cleavage process (Scheme 2), it was necessary to define the pathway for regenerating the silylmetal species from the C–CN cleaved complex **C** (Scheme 4). The approach used to address this issue was the utilization of disilanes, which would react with the complex **C** to form carbon–silicon and metal–silicon bonds via  $\sigma$ -bond metathesis or an oxidative addition/reductive elimination sequence.<sup>18</sup> Overall, it was expected that the reaction of nitriles with disilanes would result in the formation of organosilanes and silyl isocyanides. It was also expected that the use of disilanes might allow the in situ generation of the metal silyl species **A** from the readily available metal halides or their derivatives.

The studies began with an investigation of the reaction of 2-cyanonaphthalene (**1**) and hexamethyldisilane (**2a**) as a prototype for the catalysis shown in Scheme 4. A pioneering work by Bergman and Brookhart led to the initial examination of  $[\text{Cp}^*\text{RhCl}_2]_2/\text{PPh}_3$  as a catalyst precursor, and it was found that the expected 2-(trimethylsilyl)naphthalene (**3a**) was obtained in 12% yield (entry 1 in Table 1). Stimulated by this promising result, a variety of rhodium complexes were then examined. Several Rh(I) complexes, such as  $[\text{RhCl}(\text{cod})_2]$ ,  $[\text{RhCl}(\text{coe})_2]$ ,  $[\text{RhOMe}(\text{cod})_2]$ , and  $[\text{Rh}(\text{cod})_2]\text{BF}_4$ , exhibited much-improved catalytic activity (entries 2–5), while  $[\text{RhCl}(\text{CO})_2]$ ,  $[\text{IrCl}(\text{cod})_2]$ , and  $[\text{Cp}^*\text{RuCl}]_n$  were inactive under these conditions. Interestingly, the  $\text{Ni}(\text{cod})_2/\text{PBu}_3$  system, which is competent for the oxidative addition of C–CN bonds,<sup>8–10</sup> did not give any silylated products. The solvent employed also proved to be an important factor in the efficiency of the reaction. Among the solvents examined, ethylcyclohexane gave the highest yield (entry 8). Although the reaction was routinely conducted at 130 °C, it

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**Table 1.** Rh(I)-Catalyzed Silylation Reaction of Nitriles: Catalyst and Solvent Optimization<sup>a</sup>

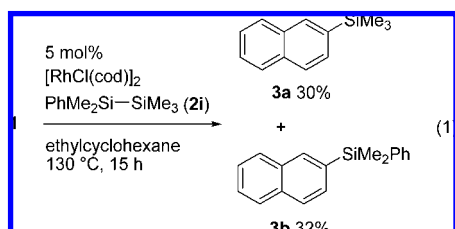
entry	catalyst	solvent	yield <sup>b</sup> (%)
1	[Cp*RhCl <sub>2</sub> ] <sub>2</sub> /2PPh <sub>3</sub>	mesitylene	12
2	[RhCl(cod)] <sub>2</sub>	mesitylene	53
3	[RhCl(coe)] <sub>2</sub>	mesitylene	62
4	[Rh(OMe)(cod)] <sub>2</sub>	mesitylene	80
5 <sup>c</sup>	[Rh(cod) <sub>2</sub> BF <sub>4</sub> ]	mesitylene	65
6	[RhCl(cod)] <sub>2</sub>	dioxane	71
7	[RhCl(cod)] <sub>2</sub>	DMA	36
8	[RhCl(cod)] <sub>2</sub>	ethylcyclohexane	87
9 <sup>d</sup>	[RhCl(cod)] <sub>2</sub>	ethylcyclohexane	49

<sup>a</sup> Reaction conditions: **1** (2.0 mmol), **2a** (4.0 mmol), catalyst (0.10 mmol) in solvent (1.0 mL) at 130 °C, 15 h. <sup>b</sup> Isolated yields. <sup>c</sup> A 10 mol % concentration of [Rh(cod)<sub>2</sub>BF<sub>4</sub>] was used. <sup>d</sup> Run at 100 °C.

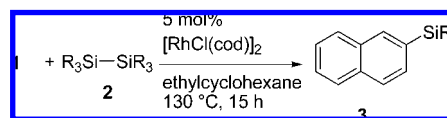
could proceed at a lower temperature (100 °C), albeit at a slower rate (entry 9). Addition of ligands, such as PPh<sub>3</sub>, PBu<sub>3</sub>, P(OPh)<sub>3</sub>, and pyridine, led to a decrease in the yield, probably due to their competitive coordination with a cyano group.

The effect of the substituents on the silicon atom of disilanes was examined next (Table 2). When one of the methyl groups on each silicon atom in **2a** was replaced with a phenyl (**2b**) or benzyl (**2c**) group, the corresponding silylated products were obtained in modest yields (entries 2 and 3). However, the use of the much bulkier *tert*-butyldimethylsilyl (**2d**), methyl diphenylsilyl (**2e**), and triethylsilyl (**2f**) groups led to no conversion at all (entries 4–6). The activation of silicon–silicon bonds is often accelerated by the introduction of electron-withdrawing groups on the silicon moiety.<sup>18</sup> However, in the present catalytic system, no desired products were formed with disilanes **2g** and **2h**, due in part to the instability of these disilanes under the reaction conditions (entries 7 and 8).

Unsymmetrically substituted disilanes were also examined. The reaction of **1** with 1,1,1,2,2-pentamethyl-2-phenyldisilane (**2i**) under standard conditions resulted in the formation of equimolar amounts of **3a** and **3b**, indicating that trimethylsilyl and dimethylphenylsilyl groups are not differentiated significantly in any of the steps involved in the present catalysis (eq 1).



The scope of the Rh-catalyzed silylation of nitriles with **2a** was then examined (Table 3). A number of functional groups, such as fluorines (entries 1, 2, and 13), esters (entries 3, 4, 7, and 11), ethers (entries 8 and 10), and amines (entry 9) proved to be compatible with this catalytic system. The presence of an acidic NH group lowered the yield of the silylated product, due to the accompanied formation of the product in which a cyano group is substituted by a hydrogen atom (entry 5). In contrast, *N,N*-disubstituted amides were well suited for this catalytic silylation (entry 6). The high functional group tolerance of the

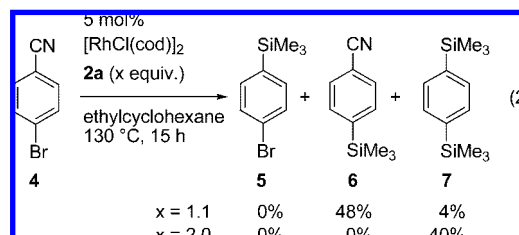
**Table 2.** Rh(I)-Catalyzed Silylation Reaction of Nitriles: Disilane Variation<sup>a</sup>

entry	disilane	yield <sup>b</sup> (%)
1	Me <sub>3</sub> Si–SiMe <sub>3</sub> ( <b>2a</b> )	87
2	PhMe <sub>2</sub> Si–SiMe <sub>2</sub> Ph ( <b>2b</b> )	46
3	BnMe <sub>2</sub> Si–SiMe <sub>2</sub> Bn ( <b>2c</b> )	41
4	<i>t</i> -BuMe <sub>2</sub> Si–SiMe <sub>2</sub> <i>t</i> -Bu ( <b>2d</b> )	0
5	Ph <sub>2</sub> MeSi–SiMePh <sub>2</sub> ( <b>2e</b> )	0
6	Et <sub>3</sub> Si–SiEt <sub>3</sub> ( <b>2f</b> )	0
7	FMe <sub>2</sub> Si–SiMe <sub>2</sub> F ( <b>2g</b> )	0
8	(EtO) <sub>3</sub> Si–Si(OEt) <sub>3</sub> ( <b>2h</b> )	0

<sup>a</sup> Reaction conditions: **1** (2.0 mmol), **2** (4.0 mmol), catalyst (0.10 mmol) in solvent (1.0 mL) at 130 °C, 15 h. <sup>b</sup> Isolated yields.

process was further demonstrated by the successful use of benzonitriles containing boronic esters (entry 14), indicating that the transfer of the aryl group on the boron to a rhodium center did not occur under these conditions.<sup>19</sup> In addition to benzonitrile derivatives, nitriles containing heteroaromatics, such as pyrroles (entry 17), indoles (entry 18), and quinolines (entry 19), and a Cp ring of ferrocene (entry 20) were all good substrates for the Rh-catalyzed reaction. On the other hand, the reaction of benzonitriles bearing nitro, acetyl, and acetamide groups did not give any silylated products. In the course of the examination of the reaction scope, a significant impact of the electronic nature of nitriles on the reaction rate was observed. In general, electron-deficient substrates were silylated faster than electron-rich nitriles. For example, 4-methoxybenzonitrile required more than 40 h for the full conversion, while the reaction of a 4-(trifluoromethyl)benzonitrile was completed within 15 h (entry 1 vs entry 8). The reaction was also sensitive to the steric environment of the nitrile moiety. Thus, the use of sterically congested substrates retarded the reaction (entries 12 and 16). Rate acceleration resulting from the introduction of an electron-withdrawing group could compensate for this unfavorable steric effect (entry 13).

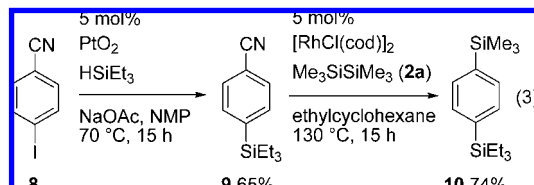
The compatibility of the aryl halide moiety was investigated next. Although aryl fluorides remained intact under the Rh-catalyzed reaction (entry 2), chlorides and bromides proved to be susceptible to silylation. For example, the reaction of 4-bromobenzonitrile (**4**) with 1.1 equiv of disilane **2a** resulted in the selective formation of compound **6**, in which the silylation took place at the bromide site (eq 4). By increasing the amount of **2a**, both functionalities were silylated, furnishing a 1,4-bis(trimethylsilyl)benzene, **7**. It has been reported that rhodium complexes can catalyze the silylation of aryl halides using hydrosilanes,<sup>20a–c</sup> but the rhodium catalysis with disilanes is unprecedented, to the best of our knowledge.<sup>21</sup>



Although the present catalysis promotes the silylation of both aryl halides and cyanides, it is known that the former function-



ality can also be silylated by other catalytic methods.<sup>20,21</sup> We envisioned that, by combining such a method with our catalytic silylation, halides and nitriles could be silylated orthogonally. As expected, the Pt-catalyzed reaction<sup>20f</sup> of 4-iodobenzonitrile (**8**) allowed the selective introduction of a triethylsilyl group at the iodide site without affecting the nitrile functionality (eq 4). The subsequent silylation of a cyano group in **9** by rhodium catalysis afforded a benzene derivative containing two different silyl groups, as in **10**.



To further extend the scope of the reaction, we examined the silylation of alkenyl cyanides (Table 4). At the time that we initiated this study, there had been no reports on catalytic reactions involving the cleavage of alkenyl C–CN bonds, irrespective of the mechanism involved. Nakao and Hiyama recently reported that a Ni(0)/Lewis acid dual catalyst system can promote the addition of alkenyl C–CN bonds to alkynes.<sup>10e</sup> We were pleased to find that the C–CN bond of *trans*-cinnamonitrile could be silylated with disilanes under these Rh-catalyzed conditions (entry 1). The silylation of the *cis*-isomer exclusively afforded the corresponding alkenylsilane with *trans* geometry (entry 2). A silylated product was not obtained with alkenyl cyanide bearing an alkyl group, presumably because the starting cyanide was prone to decompose under the reaction conditions (entry 3). On the other hand, more stable cyclohexenyl cyanide could be silylated in moderate yield (entry 4). Notably, sterically congested 2,2-disubstituted alkenyl cyanide proved to be a good substrate for this reaction (entry 5). Although alkenyl cyanide containing three phenyl groups at each vinylic position was inert (entry 6), replacing one phenyl with an ester group remarkably enhanced the reactivity of the C–CN bond to furnish the corresponding silylated product (entry 7). This indicates that an electron-deficient C–CN bond exhibits superior reactivity, as was observed in the silylation of aryl cyanides (Table 3).

Allyl cyanides are also possible substrates for this catalytic reaction, in view of some successful examples of the catalytic cleavage of their C–CN bonds via oxidative addition.<sup>8,10c</sup> As expected, the silylation of allyl cyanide **11** furnished allylsilane **12** in 59% yield (eq 5). Complete conversion was reached at a lower temperature (100 °C), although the reactions of aryl and alkenyl cyanides generally required heating at 130 °C. The

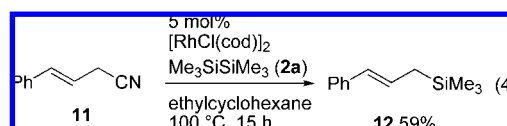
Table 3. Rh(I)-Catalyzed Silylation Reaction of Aryl Cyanides<sup>a</sup>

entry	nitrile	product	yield (%) <sup>b</sup>
1			R = CF <sub>3</sub> 94 <sup>c</sup>
2			R = F 97 <sup>c</sup>
3 <sup>d</sup>			R = CO <sub>2</sub> Et 69
4			R = CO <sub>2</sub> Bu- <i>t</i> 72
5			R = CONHBu- <i>t</i> 22 <sup>e</sup>
6			R = CONMeBu- <i>t</i> 60
7			R = OAc 54
8 <sup>f</sup>			R = OMe 69
9 <sup>g</sup>			R = NMe <sub>2</sub> 70
10			R = OMe 77
11			R = CO <sub>2</sub> Et 81
12 <sup>h</sup>			R = Me 35
13 <sup>i</sup>			R = CF <sub>3</sub> >99 <sup>c</sup>
14 <sup>g</sup>			78
15			87
16 <sup>j</sup>			57
17			78
18			81
19 <sup>d</sup>			57
20 <sup>d,f</sup>			73

<sup>a</sup> Reaction conditions: nitrile (2.0 mmol), **2a** (4.0 mmol), [RhCl(cod)]<sub>2</sub> (0.10 mmol) in ethylcyclohexane (1.0 mL) at 130 °C, 15 h. <sup>b</sup> Isolated yields. <sup>c</sup> GC yield. <sup>d</sup> [Rh(OMe)(cod)]<sub>2</sub> was used as a catalyst. <sup>e</sup> *N*-*tert*-Butylbenzamide was also isolated in 20% yield. <sup>f</sup> Run for 40 h. <sup>g</sup> [Rh(cod)<sub>2</sub>]BF<sub>4</sub> was used as a catalyst. <sup>h</sup> Run for 96 h. <sup>i</sup> Run for 60 h. <sup>j</sup> A 10 mol % concentration of the catalyst was used.

- (19) (a) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829.
- (20) For selected examples of the catalytic silylation of aryl halides using hydrosilanes, see the following references. Rh: (a) Murata, M.; Ishikura, M.; Nagata, M.; Watanabe, S.; Masuda, Y. *Org. Lett.* **2002**, *4*, 1843. (b) Murata, M.; Yamasaki, H.; Ueta, T.; Nagata, M.; Ishikura, M.; Watanabe, S.; Masuda, Y. *Tetrahedron* **2007**, *63*, 4087. (c) Yamanoi, Y.; Nishihara, H. *Tetrahedron Lett.* **2006**, *47*, 7157. Pd: (d) Seganish, W. M.; Handy, C. J.; DeShong, P. *J. Org. Chem.* **2005**, *70*, 8948. (e) Denmark, S. E.; Kallemeyn, J. M. *Org. Lett.* **2003**, *5*, 3483. Pt: (f) Hamze, A.; Provot, O.; Alami, M.; Brion, J.-D. *Org. Lett.* **2006**, *8*, 931.
- (21) Pd-catalyzed silylation of aryl halides using disilanes has been reported: (a) Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, 1895. (b) Gooßen, L. J.; Ferwanah, A.-R. S. *Synlett* **2000**, 1801. (c) Iwasawa, T.; Komano, T.; Tajima, A.; Tokunaga, M.; Obora, Y.; Fujihara, T.; Tsuji, Y. *Organometallics* **2006**, *25*, 4665.

relatively facile cleavage of C–CN bonds in the allyl cyanides might be attributed to the intermediacy of a stable  $\pi$ -allyl-rhodium complex.

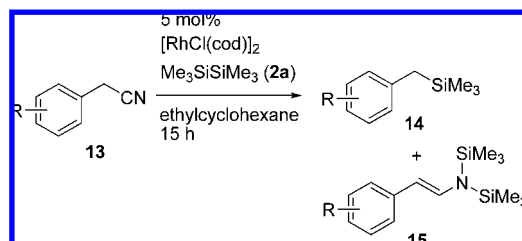


The silylation reaction of benzyl cyanides was examined next (Table 5). At 100 °C, the expected benzylsilanes **14** were obtained in low to moderate yields with an array of benzyl cyanides (entries 1–5). Since significant amounts of the starting

**Table 4.** Rh(I)-Catalyzed Silylation Reaction of Alkenyl Cyanides<sup>a</sup>

entry	nitrile	product	yield (%) <sup>b</sup>
1 <sup>c</sup>			73
2 <sup>c</sup>			44
3			0
4 <sup>c,d</sup>			55
5 <sup>d</sup>			56
6			trace
7 <sup>e</sup>			54

<sup>a</sup> Reaction conditions: nitrile (2.0 mmol), **2a** (4.0 mmol), [RhCl(cod)]<sub>2</sub> (0.10 mmol) in ethylcyclohexane (1.0 mL) at 130 °C, 15 h. <sup>b</sup> Isolated yields. <sup>c</sup> [Rh(OMe)(cod)]<sub>2</sub> was used as a catalyst. <sup>d</sup> A 10 mol % concentration of the catalyst was used. <sup>e</sup> Run for 3 h.

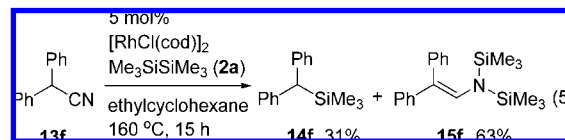
**Table 5.** Rh(I)-Catalyzed Silylation Reaction of Benzyl Cyanides<sup>a</sup>

entry	R	temp (°C)	isolated yields (%)		
			14 <sup>b</sup>	15 <sup>c</sup>	recovered 13 <sup>b</sup>
1	4-OMe ( <b>a</b> )	100	38	0	34
2	H ( <b>b</b> )	100	43	0	36
3	4-CF <sub>3</sub> ( <b>c</b> )	100	35	0	0
4	4-CO <sub>2</sub> Me ( <b>d</b> )	100	33	0	trace
5	2-Me ( <b>e</b> )	100	20	0	59
6	4-OMe ( <b>a</b> )	160	68	0	0
7	H ( <b>b</b> )	160	52	18	0
8	4-CF <sub>3</sub> ( <b>c</b> )	160	59	18	0
9	4-CO <sub>2</sub> Me ( <b>d</b> )	160	35	12	0
10	2-Me ( <b>e</b> )	160	63	17	trace

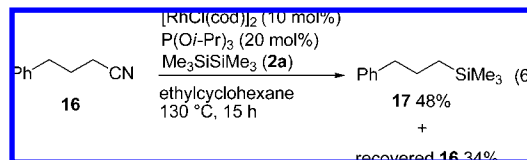
<sup>a</sup> Reaction conditions: benzyl cyanide **13** (2.0 mmol), **2a** (4.0 mmol), [RhCl(cod)]<sub>2</sub> (0.10 mmol) in ethylcyclohexane (1.0 mL) for 15 h. <sup>b</sup> Isolated yields. <sup>c</sup> Estimated by GC analysis.

benzyl cyanides were recovered in most cases, we decided to conduct the reactions at a higher temperature. At 160 °C, complete conversion was observed in all cases, and benzylsilylanes **14** were obtained in satisfactory yields (entries 6–10). Interestingly and importantly, the formation of enamine **15** (in which a C–CN bond is not cleaved) as a minor product (0–18%) was also observed in the silylation reaction of benzyl cyanides.

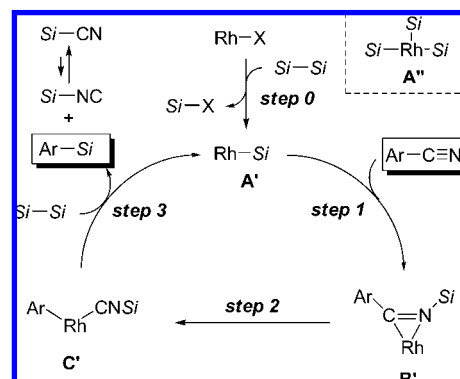
The product distribution (i.e., **14/15**) was not significantly affected by the electronic and steric nature of the aryl group of the benzyl cyanides. However, the predominant formation of the enamine product was observed in the silylation of diphenylacetonitrile **13f** at 160 °C (eq 5). The formation of unexpected side product **15** provided some insight into the reaction mechanism (vide infra).



Next, we turned our attention to the use of unactivated alkyl cyanides in this silylation reaction. Regardless of the mechanism involved, utilization of unactivated C(sp<sup>3</sup>)–CN bonds containing β-hydrogen atoms for the catalytic transformation represents a challenge, due to the difficulty in suppressing a facile β-hydrogen elimination process of the intermediate metal alkyl species.<sup>10e</sup> The ability of our catalytic system to silylate unactivated C(sp<sup>3</sup>)–CN bonds was investigated using nitrile **16** as a test substrate (eq 5). After a variety of optimization studies, the silylated product **17** was obtained in 48% yield by adding P(O-*i*-Pr)<sub>3</sub> as an additive. Although the efficiency of the reaction was unsatisfactory, it is noteworthy that byproducts arising from the β-hydrogen elimination process of the possible metal alkyl intermediate (i.e., allylbenzene or β-methylstyrene) were not observed.



**Mechanistic Considerations.** On the basis of the stoichiometric reaction reported by Bergman and Brookhard,<sup>12</sup> a possible mechanism that accounts for the silylation of C–CN bonds is illustrated in Scheme 5. The reaction of a catalyst precursor, such as [RhCl(cod)]<sub>2</sub>, with disilanes generates a rhodium(I) silyl species, **A'**, via σ-bond metathesis or an oxidative addition/reductive elimination sequence (step 0). As supporting evidence for this step, chlorotrimethylsilane, which should be generated, was observed by <sup>29</sup>Si NMR measurement of the stoichiometric reaction (see the Supporting Information for details). Migration of the silyl group in **A'** to the nitrogen atom of the substrate nitrile affords an η<sup>2</sup>-iminoacyl complex, **B'**. Migration of the silyl group in **B'** to the carbon atom of the substrate nitrile affords an η<sup>2</sup>-iminoacyl complex, **C'**. Finally, reductive elimination of the silyl group from **C'** yields the silylated product and regenerates the catalyst precursor.

**Scheme 5.** Possible Mechanism for Silylation of Aryl Cyanides

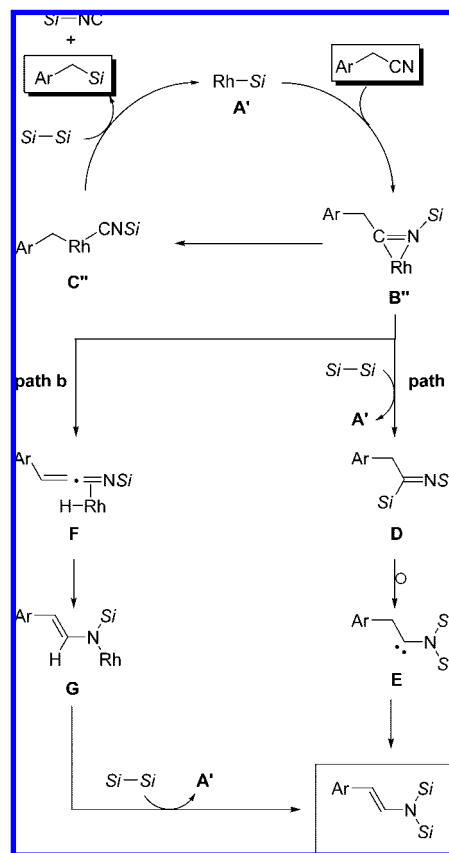
**B'** (step 1). Subsequent migration of the aryl group in **B'** to a rhodium center induces the cleavage of a C–C bond to form an arylrhodium complex, **C'** (step 2).  $\sigma$ -Bond metathesis between an Ar–Rh bond in **C'** and a Si–Si bond of disilane produces an arylsilane product and a rhodium silyl complex, **A'**, completing a catalytic cycle (step 3). As in step 0, a pathway through a Rh(III) intermediate (i.e., an oxidative addition/reductive elimination sequence) is also possible for step 3. The coordinated silyl isocyanide, which is formed in step 2, should be dissociated from a rhodium center in any of the steps for an efficient catalysis. The dissociated silyl isocyanide should isomerize, under the reaction conditions, to silyl cyanide, a more thermodynamically stable isomer.<sup>22</sup> Indeed, the formation of trimethylsilyl cyanide was confirmed by <sup>29</sup>Si NMR measurement of the crude reaction mixture obtained from the Rh-catalyzed reaction of **1** with **2a**. Furthermore, part of the dissociated trimethylsilyl cyanide could be trapped as cyanohydrin silyl ether<sup>15c</sup> by stirring the crude reaction mixture with acetophenone and I<sub>2</sub> (see the Supporting Information for details).

In addition to rhodium(I) silyl species **A'**, a rhodium(III) silyl complex, **A''**, which could be formed by oxidative addition of disilane to **A'**, is also a possible competent species for the catalytic silylation of nitriles. An iridium complex related to **A''** was proposed as a key intermediate in the catalytic silylation of C–H bonds.<sup>23</sup> No conclusive evidence is yet available concerning which of these complexes is responsible for the catalysis (**A'** and/or **A''**), although we have conducted several NMR studies on the stoichiometric reaction of [RhCl(cod)]<sub>2</sub> with **2a** in the presence or absence of nitriles (see the Supporting Information for details).

In relation to steps 1 and 2, Bergman and Brookhart investigated the effect of *para* substituents on the rate of the C–CN bond cleavage reaction of benzonitrile derivatives on a rhodium complex.<sup>12b</sup> They documented that the silyl migration reaction, which is related to step 1 in the present catalysis, is relatively insensitive to the electronic nature of the benzonitrile used. In contrast, the deinsertion of silyl isocyanide, which is related to step 2 in our catalysis, is accelerated by an electron-withdrawing group.<sup>24</sup> They noted that the rate enhancement by an electron-withdrawing group may be explained by destabilization of the Rh–N interaction in **B'** as well as the formation of a stronger Ar–Rh bond in the transition state. On the other hand, in the course of the examination of an array of nitriles in the catalytic silylation, a similar electronic effect of nitrile substrates on the overall rate was observed; the presence of electron-withdrawing groups resulted in an increased rate. Although neither experimental nor literature data concerning the sensitivity of step 3 to electronic effects are available, the observed effect of substituents can be well-rationalized by the assumption that step 2 is the turnover-limiting step in the present catalysis.

On the other hand, a small electronic effect was observed in the silylation of benzyl cyanides (Table 5). This might indicate that the turnover-limiting step in these cases lies in a different step than that in the reactions of aryl cyanides. The migratory

**Scheme 6.** Mechanistic Rationale for the Silylation of Benzyl Cyanides



extrusion of silyl isocyanide, a plausible turnover-limiting step in the case of aryl cyanides, is expected to be relatively facile in the case of benzyl cyanides, since it has been reported that the related migratory extrusion of carbon monoxide from Rh–C(=O)CH<sub>2</sub>Ph has a lower activation energy than that from Rh–C(=O)Ph.<sup>24</sup> Another important observation of the reactions of benzyl cyanides is the formation of enamine side product **15** (Table 5).<sup>25</sup> Possible routes leading to enamine are provided in Scheme 6. The  $\eta^2$ -iminoacyl complex **B''** serves as a common intermediate for the formation of both benzylsilanes and enamines. The reaction of complex **B''** with disilane affords iminosilane **D** and regenerates the active species **A'** (path a). This process (**B''** → **D**) can be related to the acylsilane formation process by the reaction of a metal acyl complex with disilane.<sup>26</sup> The silyl group at the imino carbon atom in **D** then migrates to the imino nitrogen atom via aza-Brook-type rearrangement to give  $\alpha$ -aminocarbene **E** or its metal-bound species.<sup>27</sup> Finally, insertion of the carbene moiety in **E** into a benzylic C–H bond furnishes the observed enamine product. An alternate pathway is initiated by  $\beta$ -hydrogen elimination from  $\eta^2$ -iminoacyl

(22) (a) Thayer, J. S. *Inorg. Chem.* **1968**, *7*, 2599. (b) Secker, J. A.; Thayer, J. S. *Inorg. Chem.* **1976**, *15*, 501.

(23) (a) Ishiyama, T.; Sato, K.; Nishio, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 5346. (b) Ishiyama, T.; Sato, K.; Nishio, Y.; Miyaura, N. *Chem. Commun.* **2005**, 5065. (c) Saiki, T.; Nishio, Y.; Ishiyama, T.; Miyaura, N. *Organometallics* **2006**, *25*, 6068.

(24) A similar electronic effect was also observed in mechanistically related rhodium-catalyzed decarbonylation of aldehydes: Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P.-O.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 5206.

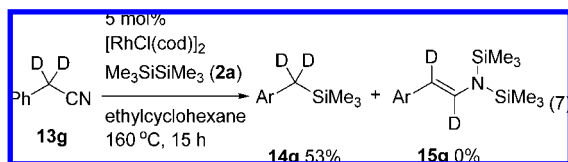
(25) For transition-metal-mediated synthesis of *N,N*-disilylenamines, see: (a) Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *Organometallics* **1985**, *4*, 623. (b) Murai, T.; Sakane, T.; Kato, S. *J. Org. Chem.* **1990**, *55*, 449.

(26) (a) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 1653–1656. (b) Eaborn, C.; Griffiths, R.; Pidcock, A. J. *Organomet. Chem.* **1982**, *225*, 331. (c) Ricci, A.; Degl'Innocenti, A.; Chimichi, S.; Fiorenza, M.; Rossini, G. *J. Org. Chem.* **1985**, *50*, 130. (d) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974.

(27) Suginome, M.; Fukuda, T.; Ito, Y. *J. Organomet. Chem.* **2002**, *643–644*, 508.

complex **B''**, resulting in the formation of ketene imine **F** (path b).<sup>28</sup> The eliminated rhodium hydride then adds to a C=N bond in **F** to give a rhodium enamide intermediate, **G**. *N*-Silylation of **G** with disilane produces an enamine and a rhodium silyl complex, **A'**.

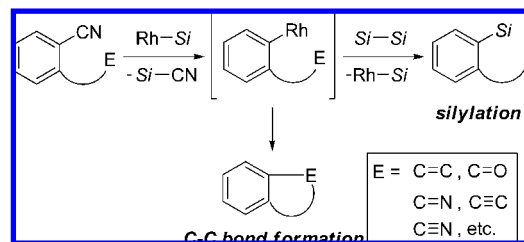
The yields of the enamine **15** were, in general, lower than those of benzylsilane **14**, and the formation of enamine was observed at a higher temperature (160 °C). These results indicate that the pathway leading to enamines is an energetically difficult process, compared with that leading to benzylsilanes. To gain more insight into the mechanism for the formation of enamines, the silylation reaction of deuterated benzyl cyanide **13g** was examined (eq 7). In contrast to the results using nonlabeled benzyl cyanide **13b**, enamine **15g** was not detected, while benzylsilane **14g** was obtained in 53% yield. This observation suggests that there is a moderately large kinetic isotope effect in the C–H bond cleavage step (**E** → enamine in path a or **B''** → **F** in path b) and the deuterium elimination is not competitive with silylation. In the case of silylation of **13f**, the activation energy for the C–H bond cleavage is lowered due to the formation of more stable trisubstituted enamine **15f**. Although there is no firm evidence to distinguish paths a and b at this point, we currently favor the latter mechanism involving  $\beta$ -hydrogen elimination, since iminosilane **D** would be detected during the course of the reaction if enamine is formed through path a. Irrespective of the mechanism involved, a key point is that the formation of the enamines strongly supports the intermediacy of  $\eta^2$ -iminoacyl complex **B''** in the rhodium-catalyzed C–CN bond cleavage reaction.



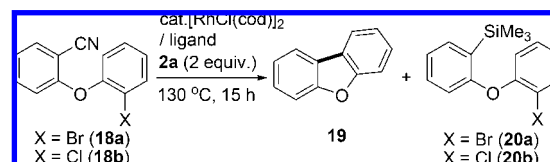
**Intramolecular Arylation of Nitriles.** As discussed above, we postulated an arylrhodium intermediate (**C'** in Scheme 5) in the silylation of aryl cyanides. In view of a number of reactions of such intermediates with diverse electrophiles,<sup>29,30</sup> it was envisaged that the postulated arylrhodium species in the catalysis should be intercepted by tethered electrophiles, such as enones, aldehydes, and nitriles, resulting in an intramolecular cyclization (Scheme 7).

To realize the carbon–carbon bond formation process depicted in Scheme 7, a variety of tethered electrophiles were examined. It was found that benzonitrile **18a**, which contains a bromophenyl moiety, afforded the desired cyclization product **19** in 10% yield (entry 1 in Table 6).<sup>31</sup> However, the major product was a disilylated compound in which both C–CN and C–Br bonds were silylated. The use of the chloride analogue **18b** increased the yield of **19** to 42% by suppressing the

**Scheme 7.** Utilization of an Arylrhodium Complex for Intramolecular Cyclizations



**Table 6.** Rhodium-Catalyzed Intramolecular Arylation of Nitrile **18**<sup>a</sup>



entry	X	ligand	isolated yields (%)		
			19	20	recovered 18
1	Br	none	10	0 (57) <sup>b</sup>	0
2	Cl	none	42	10	40
3	Cl	P(O <i>i</i> -Pr) <sub>3</sub>	45	6	31
4	Cl	P(4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	35	trace	61
5 <sup>c</sup>	Cl	P(4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	71	trace	27

<sup>a</sup> Reaction conditions: **18** (0.5 mmol), **2a** (1.0 mmol), [RhCl(cod)]<sub>2</sub> (0.025 mmol), and ligand (0.050 mmol) in ethylcyclohexane (1.0 mL) at 130 °C, 15 h. <sup>b</sup> Yield of bis[2-(trimethylsilyl)phenyl] ether. <sup>c</sup> [RhCl(cod)]<sub>2</sub> (0.050 mmol) was used.

undesired C–X bond silylation, although silylation at the C–CN bond accompanied to give **20b** in 10% yield (entry 2). Screening of the ligand revealed that the addition of P(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> effectively suppressed the formation of **20b** (entry 4). The yield of the cyclization product **19** was improved by increasing the catalyst loading without deteriorating the selectivity (entry 5).

Under these conditions, intramolecular arylation involving C–CN bond cleavage proceeded with several substrates to furnish tricyclic systems (Table 7). Substituted dibenzofurans could be synthesized in satisfactory yields via the intramolecular cross-coupling of aryl cyanides and aryl chlorides (entries 1–4). An attempt to apply this methodology to a pyridine-containing system failed under the standard conditions, probably due to the catalyst deactivation through the coordination of pyridine to rhodium. However, the addition of a catalytic amount of InCl<sub>3</sub> in place of P(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, dramatically increased the yield of the product (entry 5). Since this acceleration effect of InCl<sub>3</sub> was not observed in other substrates shown in Table 7, we consider that the effect is brought by the suppression of catalyst deactivation through the coordination of pyridine to InCl<sub>3</sub>, rather than by the nitrile activation.<sup>10e</sup> A nitrogen-tethered substrate could also be applied successfully to form a carbazole derivative (entry 6). In addition to aryl C–CN bonds, a benzylic C–CN bond could be arylated under these conditions, providing access to a fluorene framework (entry 7).

The construction of an aryl–aryl linkage is one of the most important synthetic processes. The metal-catalyzed cross-coupling reactions of aryl (pseudo)halides and arylmetal reagents, such as Grignard reagents and boronic acids, are currently the methods of widespread utility.<sup>32</sup> Considering the

- (28) (a) Torii, S.; Okumoto, H.; Sadakane, M.; Hai, A. K. M. A.; Tanaka, H. *Tetrahedron Lett.* **1991**, *34*, 6553. (b) Tanaka, H.; Hai, A. K. M. A.; Sadakane, M.; Okumoto, H.; Torii, S. *J. Org. Chem.* **1994**, *59*, 3040. (c) Zhou, Z.; Alper, H. *J. Org. Chem.* **1996**, *61*, 1256.  
 (29) Miura, T.; Murakami, M. *Chem. Commun.* **2007**, 217. See also ref 19.  
 (30) For our works along this line, see: (a) Harada, Y.; Nakanishi, J.; Fujihara, H.; Tobisu, M.; Fukumoto, Y.; Chatani, N. *J. Am. Chem. Soc.* **2007**, *129*, 5766. (b) Miyamoto, M.; Harada, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2008**, *10*, 2975.  
 (31) The reaction of arylrhodium species, generated from arylboron compounds, with aryl halides leading to biaryls has been reported: Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2005**, *7*, 2229.

- (32) For a review on industrial application of metal-catalyzed cross-coupling reactions, see: Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651.



Table 7. Rhodium-Catalyzed Intramolecular Arylation of Nitriles<sup>a</sup>

entry	nitrile	product	yield (%) <sup>b</sup>
1			71
2 <sup>c</sup>			78
3 <sup>c</sup>			68
4 <sup>c</sup>			65
5 <sup>d</sup>			53
6 <sup>e</sup>			55 <sup>f</sup>
7 <sup>g</sup>			60 <sup>h</sup>

<sup>a</sup> Reaction conditions: nitrile (0.5 mmol), **2a** (1.0 mmol), [RhCl(cod)]<sub>2</sub> (0.05 mmol), and P(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> (0.10 mmol) in ethylcyclohexane (1.0 mL) at 130 °C, 15 h. <sup>b</sup> Isolated yield. <sup>c</sup> P(O-*i*-Pr)<sub>3</sub> (0.10 mmol) was used in place of P(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. <sup>d</sup> InCl<sub>3</sub> (0.10 mmol), in place of P(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, and dioxane (2 mL), in place of ethylcyclohexane, were used. A 6–7% yield of the silylated product was also formed. <sup>e</sup> Run at 160 °C using **2a** (2.0 mmol). <sup>f</sup> (2-Chlorophenyl)phenylamine was also obtained in 18% yield. <sup>g</sup> P(O-*i*-Pr)<sub>3</sub> (0.10 mmol) was used in place of P(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. Run at 160 °C for 40 h. <sup>h</sup> The silylated product was also obtained in 15% yield.

cost, availability, and stability of the organometallic coupling partners, recent efforts have been devoted to replacing the organometallic reagents with simple organic compounds in such cross-coupling reactions. Although simple arenes are the most ideal coupling partners to this end, the issue of regioselectivity must be addressed.<sup>33</sup> In this context, decarboxylative coupling, in which aryl carboxylic acids can serve as an aryl source in the cross-coupling with aryl halides, represents a notable method.<sup>34</sup> The results shown in Table 7 lay the foundation for

(33) For recent reviews, see: (a) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (b) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (c) Campeau, L.-C.; Stuart, D. R.; Fagnou, K. *Aldrichimica Acta* **2007**, *24*. (d) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 200. (e) Li, B.-J.; Yang, S.-D.; Shi, Z.-J. *Synlett* **2008**, *7*, 949.

the establishment of metal-catalyzed cross-coupling processes that utilize aryl cyanides as nucleophilic coupling partners in place of organometallic reagents.

## Conclusion

We have developed a rhodium-catalyzed silylation of nitriles with disilanes in which an unreactive C–CN bond is cleaved in a catalytic manner. Under the catalytic conditions, a diverse array of functional groups, including esters, amides, amines, ethers, and boronic esters, as well as heterocycles, are tolerated. In addition to the C–CN bonds of aryl, alkenyl, allyl, and benzyl cyanides, those of alkyl cyanides, a challenging class of substrates for the catalytic transformation, can be cleaved and silylated with this catalytic system. One of the most intriguing features of this reaction is the mechanism for the cleavage of C–CN bonds. On the basis of related stoichiometric reactions, it is proposed that the catalytic reaction proceeds through the deinsertion of silyl isocyanide of  $\eta^2$ -iminoacyl complex **B'** (Scheme 5). The observation of enamine side products in the silylation of benzyl cyanides also supports the intermediacy of **B'**. This silicon-assisted strategy for the activation of C–CN bonds is further applied to an intramolecular cyclization process in which the Ar–Ar bond is constructed by the cross-coupling reaction between Ar–CN and Ar–Cl. Current efforts are directed toward further application of the postulated rhodium silyl species to the cleavage of other unreactive bonds.<sup>35</sup>

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**Supporting Information Available:** Complete experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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