

Rhodium-Catalyzed Reductive Decyanation of Nitriles Using Hydrosilane as a Reducing Agent: Scope, Mechanism and Synthetic Application[†]

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Received October 26, 2009, Accepted November 20, 2009

A rhodium-catalyzed reductive cleavage reaction of carbon-cyano bonds is developed using hydrosilane as a mild reducing agent. A wide range of nitriles, including aryl, benzyl, and β -hydrogen containing alkyl cyanides are applicable to this decyanation reaction. The method is also applicable to organic synthesis, in which benzyl cyanide is used as a benzyl anion equivalent and a cyano group functions as a removable ortho-directing group.

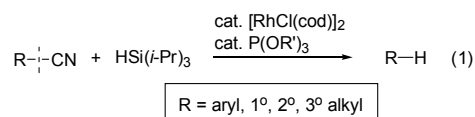
Key Words: Reductive decyanation, Carbon-carbon bond activation, Rhodium catalyst, Hydrosilane

Introduction

Functional group transformation is a central issue in organic synthesis. In addition to introduction and interconversion of functional groups, their removal has long been utilized as a key transformation for the synthesis of complex organic molecules. In this context, several powerful methods, including Barton-Macombie deoxygenation,^{1a} Krapcho decarboxylation in acetoacetic and malonic ester synthesis,^{1b} Tsuji-Wilkinson decarbonylation,^{1c,d} and many others^{1e-i} have been developed. In view of the widespread utility of functional group removal, it was expected that a method that transforms organic nitriles into the parent alkanes or arenes should find numerous applications since such a process enables the temporary use of the beneficial features of a cyano functionality, such as α -C-H acidity² and the *ortho*-directing effect.³ However, this type of reductive decyanation reaction is less common and generally requires a strong reducing agent (Na/NH₃, K, or LiAlH₄), which considerably limits the scope of applicable nitriles.⁴

On the other hand, several transition metal complexes are known to mediate the cleavage of the carbon-cyano bond in nitriles *via* oxidative addition or silicon-assisted mechanism.^{5,6} Although the former process has been successfully applied to several catalytic reactions,^{5b-d} catalysis *via* the latter mechanism had been limited to the work of Nakazawa, in which the reductive cleavage of nitriles with hydrosilane is catalyzed by an iron complex under irradiation.^{6d-f} Subsequently, we reported a rhodium-catalyzed silylation^{7a,b} and intramolecular arylation^{7b} of nitriles using disilane as a source of catalytically active silyl-metal species. We envisioned that the use of hydrosilane in place of disilane in our rhodium catalytic system would lead to the development of a catalytic reductive decyanation reaction. Results of preliminary studies proved this approach to be viable (eq 1).^{7c} Herein, we report the results of our detailed study of this rhodium-catalyzed reductive decyanation reaction, including reac-

tion optimization, scope and limitation, mechanistic studies, and synthetic applications.



Results and Discussion

The initial investigation was performed using 2-cyanonaphthalene (**1**) and triethylsilane (**2a**) in the presence of a catalytic amount of [RhCl(cod)]₂. Under the conditions that we previously identified as effective for the silylation of nitriles (in ethylcyclohexane at 130 °C),^{7a,b} the expected reduced product **3** was formed in 56% yield, along with a silylated product **4a** (**3/4a** = 83/17, entry 1 in Table 1).⁸ Encouraged by this promising result, we next examined the effect of the substituents on the hydrosilanes in the hope of improving the selectivity and efficiency of the formation of **3**. The use of the less bulky hydrosilane **2b** or the phenyl-substituted silane **2c** lowered both yield and selectivity (entries 2 and 3). A slight improvement was observed when *t*-butyldimethylsilane (**2d**) was employed (entry 4). We were pleased to find that the use of the highly bulky triisopropylsilane (**2e**) completely suppressed the undesired silylation and furnished **3** in 54% yield (entry 5). Although the yield was moderate, mass balance was much improved compared with that observed with other hydrosilanes. On the other hand, conversion was significantly reduced when alkoxy-substituted silanes **2f-h** were used (entries 6-8). Based on the results presented in Table 1, we decided to employ **2e** as the reducing agent for use in subsequent experiments to optimize this rhodium-catalyzed reductive decyanation.

To increase the conversion efficiency, the effects of the ligands were examined (Table 2). The addition of PPh₃ to the rhodium-catalyzed reaction of **1** with **2e** slightly increased the yield of **3** without the undesired silylation (entry 1). The yield was dramatically improved when P(*O*-*i*-Pr)₃ was added, and **3**

[†]This paper is dedicated to Professor Sunggak Kim on the occasion of his honorable retirement.

Table 1. Rhodium-catalyzed reaction of **1** with hydrosilanes **2a-h**^a

entry	H-Si	3 (%) ^b	3/4 ^c	recovered 1 (%) ^b
1	H-SiEt ₃ (2a)	56	83/17	trace
2	H-SiEt ₂ Me (2b)	36	78/22	16
3	H-SiMe ₂ Ph (2c)	13	58/42	33
4	H-SiMe ₂ (<i>t</i> -Bu) (2d)	65	85/15	0
5	H-Si(<i>i</i> -Pr) ₃ (2e)	54	100/0	42
6 ^d	H-SiMe ₂ (OEt) ₂ (2f)	9	70/30	49
7 ^d	H-SiMe(OEt) ₂ (2g)	20	74/26	56
8 ^d	H-Si(OEt) ₃ (2h)	30	55/45	trace

^aReaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), and [RhCl(cod)]₂ (0.025 mmol) in ethylcyclohexane (0.25 mL) at 130 °C for 15 h. ^bGC yield. ^cGC area ratio. ^dWith 10 mol % of catalyst.

Table 2. Optimization studies for the rhodium-catalyzed reaction of **1** with **2e**^a

entry	additive	x	y	temp.	3 (%) ^b
1	none	5	-	130	54
2	PPh ₃	5	10	130	64
3	P(O- <i>i</i> -Pr) ₃	5	10	130	> 99
4	P(O- <i>i</i> -Pr) ₃	5	10	100	92
5	P(O- <i>i</i> -Pr) ₃	2	4	100	11
6	P(O- <i>i</i> -Pr) ₃	5	10	80	trace
7	P(OBu) ₃	5	10	130	> 99
8	P(OPh) ₃	5	10	130	52

^aReaction conditions: **1** (0.5 mmol), **2e** (1.0 mmol), [RhCl(cod)]₂ (0.025 or 0.010 mmol), and ligand (0.050 or 0.020 mmol) in ethylcyclohexane (0.25 mL) at 130 °C for 15 h. ^bGC yield. ^cIsolated yield.

was formed quantitatively (entry 2). Further evaluation of the phosphite ligands revealed that P(OBu)₃ exhibited a comparable effect (entry 7), while P(OPh)₃ did not accelerate the reaction (entry 8). The reaction temperature could be lowered to 100 °C without a significant reduction in the yield of **3** (entry 4), while almost no reaction occurred at 80 °C (entry 6). Decreasing the catalyst loading at 100 °C resulted in a significant drop in yield (entry 5). Based on the excellent performance of P(O-*i*-Pr)₃ or P(OBu)₃ in the catalytic decyanation of **1** with **2e**, we decided to explore the scope of this reaction using these ligands.

Under the optimal reaction conditions described above, the cyano groups in a number of substituted benzonitriles could be removed efficiently (Table 3). Utilization of hydrosilane as a mild reducing agent allowed a high functional group tolerance. For example, ethers (entries 3-5, 10, 11, 15, 16), amines (entry

Table 3. Rh-catalyzed reductive decyanation of aromatic nitriles^a

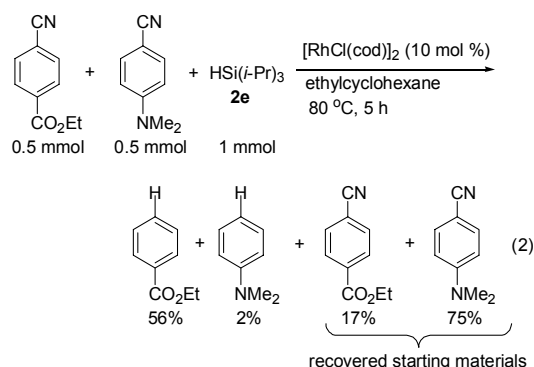
entry	Ar	yield (%) ^b	entry	Ar	yield (%) ^b
1		99 ^c	10		95 ^c
2		96 ^c	11		95
3		74 ^c	12		89
4		64 ^c	13 ^d		81
5		76	14 ^{d,e}		94
6		76 ^c	15		98
7		85	16		77
8		84	17		48
9		94	18 ^f		81

^aReaction conditions: aryl cyanide (0.5 mmol), **2e** (1.0 mmol), [RhCl(cod)]₂ (0.025 mmol), P(OBu)₃ (0.05 mmol) in ethylcyclohexane (0.25 mL) at 130 °C for 15 h. ^bIsolated yields are based on aryl cyanides unless otherwise noted. ^cDetermined by GC due to the volatility of the product. ^dRun at 160 °C using [RhCl(cod)]₂ (0.05 mmol) in the presence of P(O-*i*-Pr)₃ (0.10 mmol). ^eToluene was used as a solvent. ^fRun at 100 °C in the absence of P(OBu)₃.

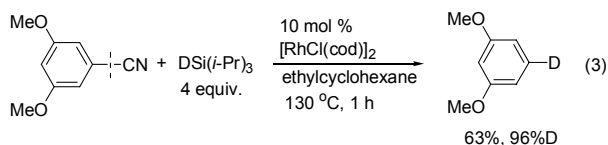
6), amides (entry 7), and esters (entries 8 and 16) remained unaffected. Moreover, a boronic ester, which can undergo transmetalation with a rhodium complex,⁹ survived under these conditions (entry 9). Although both electron-rich and electron-deficient aryl cyanides afforded the corresponding decyanated products in good to excellent yield at 130 °C, the electronic nature of the substrates proved to affect the reaction rate significantly. Thus, an intermolecular competition experiment was performed. The reaction of a 1:1 mixture of electron-rich and electron-deficient aryl cyanides at 80 °C resulted in selective decyanation of the latter substrate (eq 2). We observed a similar electronic effect in the rhodium-catalyzed decyanative silylation

reaction.^{7a,b} It should also be noted that both electron-deficient and electron-rich heteroaromatic substrates can be applied to this catalytic reaction (entries 17–18).

One notable feature of this catalysis is its insensitivity to steric demands. Under identical conditions, *ortho*-substituted benzonitriles smoothly underwent reductive decyanation to afford the corresponding arenes in excellent yield (entries 10–12). Even more sterically encumbered cyano groups, as in 2,6-disubstituted benzonitrile (entry 13) and 9-cyanoanthracene (entry 14), were successfully removed by increasing both the catalyst loading and reaction temperature. It is important to mention that, in each case presented in Table 3, formation of decyanative silylation products, similar to **4**, was not observed.



Our rhodium-catalyzed reductive decyanation reaction provides an alternative route to labeled arenes from nitriles. Thus, the use of deuterated triisopropylsilane allows for substitution of a cyano group with a deuterium atom under neutral conditions (eq 3).



We next investigated benzyl cyanides as possible substrates for this catalytic reductive decyanation, expecting that the cleavage of a benzylic carbon-cyano bond could proceed relatively facilely.¹⁰ Indeed, treatment of benzyl cyanides with **2e** and a rhodium catalyst afforded the corresponding decyanated products in good to excellent yields (entries 1–6 in Table 4). These reactions proceeded smoothly even in the absence of added phosphite ligands, while a slight improvement in yield was achieved by use of $P(O-i-Pr)_3$ for some of the benzyl cyanides. In our previous studies of rhodium-catalyzed decyanative silylation using disilane, the use of benzyl cyanides resulted in an enamine-type byproduct, in which the carbon-cyano bond is not cleaved.^{7b} In contrast to this observation, no such byproducts were observed in the present study. Cyano groups located at both the primary and secondary benzylic positions were removed under these conditions (entries 3 and 4). Notably, highly congested tertiary benzyl cyanides furnished the corresponding decyanated products in good yields (entries 5 and 6). Interestingly, introducing an ester group at the α position of benzyl cyanides increased reactivity. The sterically demanding α,α -disubstituted cyanoacetates efficiently underwent catalytic reductive decy-

lation even at 80 °C (entry 6). This process is complementary to the well-established decarboxylation reaction, in which an ester group in cyanoacetate derivatives is finally removed to afford substituted acetonitriles.^{1b,11}

Because benzylic substrates, especially those containing β -hydrogen atoms (i.e., entries 3, 4, and 6) were successfully employed in the reductive decyanation reaction, we next turned our attention to the reactivity of simple alkyl cyanides. Analogous to the difficulty encountered in the catalytic transformation of $C(sp^3)$ -X bonds,¹² developing the catalytic cleavage of unactivated $C(sp^3)$ -CN bonds, especially those containing a β -hydrogen, represents a challenge due, in part, to their thermodynamic stability and the susceptibility of the alkyl-metal intermediates to β -hydrogen elimination. Indeed, the formation of by-products from undesired β -hydrogen elimination was reported for the nickel-catalyzed reaction of alkyl cyanides, in which cleavage of the C-CN bond proceeds through oxidative addition.¹³ By contrast, when the C-CN bond is cleaved *via* a silicon-assisted mechanism, the reaction is likely to be applicable to β -hydrogen containing, unactivated alkyl cyanides. Bergman and Brookhart demonstrated that $Cp^*Rh(SiPh_3)(PMe_3)_3$ can cleave the C-CN bond of *i*-PrCN to form the corresponding σ -alkylrhodium complexes.^{6a,b} Nakazawa also reported that a few unactivated primary alkyl cyanides (EtCN, *i*-PrCH₂CN, and NCCH₂CH₂CN) are applicable to the iron-catalyzed reductive cleavage reaction under irradiation.^{6f} In spite of these studies, the full potential of this silicon-assisted strategy for the catalytic cleavage of unactivated $C(sp^3)$ -CN bonds remains to be elucidated. Thus, we began with the examination of several simple primary alkyl cyanides. To our delight, the reductive decyanation proceeded quite efficiently (entries 7–10 in Table 4). Compared with the reactions of aryl or activated alkyl cyanides, a higher reaction temperature (160 °C) was required to reach high conversion efficiency. Nevertheless, complete suppression of the formation of alkenes *via* β -hydrogen elimination at this temperature is noteworthy. Primary alkyl cyanides bearing a bulky substituent at the β -position also underwent reductive decyanation to afford the product in excellent yield (entry 11). Furthermore, the more challenging secondary alkyl cyanides also were suitable substrates. The reaction of 2-methyl-4-phenylbutanenitrile with **2e** in the presence of the $[RhCl(cod)]_2/P(O-i-Pr)_3$ catalyst at 160 °C successfully furnished butylbenzene without the formation of alkenes (entry 12). On the other hand, when 2-ethyl-4-phenylbutanenitrile was exposed to the identical conditions, the desired decyanated product (i.e., pentylbenzene) was obtained in 64% yield (data not shown in Table 4) along with a β -hydrogen elimination product (*E*-pent-1-enylbenzene, 28%). This result indicates that, for the secondary alkyl cyanides, the steric nature of the substrates has a significant impact on the selectivity. The undesired β -hydrogen elimination observed with this sterically demanding substrate could be avoided by increasing the amount of **2e** (entry 13). Currently, a limitation of the present reaction is its inapplicability to unactivated tertiary alkyl cyanides, which afforded a complicated mixture, including alkenes *via* dehydrocyanation. However, in the one case that precluded β -hydrogen elimination for geometric reasons, a tertiary alkyl cyanide (i.e., 1-cyanoadamantane) furnished the corresponding decyanated product selectively, albeit in modest yield (entry 14).

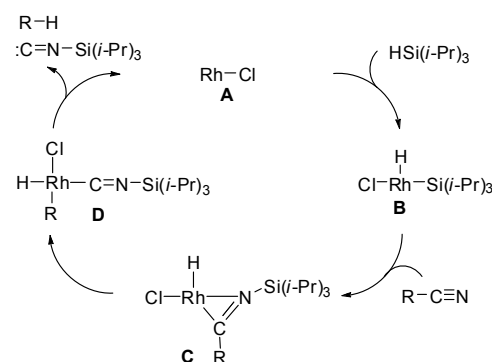
Table 4. Rh-catalyzed reductive decyanation of aliphatic nitriles^a

$\text{R}-\text{C}\equiv\text{N} + \text{H}-\text{Si}(\text{i-Pr})_3 \xrightarrow[\text{ethylcyclohexane, 160 }^\circ\text{C, 15 h}]{[\text{RhCl}(\text{cod})]_2 (10 \text{ mol } \%), \text{P}(\text{O-}i\text{-Pr})_3 (20 \text{ mol } \%), \text{2e (2 equiv.)}} \text{R}-\text{H}$					
entry	R-CN	yield (%) ^b	entry	R-CN	yield (%) ^b
1 ^{c,d}		75	8		99 ^e
2 ^c		69	9		99 ^e
3 ^c		90 ^e	10		99 ^e
4 ^{c,d}		81	11		95
5		91	12		98 ^e
6 ^f		91	13 ^g		93
7		78 ^e	14		43 ^e

^aReaction conditions: alkyl cyanide (0.5 mmol), **2e** (1.0 mmol), [RhCl(cod)]₂ (0.05 mmol), and P(O-*i*-Pr)₃ (0.10 mmol) in ethylcyclohexane (0.25 mL) at 160 °C, 15 h. ^bIsolated yields based on alkyl cyanides unless otherwise noted. ^cRun at 130 °C. ^dRun in the absence of P(O-*i*-Pr)₃. ^eDetermined by GC due to the volatility of the product. ^fRun using **2e** (2.0 mmol), [RhCl(cod)]₂ (0.10 mmol) at 80 °C in the absence of P(O-*i*-Pr)₃. ^gRun at 170 °C using **2e** (2.5 mmol) in the absence of solvent.

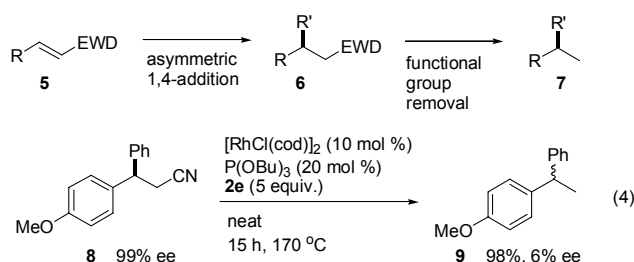
Based on the previously reported silicon-assisted carbon-cyano bond cleavage reactions,^{6,7} we propose a simplified catalytic cycle that can account for the reductive decyanation using **2e** as depicted in Scheme 1. Oxidative addition of **2e** to a rhodium center affords silyl-rhodium species **B**, which then adds across the carbon-nitrogen triple bond in nitriles to form an η^2 -iminoacyl intermediate **C**. Deinsertion of silyl isocyanide from **C** induces cleavage of the carbon-carbon bond, which is derived from the carbon-cyano bond, to afford complex **D**. Reductive elimination of a decyanated product (R-H) and dissociation of silyl isocyanide completes the catalytic cycle.¹⁴ Although we show Rh(III) complexes as key intermediates in Scheme 1, silyl complexes in higher oxidation states, which can be generated by further oxidative addition of **2e** to a Rh(III) center,¹⁵ could also be involved.¹⁶

Asymmetric 1,4-addition reactions have been recognized as a powerful method for the construction of functionalized chiral building blocks (**5**→**6**). Although the chiral molecules containing electron-withdrawing groups, as in **6**, act as versatile synthetic intermediates, a more diverse array of optically active compounds that are difficult to access by other methods would be made available, if the electron-withdrawing groups in **6** could be removed without loss of optical purity. In this context, Carr-

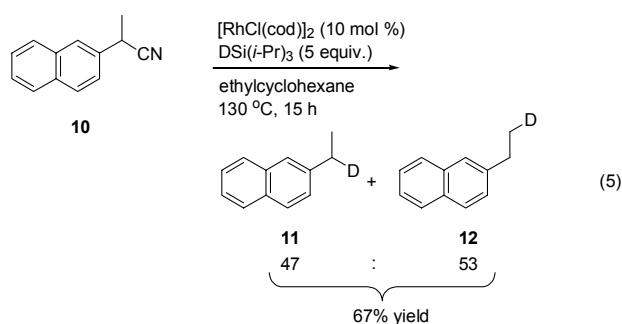


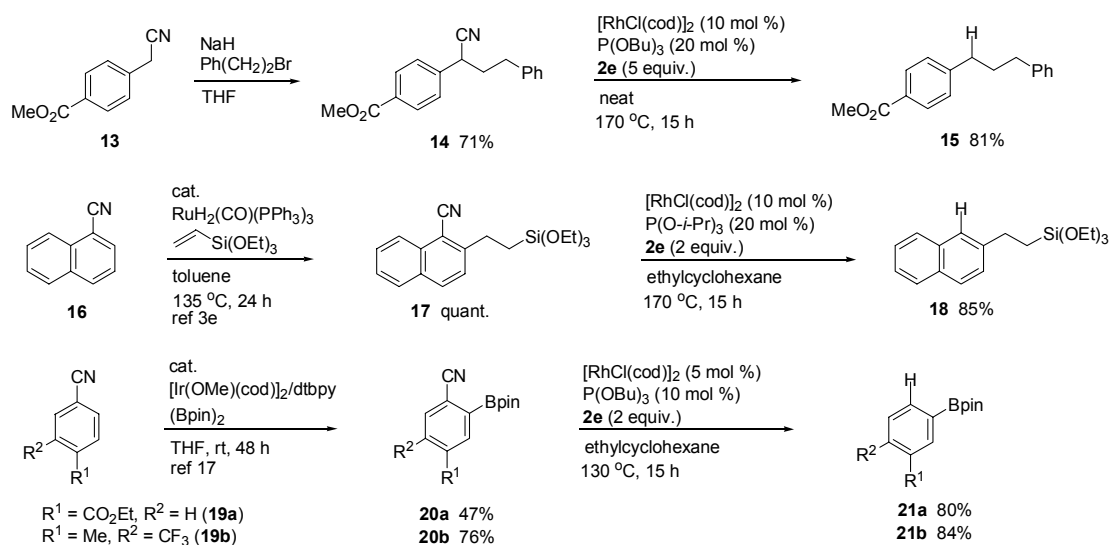
Scheme 1. A plausible mechanism^a: ^aOther possible ligands, such as cod and P(OR')₃, are omitted for simplicity. Geometry around the rhodium center in each intermediate is one of several possibilities.

eira and coworkers successfully developed procedures for removal of nitro and formyl groups after their use in asymmetric 1,4-addition.^{9b,17} In view of the successful catalytic asymmetric 1,4-addition of arylboronic acids to α,β -unsaturated nitriles recently reported by Hayashi *et al.*,¹⁸ we attempted the rhodium-catalyzed reductive decyanation of the chiral nitrile **8**. However, to our disappointment, the product **9** was obtained as a nearly racemic form, although the chemical yield was excellent (eq 4).



The fact that, under our catalytic conditions, nearly complete racemization occurred with **8**-though β -hydrogen elimination products were not observed-motivated us to conduct the labeling experiment shown in eq 5. Thus, treatment of the β -hydrogen-containing benzyl cyanide **10** with deuterated silane in the presence of a rhodium catalyst afforded the decyanated product. ¹H NMR analysis of the isolated product revealed that the deuterium atom was incorporated at both the benzylic and terminal positions in an approximately 1:1 ratio. The results obtained in eqs 4 and 5 clearly indicate that isomerization of a rhodium center *via* a β -hydrogen elimination/hydrometalation sequence occurs during catalysis, even when dissociation of the β -hydrogen elimination products (i.e., alkenes) was not detected.





Scheme 2. Synthetic applications

Similar to other defunctionalization reactions,¹ our catalytic reductive decyanation offers numerous opportunities for application in organic synthesis (Scheme 2). For example, the α -C-H acidity of aliphatic nitriles² can be utilized temporarily. Treatment of the benzyl cyanide **13** with NaH, followed by the addition of 2-bromoethylbenzene afforded the alkylated product **14**. The cyano group in **14** was efficiently removed by the rhodium-catalyzed reaction with **2e**. This protocol opens up the utility of benzyl cyanides as benzyl anion equivalents. Another useful function of cyano groups in organic synthesis is the *ortho*-directing effect in some metal-mediated C-H bond functionalization reactions.^{3,19} Our catalytic reductive decyanation reaction enables a cyano group to serve as a removable directing group,²⁰ providing a new strategy for regioselective functionalization of aromatic C-H bonds. The cyano group in **16** directs the ruthenium-catalyzed alkylation using vinylsilane to proceed at the 2-position in a regioselective manner.^{3c} The cyano group in **17** was removed by our method to furnish **18**, accomplishing a formal direct C-H bond alkylation of naphthalene at the 2-position. This strategy was extended to C-H borylation reactions. It has been reported that the iridium-catalyzed reaction of the benzonitrile derivatives **19** with diboron affords the borylated products **20** regioselectively due to the steric directive effect of the cyano group.¹⁹ Subsequent decyanation furnished borylated arenes **21**, which cannot be synthesized regioselectively by the direct borylation of **19**.

Conclusions

In summary, we developed a rhodium-catalyzed reductive decyanation reaction that uses triisopropylsilane as a mild reducing agent. A notable aspect of this reaction is its wide scope of substrates, including aromatic, β -hydrogen-containing primary and secondary, and some tertiary alkyl cyanides that bear a variety of functional groups and substantial steric bulk. We believe that the advantage of the reaction can be attributed to the unique silicon-assisted mechanism by which the carbon-cyano

bond is cleaved. The utility of this method in organic synthesis also was demonstrated in the α -substitution of benzyl cyanides and cyano-directed C-H bond functionalization reactions. Thus, the reaction offers a new strategy based on the use of a cyano group as a removable steering group. Further exploration of catalytic reactions that proceed *via* silicon-assisted cleavage of carbon-cyano bonds is ongoing in our laboratory.

Experimental

General procedure for Rh-catalyzed reductive decyanation (entry 12, Table 3). An oven-dried, 5 mL, screw-capped vial was charged with 2-phenylbenzonitrile (89.6 mg, 0.5 mmol), triisopropylsilane (158.4 mg, 1 mmol), [RhCl(cod)]₂ (12.3 mg, 0.025 mmol), tributylphosphite (12.5 mg, 0.05 mmol) and ethylcyclohexane (0.25 mL) under a gentle stream of nitrogen. The vessel was heated in an oil bath at 130 °C for 15 h followed by cooling. The contents were subjected to flash chromatography (hexane) to give biphenyl as a white solid (68.4 mg, 89%).

Acknowledgments. We thank Prof. Tamio Hayashi and Mr. Keigo Sasaki for the generous gift of **8**. This work has been supported by the Program of Promotion of Environmental Improvement to Enhance Young Researchers' Independence, the Special Coordination Funds for Promoting Science and Technology, and by a Grant-in-Aid for Science Research on Priority Areas (No. 20036035, Synergy of Elements) from MEXT, Japan. M.T. also acknowledges the Nagase Science and Technology Foundation. We also thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance with the MS, HRMS and elemental analyses.

Supporting Information. Supporting Information which includes detailed experimental procedures and spectroscopic data for new compounds, is available on request from the corresponding authors (fax: +81-6-6879-7396; e-mail: tobisu@chem.eng.osaka-u.ac.jp or chatani@chem.eng.osaka-u.ac.jp).

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