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Rh(I)-Catalyzed Silylation of Aryl and Alkenyl Cyanides Involving the Cleavage of C−C and Si−Si Bonds

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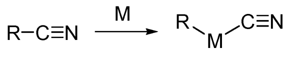
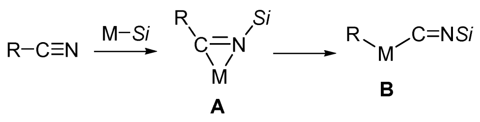
The cleavage of C−C σ bonds by transition-metal complexes represents a fundamental challenge in the field of organometallic chemistry. Success has primarily been limited to systems that rely on relatively specific driving forces, such as relief of ring strain and aromatization or on chelation assistance.[1] A notable exception to this is the cleavage of C−C σ bonds of nitriles, in which unstrained C−CN bonds can be cleaved in the absence of neighboring coordinating groups.[2−8] Mechanistic studies of such transition-metal-mediated C−CN bond-cleavage reactions have revealed two distinct pathways (eqs 1 and 2). One is the oxidative addition of a C−CN bond to a low-valent metal center to afford an alkyl(aryl)−cyano complex (eq 1). The majority of C−CN bond cleavage reactions appear to proceed through this mechanism, and several alkyl(aryl)−cyano complexes have been synthesized from alkyl(aryl) cyanides.[1−5] In addition, the oxidative addition of a C−CN bond has also been postulated as a key step in some *catalytic* reactions.[9,10] On the other hand, it has been reported that silyl−metal species mediate C−CN bond cleavage via an alternate mechanism, which consists of the formal silylmetalation of a cyano group to form η^2-iminoacyl complex **A** and the subsequent deinsertion of silyl isocyanide (eq 2). This silicon-assisted mechanism was first reported by Bergman and Brookhart by employing a silyl−rhodium complex.[11] Nakazawa reported that a similar mechanism operates in the photochemically induced C−CN bond cleavage reaction mediated by iron complexes, representing, to the best of our knowledge, the only *catalytic* reaction that proceeds through the pathway shown in eq 2.[12] In this Communication, we describe a new silylation reaction of nitriles based on eq 2, in which C−CN and Si−Si bonds are cleaved nonphotochemically in a *catalytic* manner.



(1)



(2)

To incorporate the silicon-assisted C−CN bond-cleavage process into a catalytic cycle, the critical issue is establishing the pathway for regenerating the silyl−metal complex from the alkyl(aryl)−metal complex **B**. The potential reactivity of a Si−Si bond toward metal−carbon bonds[13,14] led us to consider the catalytic cycle outlined in Scheme 1, in which complex **B** reacts with a disilane to regenerate a silyl−metal complex with the concomitant formation of an alkyl(aryl)silane and silyl isocyanide, which should isomerize to thermodynamically stable silyl cyanide.[12,15] In addition, because disilanes would also be expected to exhibit a similar reactivity toward metal halide complexes to form a silyl−metal complex, we surmised that some of the more common metal halide (or related) complexes could be employed as catalyst precursors in place of silyl−metal complexes.

Scheme 1. Design of a Catalytic Cycle Involving Silicon-Assisted C−CN Bond Cleavage

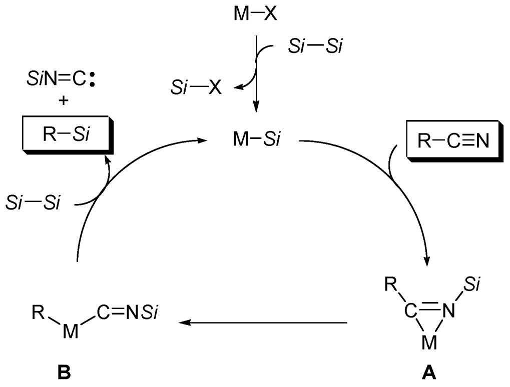
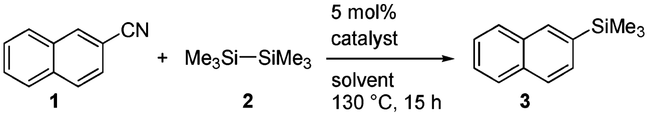


Table 1. Rh(I)-Catalyzed Silylation Reaction of Nitriles: Catalyst and Solvent Screening[a]



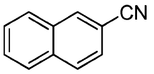
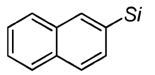
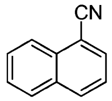
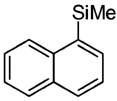
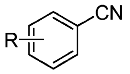
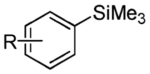
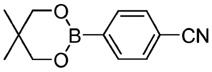
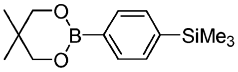
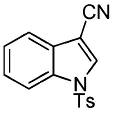
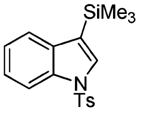
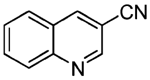
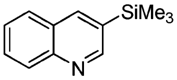
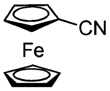
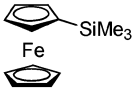
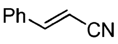
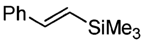
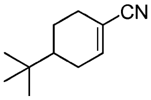
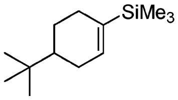
entry	catalyst	solvent	yield[b] (%)
1	$[Cp^*RhCl_2]_2/2PPh_3$	mesitylene	12
2	$[RhCl(cod)]_2$	mesitylene	53
3	$[RhCl(coe)_2]_2$	mesitylene	62
4	$[Rh(OMe)(cod)]_2$	mesitylene	80
5[c]	$[Rh(cod)_2]BF_4$	mesitylene	65
6	$[RhCl(cod)]_2$	dioxane	71
7	$[RhCl(cod)]_2$	DMA	36
8	$[RhCl(cod)]_2$	ethylcyclohexane	87
9[d]	$[RhCl(cod)]_2$	ethylcyclohexane	49

[a] Reaction conditions: **1** (2.0 mmol), **2** (4.0 mmol), catalyst (0.10 mmol) in solvent (1.0 mL) at 130 °C, 15 h. [b] Isolated yields. [c] 10 mol % of $[Rh(cod)_2]BF_4$ was used. [d] Run at 100 °C.

To investigate the feasibility of our working hypothesis, we examined the reaction of 2-cyanonaphthalene (**1**) with hexamethyldisilane (**2**) in detail. In light of the pioneering work by Bergman and Brookhart,[11] we initially used $[Cp^*RhCl_2]_2/PPh_3$ as a catalyst precursor and found that the reaction did indeed proceed, furnishing 2-trimethysilylnaphthalene (**3**) in 12% yield (Table 1, entry 1). Further screening of catalysts indicated that several Rh(I) complexes, such as $[RhCl(cod)]_2$, $[RhCl(coe)_2]_2$, $[Rh(OMe)(cod)]_2$, and $[Rh(cod)_2]BF_4$, are more effective catalysts (entries 2−5).[16] $[RhCl(CO)_2]_2$, $[IrCl(cod)]_2$, $[Cp^*RuCl]_n$, and $Ni(cod)_2/PBu_3$ were completely inactive in this reaction under otherwise identical conditions. The effect of solvents was also investigated using $[RhCl(cod)]_2$ as a catalyst. The use of ethylcyclohexane led to a dramatic increase in the yield of **3** (entry 8). The reaction can be conducted at a lower temperature (100 °C) at the expense of reaction rate (entry 9).

10.1021/ja062745w CCC: $33.50

Table 2. Rh(I)-Catalyzed Silylation Reaction of Nitriles[a]

entry	nitrile	product	yield (%)[b]
			
1		*Si* = $SiMe_3$	87
2[c,d]		*Si* = $SiMe_2Ph$	46
3[c,e]		*Si* = $SiMe_2(CH_2Ph)$	41
4[f]			57
			
5	R = 4-CF_3		94[g]
6[h]	R = 4-CO_2Me		70
7	R = 4-CO_2Bu^t		72
8	R = 4-OAc		54
9	R = 4-F		97[g]
10[i]	R = 4-OMe		69
11[j]	R = 4-NMe_2		70
12[k]	R = 2-Me		35
13[j]			78
14			81
15[h]			57
16[h,i]			73
17[h]			73
18[f]			55

[a] Reaction conditions: nitrile (2.0 mmol), hexamethyldisilane (4.0 mmol), $[RhCl(cod)]_2$ (0.10 mmol) in ethylcyclohexane (1.0 mL) at 130 °C, 15 h.
[b] Isolated yields.
[c] Run on a 1-mmol scale.
[d] 1,1,2,2-Tetramethyl-1,2-diphenyldisilane was used in place of **2**.
[e] 1,2-Dibenzyl-1,1,2,2-tetramethyldisilane was used in place of **2**.
[f] 10 mol % of the catalyst was used.
[g] GC yield.
[h] $[Rh(OMe)(cod)]_2$ was used as a catalyst.
[i] Run for 40 h.
[j] $[Rh(cod)_2]BF_4$ was used as a catalyst.
[k] Run for 96 h.

We next turned our attention to the scope of this catalytic silylation reaction (Table 2). With respect to disilanes, it was also possible to introduce dimethylphenylsilyl and benzyldimethylsilyl groups in modest yields by employing the corresponding disilanes (entries 2 and 3). We were pleased to find that a diverse array of aryl cyanides can be silylated. Thus, the catalytic process tolerates a number of functional groups, including fluorides (entries 5 and 9), esters (entries 6−8), ethers (entry 10), tertiary amines (entry 11), and, notably, boronic esters (entry 13). The reaction is sensitive to sterics surrounding the nitrile, as demonstrated by the reduced yields for 1-naphthalenecarbonitrile (entry 4) and 2-methylbenzonitrile (entry 12). Heteroaryl cyanides (entries 14 and 15) and cyanoferrocene (entry 16) were found to be good substrates for this silylation reaction. It is noteworthy that the method can be applied not only to aryl cyanides, but also to alkenyl cyanides, affording disubstituted (entry 17) and trisubstituted (entry 18) alkenylsilanes. To the best of our knowledge, this is the first example of the catalytic cleavage of the C−CN bond of *alkenyl* cyanides.

In summary, we report herein on the Rh(I)-catalyzed silylation reaction of aryl and alkenyl cyanides involving the cleavage of unreactive C−CN and Si−Si bonds.[17] Expanding the scope of the reaction and applying this concept to other functional group transformations are currently in progress.

Acknowledgment. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining MS, HRMS, and elemental analyses. We also acknowledge Prof. Baba and Prof. Yasuda (Osaka University) for obtaining ^{29}Si NMR spectra.

Supporting Information Available: Detailed experimental procedures and the characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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