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# Si-CN Bond Cleavage of Silyl Cyanides by an Iron Catalyst. A New Route of Silyl Cyanide Formation

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The reaction of silyl cyanide (R<sub>3</sub>SiCN) with hydrosilane (R'<sub>3</sub>SiH) in the presence of a catalytic amount of  $[(\eta^5-C_5H_5)Fe(CO)_2Me]$  formed R'<sub>3</sub>SiCN and R<sub>3</sub>SiH. This reaction involves Si–CN bond cleavage and provides a new method for the preparation of silyl cyanides. DFT calculation showed that coordinatively unsaturated  $[(\eta^5-C_5H_5)Fe(CO)(SiMe_3)]$  reacts exothermically with Me<sub>3</sub>SiCN to give the CN  $\pi$ -coordinated complex,  $[(\eta^5-C_5H_5)Fe(CO)(\eta^2-Me_3SiCN)(SiMe_3)]$ , followed by exothermic silyl migration from the iron to the nitrogen atom of the  $\eta^2$ -coordinated Me<sub>3</sub>SiCN with the activation energy of 8.8 kcal mol<sup>-1</sup> to give  $[(\eta^5-C_5H_5)Fe(CO)(Me_3SiC=NSiMe_3-\kappa C,\kappa N)]$ . The complex is one of the intermediates in the catalytic cycle. The related complex  $[(\eta^5-C_5Me_5)Fe(CO)(\kappa-C,N-t-BuMe_2SiC=NSiPh_3)]$  was isolated in the reaction of  $[(\eta^5-C_5Me_5)Fe(CO)(py)(SiPh_3)]$  with *t*-BuMe\_2SiCN and characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy. The activation energy of the Si–CN bond cleavage in  $[(\eta^5-C_5H_5)Fe(CO)(\kappa-C,N-Me_3SiC=NSiMe_3)]$  was evaluated by DFT calculation to be 33.7 kcal mol<sup>-1</sup> which is comparable to that in the reaction of acetonitrile (32.9 kcal mol<sup>-1</sup>).

Most chemical reactions consist of bond cleavage and formation. Finding suitable reaction conditions that allow breaking of a particular bond in a reagent and forming a new bond selectively is a challenging task. Bond cleavage is an important topic in organic chemistry as much as bond formation.<sup>1</sup> Selective cleavage of weak bonds is relatively easy, whereas that of strong bonds is difficult and usually requires the use of a transition-metal catalyst to reduce the activation energy of bond breaking. In this context, we have reported a C-CN bond cleavage reaction of organonitriles catalyzed by an iron complex.<sup>2</sup> The reaction is noteworthy as the C--CN bond is one of the strongest C-C single bonds: the bond energy of C-C bond in acetonitrile is  $133 \text{ kcal mol}^{-1}$ , whereas that of C-C bond in alkanes is ca.  $83 \text{ kcal mol}^{-1}$ . The key steps of the catalytic cycle are shown in Scheme 1. The cyano group coordinates in  $\eta^1$ -fashion to a 16e iron complex bearing a silvl group. Then, the organonitrile changes its coordination mode from  $\eta^1$  to  $\eta^2$ . The silvl group migrates from iron to nitrile nitrogen to form an N-silvlimino complex. Finally, C-R bond cleavage affords the iron complex bearing silyl isocyanide and R ligands. N-CN bond cleavage of cyanamides (R<sub>2</sub>N-CN)<sup>3</sup> and O-CN bond cleavage of cyanates (RO-CN)<sup>3b,4</sup> have been reported using a molybdenum catalyst, and a catalytic cycle similar to that for C-CN bond cleavage has been proposed. In all cases above, the silvl group plays a key role because its migration triggers the cleavage of strong C-CN, N-CN, and O-CN bonds. We reasoned that this type of reaction, called Silyl-Migration-Induced reaction (SiMI reaction), has general validity and can be applied to the cleavage of E-CN bonds where E is other than alkyl, aryl, amino, and alkoxy groups. Based on this hypothesis, we investigated the cleavage of strong Si–CN bonds in silvl cyanides (BDE<sub>Si–CN</sub> = 85



Scheme 1. Key step in the catalytic cycle of R–CN bond cleavage by an iron complex.

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kcal mol<sup>-1</sup>).<sup>5</sup> We examined the reaction shown in Scheme 2, where silyl cyanide and hydrosilane bear different silyl groups, causing the formation of a new Si–CN bond if Si–CN bond cleavage occurs.

### **Results and Discussion**

A mixture of t-BuMe<sub>2</sub>SiCN (10 equiv), Et<sub>3</sub>SiH (100 equiv), and  $[CpFe(CO)_2Me]$  (1 equiv) (Cp:  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) in deuterated benzene was photoirradiated under nitrogen at room temperature for 12 h. The <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra of the reaction mixture showed the formation of Et<sub>3</sub>SiCN and t-BuMe<sub>2</sub>-SiH in 44% yield based on the amount of t-BuMe<sub>2</sub>SiCN used (Scheme 3). The remaining part of the reaction mixture was unreacted starting materials, indicating that no side reaction occurred. After the sample was exposed to air. (t-BuMe<sub>2</sub>Si)<sub>2</sub>O. (Et<sub>3</sub>Si)<sub>2</sub>O, and Et<sub>3</sub>SiOH coming from the hydrolysis of t-BuMe<sub>2</sub>SiCN and Et<sub>3</sub>SiCN were observed by GC-MS.<sup>6</sup> Et<sub>3</sub>SiCN could be isolated by distillation under reduced pressure, exploiting the large difference in boiling point between silane (108 °C for Et<sub>3</sub>SiH, 83 °C for t-BuMe<sub>2</sub>SiH) and Et<sub>3</sub>SiCN (183 °C), and the fact that t-BuMe<sub>2</sub>SiCN is a solid. These results show that the starting silvl cvanide and hydrosilane underwent a recombination of their Si-CN and Si-H bonds, affording a new silvl cyanide and a new silane. This reaction is the first example of metathesis between Si-CN and Si-H bonds. It is also one of a few examples of Si-CN bondbreaking reactions promoted by organometallic complexes.<sup>7</sup> Moreover, the reaction should be noted because it involves Si-CN bond cleavage without Si-O bond formation, which is the driving force in the majority of reactions of silyl cyanides.

In the reaction shown in Scheme 3, silyl cyanide reacts with hydrosilane to give a different silyl cyanide and hydrosilane. As the reaction involves Si–CN bond cleavage and Si–CN bond formation, we reasoned that the reverse reaction may occur, in other words, the reaction would reach an equilibrium point. In order to check whether the reverse reaction takes place, Et<sub>3</sub>SiCN (10 equiv), *t*-BuMe<sub>2</sub>SiH (20 equiv), and [CpFe(CO)<sub>2</sub>Me] (1 equiv) were treated under the same reaction conditions. The formation of *t*-BuMe<sub>2</sub>SiCN (28% NMR yield based on the amount of Et<sub>3</sub>SiCN) was observed, confirming that the metathesis reaction is reversible.

The catalytic activity was examined for several related iron complexes and  $[CpM(CO)_3Me]$  (M = Mo, W). Results are shown in Table 1. No reaction took place in the absence of metal complex (Entries 1 and 2), indicating that a catalyst is necessary for the reaction. Complexes in Entries 3–14 were tested under both photoirradiation at room temperature and heating at 80 °C. In all cases, photoirradiation turned out to be more effective than heating. The only exception was provided

$$R_3SiCN + R'_3SiH \longrightarrow R'_3SiCN + R_3SiH$$

Scheme 2. Reaction investigated in this work.

by ferrocene, which showed no activity under both conditions probably due to its high stability (Entries 3 and 4). In the light of this observation, complexes in Entries 15-22 were only used under photoirradiation. [CpFe(CO)<sub>2</sub>Me] proved to be a better catalyst than the analogous complexes of molybdenum and tungsten (compare Entries 9 and 10 with 11–14). Replacement of methyl group in [CpFe(CO)<sub>2</sub>Me] with other groups, as well as the introduction of substituents into the cyclopentadienyl ring, caused a marked decrease in catalytic activity (compare Entries 15–18 and 19–22 with Entry 9, respectively). Overall, [CpFe(CO)<sub>2</sub>Me] under photoirradiation was the best catalytic system among those tested. The same trend was observed for C–CN bond cleavage of organonitriles.<sup>2</sup>

Next, we varied the amount of catalyst and reactants (Table 2). A progressive decrease in the catalyst amount from 0.1 to 0.01 equiv with respect to silyl cyanide caused a dramatic lowering in reaction yield from 62 to 3% (Entries 1–4). However, the amount of silane could be reduced from 100 to

Table	1.	Rea	ction	of	Et <sub>3</sub> SiH	and	t-BuMe <sub>2</sub> SiCN	in	the
Pres	enc	ce of	Vari	ous '	Transitio	n-Me	tal Catalysts		
	2:1			4 D.					

 $Et_3SiH + t-BuMe_2SiCN$ 

(100 equiv) (10 equiv)

Metal catalyst (1 equiv)	Et-SiCN		t-BuMe-SiH
$C_6 D_6$ , conditions, 12 h	Ligolon	т	

Entry	Metal catalyst	Conditions	Yield/% <sup>a)</sup>
1	none	<i>hν</i> , 25 °C	0 <sup>b)</sup>
2	none	Δ, 80 °C	0 <sup>b)</sup>
3	[Cp <sub>2</sub> Fe]	<i>hν</i> , 25 °C	0 <sup>b)</sup>
4	[Cp <sub>2</sub> Fe]	Δ, 80 °C	$0^{b)}(0)^{c)}$
5	[Fe(CO) <sub>5</sub> ]	<i>hν</i> , 25 °C	12
6	[Fe(CO) <sub>5</sub> ]	Δ, 80 °C	6 (15) <sup>c)</sup>
7	Fp <sub>2</sub>	<i>hν</i> , 25 °C	36
8	Fp <sub>2</sub>	Δ, 80 °C	5 (4) <sup>c)</sup>
9	[CpFe(CO) <sub>2</sub> Me]	<i>hν</i> , 25 °C	44
10	[CpFe(CO) <sub>2</sub> Me]	Δ, 80 °C	$0^{b)} (0)^{c),d)}$
11	[CpMo(CO) <sub>3</sub> Me]	<i>hν</i> , 25 °C	22
12	[CpMo(CO) <sub>3</sub> Me]	Δ, 80 °C	$4 (0)^{c),d}$
13	[CpW(CO) <sub>3</sub> Me]	<i>hν</i> , 25 °C	24
14	[CpW(CO) <sub>3</sub> Me]	Δ, 80 °C	$0^{b)}(0)^{c)}$
15	[CpFe(CO) <sub>2</sub> CH <sub>2</sub> Ph]	<i>hν</i> , 25 °C	25
16	[CpFe(CO) <sub>2</sub> SiMe <sub>3</sub> ]	<i>hν</i> , 25 °C	25
17	[CpFe(CO) <sub>2</sub> Cl]	<i>hν</i> , 25 °C	17
18	[CpFe(CO) <sub>2</sub> I]	<i>hν</i> , 25 °C	5
19	$[(C_5H_4Me)Fe(CO)_2Me]$	<i>hν</i> , 25 °C	3
20	$[(C_5H_4SiMe_3)Fe(CO)_2Me]$	<i>hν</i> , 25 °C	25
21	$[(C_5H_4I)Fe(CO)_2Me]$	<i>hν</i> , 25 °C	9
22	$[(C_5Me_5)Fe(CO)_2Me]$	<i>hν</i> , 25 °C	8

a) Yield calculated by <sup>1</sup>H NMR using 50 equiv of toluene as an internal standard. b) No reaction. c) Yields after 120 h are in parentheses. d) Metal complex decomposed.

 $t-\text{BuMe}_2\text{SiCN} + \text{Et}_3\text{SiH} \xrightarrow{[CpFe(CO)_2\text{Me}] (1 \text{ equiv})} Et_3\text{SiCN} + t-\text{BuMe}_2\text{SiH}$   $(10 \text{ equiv}) \quad (100 \text{ equiv}) \xrightarrow{C_6\text{D}_6, hv, 25 \text{ °C}, 12 \text{ h}} 44\% \text{ NMR yield}$ 

**Scheme 3.** Metathesis reaction of *t*-BuMe<sub>2</sub>SiCN and Et<sub>3</sub>SiH.

Table 2.	. Phot	oreaction	of <i>t</i> -Bu	Me <sub>2</sub> SiCN	with E	t₃SiH	in the
Preser	nce of	Various A	Amounts	of React	ants and	d Cata	lyst

t-BuMe<sub>2</sub>SiCN + Et<sub>3</sub>SiH

	[CpFe(CO) <sub>2</sub> Me] C <sub>6</sub> D <sub>6</sub> , <i>hv</i> , 25 °C	Et <sub>3</sub> SiCN -	⊦ <i>t-</i> BuMe₂SiH
Entry	[M]:[CN]:[SiH] <sup>a)</sup>	Time/h	Yield/% <sup>b)</sup>
1	1:10:100	78	62
2	1:20:200	78	18
3 <sup>c)</sup>	1:50:500	78	9
4 <sup>c)</sup>	1:100:1000	78	3
5	1:10:10	24	37
6	1:10:20	24	60
7	1:10:50	24	48
8	1:10:500	24	1
9	1:20:10	24	2

a) Molar ratio of  $[CpFe(CO)_2Me]$  (M), *t*-BuMe<sub>2</sub>SiCN (CN), and Et<sub>3</sub>SiH (SiH). b) Yield calculated by <sup>1</sup>H NMR using 50 equiv of toluene as an internal standard. c) Reaction was performed in neat.

**Table 3.** Reaction of Et<sub>3</sub>SiH and *t*-BuMe<sub>2</sub>SiCN in Various Solvents

Et <sub>3</sub> SiH +	t-BuMe <sub>2</sub> SiCN
(20 equiv)	(10 equiv)

[CpFe(CO)<sub>2</sub>Me] (1 equiv)

solvent. hv, 25 °C, 24 h

Entry	Solvent	$\varepsilon^{a)}$	Yield/% <sup>b)</sup>
1	neat		30
2	$C_6D_6$	2.27	60
3	PhCH <sub>3</sub> - $d_8$	2.38	62
4	cyclohexane- $d_{12}$	2.02	41
5	1,4-dioxane- $d_8$	2.21	69
6	$Et_2O-d_{10}$	4.20	67
7	$\text{THF-}d_8$	7.58	24
8	CCl <sub>4</sub>	2.24	c.m. <sup>c)</sup>
9	CDCl <sub>3</sub>	4.89	c.m. <sup>c)</sup>
10	$CD_2Cl_2$	8.93	c.m. <sup>c)</sup>
11	pyridine-d5	12.4	0 <sup>d)</sup>
12	PhNO <sub>2</sub> -d <sub>5</sub>	34.8	0 <sup>c)</sup>

a)  $\varepsilon$ : dielectric constant. Values refer to the corresponding nondeuterated solvents and were taken from Ref. 8. b) Yield calculated by <sup>1</sup>H NMR using 50 equiv of toluene as an internal standard. c) c.m.: complex mixture of compounds. d) A ligandexchange reaction between pyridine and CO was observed by <sup>13</sup>C NMR spectroscopy.

20 equiv without a significant effect on the conversion (compare Entries 1 and 6). Almost no reaction took place using a large excess (500 equiv) of silane (Entry 8). The reason will be discussed later. The use of an excess of silyl cyanide also provided a low yield (Entry 9).

Solvent effect was also investigated (Table 3). The choice was mainly limited to apolar solvents, as most polar solvents are chemically incompatible with reactants or catalyst.<sup>9</sup> Reaction



**Figure 1.** <sup>1</sup>HNMR spectral monitoring of the reaction between  $Et_3SiH$  (20 equiv) and *t*-BuMe<sub>2</sub>SiCN (10 equiv) in  $C_6D_6$  at 25 °C in the presence of [CpFe(CO)<sub>2</sub>Me] (1 equiv).

yield in benzene was twice that of neat, indicating that a solvent is necessary to assist the reaction (compare Entries 2 and 1, respectively). Benzene, toluene, 1,4-dioxane, and diethyl ether proved to be the best solvents among those tested, affording the products in 60–69% yield (Entries 2, 3, 5, and 6). Their effect can be attributed to the stabilization of reaction intermediates and/or transition states through coordination of  $\pi$ -bonds (in aromatic solvents) and oxygen lone pairs (in oxygenated solvents). Chlorinated solvents afforded a complex mixture of compounds, presumably by the reaction of solvent with catalyst and/or with reactants/products (Entries 8–10). Coordinative solvents such as THF, pyridine, and nitrobenzene also turned out not to be good solvents, probably because they coordinate to catalyst reducing or killing its activity (Entries 7, 11, and 12).

In order to optimize reaction time, the reaction was monitored by <sup>1</sup>H NMR spectroscopy under appropriate reaction conditions [Et<sub>3</sub>SiH (20 equiv), *t*-BuMe<sub>2</sub>SiCN (10 equiv), and [CpFe(CO)<sub>2</sub>Me] (1 equiv) in C<sub>6</sub>D<sub>6</sub> at 25 °C; Figure 1]. An induction period of a few minutes was observed which may be used to create a catalytically active species (see below). After 60 h, 80% of *t*-BuMe<sub>2</sub>SiCN was converted into *t*-BuMe<sub>2</sub>SiH and the reaction reached equilibrium.

Finally, we varied the reactants to explore the reaction scope and limitations. Various tertiary silanes were used (Table 4). Because the metathesis was reversible, each reaction gave a mixture of four compounds (two silanes and two silyl cyanides). Results show that the reaction is quite sensitive to steric hindrance, because it becomes slower by increasing the length of the alkyl chain of silane or using a branched silane (compare Entries 2-5 with Entry 1). The same trend was observed for aromatic compounds upon increasing the number of phenyl rings on silicon (Entries 6-8), although Ph<sub>3</sub>SiH performed slightly better than MePh<sub>2</sub>SiH (Entries 8 and 7, respectively). In all cases the reaction was clean, with <sup>29</sup>Si NMR spectrum of the reaction mixture only displaying four signals: two for the starting hydrosilane and silyl cyanide, two for the products hydrosilane and silyl cyanide. Because the reaction was clean and was monitored until equilibrium was attained, the relatively low yield of new hydrosilane and silyl cyanide is due to the equilibrium shifting toward the starring position and not due to the formation of side products. This metathesis reaction

allowed formation of some silvl cyanides that have not been synthesized so far (Entries 9-12). Unfortunately, the new compounds could not be isolated due to their high boiling point that made purification by distillation difficult. Therefore, elemental analysis data or mass data could not be obtained for these compounds. However, expected products were observed in the reaction mixture by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy.

Silvl cyanides are a very useful class of compounds in

Table 4. Catalytic Reaction of Various Silanes with t-BuMe2SiCN

t-BuMe<sub>2</sub>SiCN + Silane (10 equiv) (20 equiv)

 $\frac{[CpFe(CO)_2Me] (1 \text{ equiv})}{1,4-\text{dioxane-}d_8, hv, 25 °C}$ Silyl cyanide + *t*-BuMe<sub>2</sub>SiH

Entry	Silane	Time/h	Yield/% <sup>a)</sup>
1	Et <sub>3</sub> SiH	24	69
2	<i>n</i> -Pr <sub>3</sub> SiH	81	64
3	<i>n</i> -Bu <sub>3</sub> SiH	81	41
4	n-Hex <sub>3</sub> SiH	81	25
5	<i>i</i> -Pr <sub>3</sub> SiH	81	13
6	Me <sub>2</sub> PhSiH	64	57
7	MePh <sub>2</sub> SiH	103	28
8	Ph <sub>3</sub> SiH	103	36
9	(PhCH <sub>2</sub> )Me <sub>2</sub> SiH	148	25
10	(allyl)Me <sub>2</sub> SiH	124	5
11	Me(Ph)(vinyl)SiH	124	37
12	(EtO) <sub>2</sub> MeSiH	130	58

a) Yield calculated by <sup>1</sup>H NMR using 50 equiv of toluene as an internal standard.

organic synthesis. They are mainly used as sources of cyanide group in nucleophilic substitution and addition reactions.<sup>10</sup> For example, they react with aldehydes and ketones to form silylated cyanohydrins,<sup>11</sup> which can be readily converted into  $\beta$ -amino alcohols and  $\alpha$ -hydroxy acids, two important precursors of drugs.<sup>12</sup> They are also used in silvlation reactions for the protection of functional groups, especially alcohols, phenols, and carboxylic acids.<sup>10</sup> Several methods for the synthesis of silvl cvanides have been developed so far.<sup>10</sup> The most common one is the reaction of silvl halides with a metal cyanide (lithium, sodium, potassium, or silver cyanide). This method affords yields up to 90%, but usually requires an excess of metal cyanide,<sup>13,14</sup> expensive catalysts (solid polymer<sup>15</sup> or KI<sup>16</sup>) or high-boiling point solvents (N-methylpyrrolidone<sup>13,14</sup> or DMF<sup>17</sup>) that are difficult to recycle. Therefore, an alternative method for the synthesis of silvl cyanides is needed. The reaction mentioned in this paper opens new perspectives in silvl cyanide formation, although it needs further development before finding broad synthetic applications.

A plausible catalytic mechanism for the metathesis reaction between silvl cyanides and silanes is shown in Scheme 4. The cycle involves the following steps: (1) dissociation of CO from Fe in [CpFe(CO)<sub>2</sub>Me], (2) oxidative addition of silane, (3) reductive elimination of methane to generate the 16e active species, (4)  $\eta^1$ -coordination of silvl cyanide to iron, (5) change in the coordination mode from  $\eta^1$  to  $\eta^2$ , (6) migration of the silyl group from iron to nitrogen (through a concerted mechanism or a two-step process involving the formation of a pentacoordinated silicon species), (7) cleavage of Si-CN bond with migration of the silyl group to the iron center, (8) dissociation of silyl isocyanide, that isomerizes to the thermodynamically more stable silvl cyanide,<sup>2a,3c,18</sup> (9) oxidative addition of a



Scheme 4. Proposed catalytic cycle.





Figure 2. Optimized structures in the reaction of the Si-CN bond cleavage by an iron complex. All bond lengths are in Å.

second molecule of silane ( $R_3$ SiH), and (10) reductive elimination of the new silane ( $R'_3$ SiH) with regeneration of the active species. This reaction mechanism is similar to that proposed for C–CN bond cleavage of organonitriles by an iron complex,<sup>2</sup> and N–CN bond cleavage of cyanamides,<sup>3</sup> and O–CN bond cleavage of cyanates<sup>4</sup> by a molybdenum complex. The cleavage of the strong Si–CN bond is presumably triggered by a silyl migration from iron to nitrogen (step (6) in Scheme 4).

Density functional theory (DFT) calculations were performed to verify the feasibility of the cycles in Scheme 4, especially focusing on the Si–CN bond cleavage. SiMe<sub>3</sub> was used as a silyl group of R<sub>3</sub>SiH and R'<sub>3</sub>SiCN in the calculations, analogously to our previous theoretical studies.<sup>2a,3b,3c,4</sup> Accordingly, the active species in step (4) is coordinatively unsaturated [CpFe(CO)SiMe<sub>3</sub>] (complex **A** in Figure 2). The optimized structures of the intermediates and transition states (TSs) of the reactions and the associated energy profile are shown in Figures 2 and 3, respectively.

In the first step of the reaction pathway, silyl cyanide coordinates to **A** in the  $\eta^1$ -coordination mode via the lone pair of electrons on the N atom (step (4)) with a binding energy of 30.0 kcal mol<sup>-1</sup> (Figure 3). Then, silyl cyanide complex **B** isomerizes to silyl cyanide complex **C** in the  $\eta^2$ -coordination mode through **TS**<sub>BC</sub> (step (5)). This reaction is endothermic by 8.5 kcal mol<sup>-1</sup> and requires an activation energy of 15.5 kcal mol<sup>-1</sup>. We have shown that the energy of this reaction step is dependent on the electronic effect of the R<sub>n</sub>E group in cyanide R<sub>n</sub>E–CN (R<sub>3</sub>C–CN, R<sub>2</sub>N–CN, and RO–CN).<sup>3b</sup> An electron-withdrawing group enhances back-donation from metal to cyano group, stabilizing the side-on complex and





making the reaction less endothermic. In the present case, the electron-donating silyl group makes back-donation in C difficult and thus this rearrangement is more endothermic compared



Scheme 5. C-E bond cleavage in an iron coordination sphere.

with the rearrangement of other nitriles. For instance, the rearrangement of acetonitrile is  $7.1 \text{ kcal mol}^{-1}$  exothermic at the present level of calculations.

In the next step (step (6)), the silyl group migrates from iron to the nitrile N atom, converting C to the *N*-silylated  $\eta^2$ silylimino intermediate **D** with a dative N–Fe bond. The activation energy of this step was calculated to be 8.8 kcal mol<sup>-1</sup>. The relatively small activation energy for this silyl migration can be ascribed to the hypervalent character of the migrating Si atom and the electrostatic attractive interaction between a significant positive charge on the Si and a negative charge on nitrile N.<sup>2a</sup> This reaction is less exothermic (3.9 kcal mol<sup>-1</sup>) than the reactions of the other nitriles; for instance the silyl migration in the case of acetonitrile is 9.7 kcal mol<sup>-1</sup> exothermic. This is presumably because of the steric hindrance between the bulky silyl groups in **D**.

In step (7), the Si-CN bond is cleaved. Theoretical calculations for the reaction of acetonitrile, cyanamide, and cyanate showed that in this step there is an intermediate  $\mathbf{I}'$  bearing the interaction between the Fe atom and the  $ER_n$  group as shown in Scheme 5. Thus, for instance, the reaction of acetonitrile requires two reaction steps, the N dissociation from the Fe atom and the C-CN bond cleavage. However, in the reaction of silvl cvanide such an intermediate does not exist. Instead, D transforms directly to the silvl isocyanide complex E through TS<sub>DE</sub>. The structural feature in  $TS_{DE}$  is similar to that in the TS structures leading to I' in the reactions of acetonitrile, cyanamide, and cyanate, suggesting that  $TS_{DE}$  is a transition state for the N dissociation. However, an investigation of the reaction coordinate vector shows that the Si-CN bond lengthening is also an important structural feature of TSDE. Actually, the Si-CN bond is stretched from 1.885 Å at D to 1.921 Å at  $TS_{DE}$ . Analysis of the electronic structure of I' in the case of acetonitrile showed that agostic interactions between both the C-H and C-CN sigma bonds and the Fe vacant d orbital activate the C-CN sigma bond.3b Because the Si-CN bond orbital is larger and higher in energy than the C-CN bond orbital, its interaction with iron is stronger and more effectively activates the Si-CN bond.<sup>19</sup> This merges the two steps, N dissociation and Si-CN bond cleavage, into a single step. Activation energy of this step was calculated to be 33.7 kcal mol<sup>-1</sup> which is comparable to that in the reaction of acetonitrile  $(32.9 \text{ kcal mol}^{-1})$ at the present level of calculations). The N dissociation is a dominant structure change before reaching the  $TS_{DF}$ , and the energy required by the N dissociation does not depend on the nature of the  $ER_n$  group so much. Accordingly, the activation energy for this step is similar to that of the other nitriles.

The formation of the isocyanide complex **E** is exothermic by 48.6 kcal mol<sup>-1</sup>, relative to  $\mathbf{A} + \text{Me}_3\text{SiCN}$ , and **E** is much more stable than other intermediates such as **B** and **D**. This is different from the reactions of acetonitrile, cyanamide, and cyanate (Scheme 5).<sup>3b</sup> **E**'(Me) is only 3.4 kcal mol<sup>-1</sup> more stable than three-membered intermediate **D**'(Me). In the reactions of cyanamides, **E**'(NR<sub>2</sub>) is even less stable than the three-membered intermediate **D**'(NR<sub>2</sub>). This difference can be explained using the difference in the bond dissociation energies. Me<sub>3</sub>Si–CN bond is only 2.4 kcal mol<sup>-1</sup> stronger than H<sub>3</sub>C–CN bond, whereas Fe–Si bond in **E** is 18.7 kcal mol<sup>-1</sup> stronger than the Fe–C bond in **E**'(Me). The above results show that the reaction pathway including the SiMI reaction is feasible for Si–CN bond cleavage.

After **E** is formed, the isomerization of silyl isocyanide to silyl cyanide which is detected experimentally takes place. We have previously shown that this isomerization takes place out of the coordination sphere after the dissociation of silyl isocyanide from the Fe atom.<sup>2a</sup>

Dissociation of silyl isocyanide from **E** forms a 16e species **A**, which in principle can react in two ways: (i) a reaction with Me<sub>3</sub>SiCN to give **B** and (ii) a reaction with Me<sub>3</sub>SiH to give [CpFe(CO)(H)(SiMe<sub>3</sub>)<sub>2</sub>] (**F**). We performed the calculation and found that the reaction  $\mathbf{E} + \text{Me}_3\text{SiCN} \rightarrow \mathbf{B} + \text{Me}_3\text{SiNC}$  is 19.5 kcal mol<sup>-1</sup> endothermic, whereas  $\mathbf{E} + \text{HSiMe}_3 \rightarrow \mathbf{F} + \text{Me}_3\text{SiNC}$  is 21.7 kcal mol<sup>-1</sup> endothermic (Figure 4). The results show that [CpFe(CO)SiR<sub>3</sub>] reacts more feasibly with R'<sub>3</sub>SiCN than with R<sub>3</sub>SiH, as is shown in Scheme 4.

Experimental evidence is in agreement with theoretical calculations. Methane was detected in the reaction mixture by <sup>1</sup>H NMR spectroscopy, confirming the reductive elimination of step (3) and hence the formation of the active species [CpFe(CO)SiR<sub>3</sub>].

In order to isolate any of the intermediates in the catalytic cycle, we replaced [CpFe(CO)<sub>2</sub>Me] with pyridine complexes **1** and **3** (Scheme 6). Such complexes are also precursors of the active species, as they can easily generate a 16e complex by dissociation of pyridine.<sup>3a</sup> Heating a solution of **1** and *t*-BuMe<sub>2</sub>SiCN in equimolar amounts in benzene at 80 °C for 3 h yielded **2** quantitatively according to NMR measurements, but the isolation as a solid failed. In contrast, reaction of **3** with *t*-BuMe<sub>2</sub>SiCN yielded **4**, which was isolated as a brown powder in 86% yield. Although **4** was not obtained in crystalline form suitable for X-ray analysis, its structure in solution could be determined by comparison of its NMR data with an analogous intermediate whose crystalline structure is known. The <sup>29</sup>Si NMR spectrum of **4** displays two signals (see Experimental



Figure 4. Energy profile in kcal mol<sup>-1</sup> for exchange of Me<sub>3</sub>SiNC ligand by Me<sub>3</sub>SiCN and Me<sub>3</sub>SiH. All energies are ZPE-corrected and relative to  $E + Me_3SiCN + Me_3$ -SiH. Energies in parenthesis are free energies.

assigned to the t-BuMe<sub>2</sub>Si group. The product coming from the reaction of t-BuMe<sub>2</sub>SiCN with pyridine complex 1 (or 3) is a resonance hybrid of two contributing forms: the imino complex 2 (or 4), bearing a C=N double bond and a N $\rightarrow$ Fe dative bond, and the Fisher-type carbene 2' (or 4'), with an Fe=C double bond and a N-Fe covalent bond (Scheme 7). In the absence of data on the crystalline structure of 2 and 4, one has to rely on NMR to evaluate the contribution of the resonance forms to the hybrid structure. The <sup>13</sup>CNMR spectra of carbene complexes are characterized by marked deshielding of the carbene carbon atom.<sup>20</sup> The chemical shift of the carbon atom in two cyclopentadienyl iron carbene complexes related to 2 and 4 {[ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>(CO)<sub>2</sub>Fe=CHC<sub>6</sub>H<sub>5</sub>]PF<sub>6</sub> and [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>(CO)- $\{P(C_6H_5)_3\}Fe=CHC_6H_5]PF_6\}$  has been reported to be about 340 ppm.<sup>20d</sup> The chemical shift measured for the CN carbon atom in complexes 2 and 4 is dramatically lower ( $\delta = 144.2$ and 143.4 ppm, respectively). Although the chemical shift of the carbon atom depends on the nature of substituents on carbon, such a large difference in chemical shift of the carbon atom on iron between complexes 2 and 4 and carbene complexes above suggests that carbene forms 2' and 4' do not significantly contribute to the structure of hybrid. Photoreaction of 2 with 2 equiv of Et<sub>3</sub>SiH over 4 days generated Et<sub>3</sub>SiCN and t-BuMe<sub>2</sub>SiH in 58% yield. This result confirms that the Nsilvlated  $\eta^2$ -silvlimino iron complex is an intermediate in the catalytic cycle.

The low conversion measured in the presence of a large excess of silane (Table 2, Entry 8) can be rationalized in the light of a side reaction involving the active species [CpFe-(CO)SiR<sub>3</sub>]. This complex reacts with  $R'_3SiCN$  and also with



Scheme 6. Synthesis of *N*-silylated  $\eta^2$ -silylimino iron complex.



Scheme 7. Possible resonance structures of 2 and 4.

R<sub>3</sub>SiH. In the former case, the reaction proceeds according to the sequence shown in Scheme 4. In the latter case, Si-H bond in R<sub>3</sub>SiH undergoes oxidative addition to the iron center generating  $[CpFe(CO)(H)(SiR_3)_2]$ . This complex has been previously isolated from the reaction of [CpFe(CO)<sub>2</sub>Me] with R<sub>3</sub>SiH, and it has been characterized by NMR spectroscopy and X-ray crystallography.<sup>21</sup> In the reaction of 10 equiv of t-BuMe<sub>2</sub>SiCN, 20 equiv of Et<sub>3</sub>SiH, and 1 equiv of [CpFe(CO)<sub>2</sub>-Me], disilvl complex [CpFe(CO)(H)(SiEt<sub>3</sub>)<sub>2</sub>] was detected by <sup>1</sup>HNMR spectroscopy after 0.5 h of photoirradiation, and disappeared after a prolonged reaction time (10 h). The molar ratio of R'<sub>3</sub>SiCN and R<sub>3</sub>SiH is responsible for which reaction occurs mainly. When silane and silyl cyanide are nearly in equimolar ratio, the reaction mainly follows the catalytic cycle in Scheme 4, affording the metathesis products as shown by DFT calculation (Figure 3). When silane is in a large excess with respect to silvl cyanide, the side reaction becomes prevalent and reaction yield is low.

Another possible mechanism for the metathesis reaction involves the oxidative addition of the Si–CN bond in silyl cyanide. The oxidative addition of E–CN bond in acetonitrile and cyanamide has been investigated<sup>2a,3b</sup> and found to be disfavored for two reasons: 1) the high activation energy required for this step ( $52.7^{2a}$  and  $31.3^{3b}$  kcal mol<sup>-1</sup>, respectively), and 2) the instability of product [CpFeCO(SiR<sub>3</sub>)(E)(CN)], which would bear iron in the +4 oxidation state. Based on these findings, the oxidative addition pathway for acetonitrile and cyanamide has been ruled out. Because the E–CN bond cleavage reactions investigated in our group all proceed through silyl migration,<sup>2-4</sup> we proposed the silyl migration pathway for Si–CN bond cleavage reaction rather than Si–CN oxidative addition.

In conclusion, this paper describes an iron-catalyzed metathesis reaction of silyl cyanides and hydrosilanes involving the recombination of their Si-CN and Si-H bonds. The study of mechanism by a combination of DFT calculations and experimental techniques revealed that the reaction is triggered by the migration of a silyl group from the iron center to nitrogen of silvl cyanide, and follows a mechanism similar to that of other strong bond cleavage reactions. This work is important for two reasons. First, it is the first example of metathesis reaction of Si-H and Si-CN bonds. Therefore, it sheds new light on the activation of strong Si-CN bonds by transitionmetal complexes. Second, it is potentially a new method for the preparation of silyl cyanides. The reaction offers several advantages with respect to traditional methodologies, such as the use of cheap catalyst, low-boiling solvents, and stoichiometric amounts of cyanide source. Moreover, it allows synthesis of silvl cyanides never obtained so far, thus opening new perspectives on the use of this class of compounds.

### Experimental

**General Remarks.** All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. Toluene, hexane, and pentane were distilled from sodium and benzophenone prior to use and stored under nitrogen.  $[(C_5R_5)Fe(CO)_2Me]$   $(C_5R_5 = C_5H_5$ ,<sup>22</sup>  $C_5H_4Me$ ,<sup>23</sup>  $C_5Me$ ,<sup>24</sup>  $C_5H_4(SiMe_3)$ ,<sup>25</sup> and  $C_5H_4I^{26}$ ,  $[(C_5H_5)Fe(CO)_2X]$   $(X = Cl,^{27} I,^{28} CH_2Ph,^{29} SiMe_3,^{30} and SiEt_3^{31})$ ,  $[CpMo(CO)_3Me]$ ,<sup>22</sup>  $[CpW(CO)_3Me]$ ,<sup>22</sup> and  $[CpFe(CO)(py)SiEt_3]$ ,<sup>2c</sup> were prepared

according to literature methods. The other chemicals were commercially available and were used without further purification. Photoirradiation was performed with a 400 W mediumpressure mercury arc lamp (Pyrex filtered) at room temperature under nitrogen atmosphere. NMR spectra (<sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si) were recorded on a JNM-AL400 spectrometer. The residual peak of solvent was used as reference for <sup>1</sup>H and <sup>13</sup>C NMR spectra of pure compounds. The peak of toluene was used as reference for <sup>1</sup>H and <sup>13</sup>C NMR spectra of reaction mixtures. Peak positions in <sup>29</sup>Si NMR spectra were referenced to external tetramethylsilane ( $\delta = 0$  ppm). GC-MS spectra were acquired on a GCMS-QP2010Plus spectrometer using a temperature gradient (25–300 °C).

General Procedure for the Metathesis Reactions. A solution of [CpFe(CO)<sub>2</sub>Me] (4.1 mg, 21.4  $\mu$ mol, 1.0 equiv), silane (428  $\mu$ mol, 20 equiv), silylcyanide (214  $\mu$ mol, 10 equiv) and toluene (22.6  $\mu$ L, 214  $\mu$ mol, 10 equiv) in 1,4-dioxane- $d_8$  or benzene- $d_6$  (500  $\mu$ L)<sup>32</sup> under nitrogen was photoirradiated at 25 °C. The reaction was monitored by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy until equilibrium was attained.

**Diethoxymethylsilyl Cyanide.** The title compound was obtained from diethoxymethylsilane and *tert*-butyldimethylsilyl cyanide according to the general procedure. <sup>1</sup>H NMR ( $\delta$ , 1,4-dioxane- $d_8$ ): 0.07 (s, 3H, CH<sub>3</sub>), 1.14 (t, 6H, J = 6.8 Hz, CH<sub>3</sub>-CH<sub>2</sub>O), 3.66 (q, 4H, J = 6.8 Hz, CH<sub>3</sub>CH<sub>2</sub>O). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): -5.3 (s, CH<sub>3</sub>), 18.8 (s, CH<sub>3</sub>CH<sub>2</sub>O), 58.2 (s, CH<sub>3</sub>CH<sub>2</sub>O), 125.4 (s, CN). <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): -27.6 (s).

**Benzyldimethylsilyl Cyanide.** The title compound was obtained from benzyldimethylsilane and *tert*-butyldimethylsilyl cyanide according to the general procedure. <sup>1</sup>H NMR ( $\delta$ , 1,4-dioxane- $d_8$ ): 0.25 (s, 6H, CH<sub>3</sub>), 2.33 (s, 2H, CH<sub>2</sub>), 7.01–7.27 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): -4.3 (s, CH<sub>3</sub>), 23.6 (s, CH<sub>2</sub>), 125.1 (s, CN), 125.6 (Ph), 128.6 (Ph), 129.0 (Ph), 136.4 (Ph). <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): -12.9 (s).

Methylphenylvinylsilyl Cyanide. The title compound was obtained from methylphenylvinylsilane and *tert*-butyldimethylsilyl cyanide according to the general procedure. <sup>1</sup>H NMR (δ, 1,4-dioxane-*d*<sub>8</sub>): 0.33 (s, 1H, CH<sub>3</sub>), 5.82 (dd, 1H, *J*<sub>trans</sub> = 23.9 Hz, *J*<sub>vic</sub> = 3.4 Hz, CH=CH<sub>2</sub>), 6.06 (dd, 1H, *J*<sub>cis</sub> = 15.6 Hz, *J*<sub>vic</sub> = 3.4 Hz, CH=CH<sub>2</sub>), 6.28 (ddd, 1H, *J*<sub>trans</sub> = 23.9 Hz, *J*<sub>cis</sub> = 15.6 Hz, <sup>2</sup>*J*<sub>Si-H</sub> = 3.9 Hz, *CH*=CH<sub>2</sub>), 7.41 (m, 3H, Ph), 7.63 (m, 2H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, C<sub>6</sub>D<sub>6</sub>): -4.5 (s, CH<sub>3</sub>), 124.3 (s, CN), 128.8 (s, Ph), 130.1 (s, Ph), 131.2 (s, CH=CH<sub>2</sub>), 134.5 (s, Ph), 134.8 (s, Ph), 138.3 (s, CH=CH<sub>2</sub>). <sup>29</sup>Si NMR (δ, C<sub>6</sub>D<sub>6</sub>): -21.5 (s).

**Triethylsilyl Cyanide.** A solution of  $[CpFe(CO)_2Me]$  (41 mg, 214 mmol, 1.0 equiv), Et<sub>3</sub>SiH (4.28 mmol, 20 equiv), and *t*-BuMe<sub>2</sub>SiCN (2.14 mmol, 10 equiv) in benzene (5.0 mL) was photoirradiated at room temperature for 24 h. After removal of volatile materials at 4000 Pa, the residue was distilled at 80 °C and 100 Pa to give Et<sub>3</sub>SiCN as a colorless liquid. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra of this compound have not been described in the literature, <sup>33</sup> so they are reported below. <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): 0.31 (q, 6H, *J* = 8.0 Hz, *CH*<sub>2</sub>CH<sub>3</sub>), 0.79 (t, 9H, *J* = 8.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): 3.0 (s, *C*H<sub>2</sub>CH<sub>3</sub>), 7.1 (s, CH<sub>2</sub>CH<sub>3</sub>), 124.8 (s, CN). <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): -1.3 (s).

Preparation of  $[Cp^*Fe(CO)(py)SiPh_3]$  (py: pyridine) (3). A solution of  $[Cp^*Fe(CO)_2SiPh_3]$  (812 mg, 1.60 mmol, 1.0 equiv) in pyridine (9.0 mL, 112 mmol, 70 equiv) was photoirradiated at 5 °C for 48 h. Removal of volatile materials under reduced pressure left a dark-red solid, which was washed ten times with 2 mL of hexane at -70 °C. Recrystallization with hexane at -20 °C afforded pure crystals of **3** (495 mg, 0.89 mmol, 55% yield). <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): 1.34 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 5.91 (t, 2H, J = 6.8 Hz, *m*-py), 6.40 (t, 1H, J = 8.0 Hz, *p*-py), 7.20 (m, 9H, Ph), 7.71 (m, 6H, Ph), 8.26 (m, 2H, *o*-py). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): 9.6 (s, C<sub>5</sub>Me<sub>5</sub>), 90.9 (s, C<sub>5</sub>Me<sub>5</sub>), 123.4 (s, *m*-py), 128.2 (s, Ph), 128.9 (s, Ph), 134.0 (s, *p*-py), 136.9 (s, Ph), 145.5 (s, Ph), 157.6 (s, *o*-py), 224.2 (s, CO). <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): 38.3 (s).

Synthesis of N-Silylated  $\eta^2$ -Silylimino Complexes 2 and 4. Complex 1 (580 mg, 1.69 mmol, 1.0 equiv) was treated with t-BuMe<sub>2</sub>SiCN (239 mg, 1.69 mmol, 1.0 equiv) in toluene (5 mL) at 80 °C for 2 h. Removal of volatile materials under reduced pressure led to formation of the corresponding Nsilvlated  $\eta^2$ -amidino complex 2 as a light brown oil in 100% <sup>1</sup>HNMR yield. In a similar way, complex **3** (753 mg, 1.35 mmol, 1.0 equiv) was treated with t-BuMe<sub>2</sub>SiCN (191 mg, 1.35 mmol, 1.0 equiv) in toluene (5 mL) at 80 °C for 2 h. Removal of solvent under reduced pressure, followed by washing of residue with pentane at -70 °C, provided 4 as a brown-orange powder (1.16 mmol, 719 mg, 86%). Complex 4 was so air- and moisture-sensitive that correct elemental analysis data could not be obtained, although satisfactory spectroscopic data were obtained. 2; <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): 0.44 (q, 6H, J = 7.8 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 0.57 and 0.58 (s, 6H, t-BuMe<sub>2</sub>Si), 0.89 (t, 9H, J = 7.8 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 1.21 (s, 9H, *t*-BuMe<sub>2</sub>Si), 4.42 (s, 5H, Cp).  ${}^{13}C{}^{1}H{}NMR$  ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): -6.6 (s, *t*-BuMe<sub>2</sub>Si), -6.4 (s, t-BuMe<sub>2</sub>Si), 9.9 (s, SiCH<sub>2</sub>CH<sub>3</sub>), 11.2 (s, SiCH<sub>2</sub>CH<sub>3</sub>), 16.6 (s, Me<sub>3</sub>CSi), 25.4 (s, Me<sub>3</sub>CSi), 81.9 (s, Cp), 144.2 (s, CN), 222.3 (s, CO). <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): -4.7 (s, *t*-BuMe<sub>2</sub>Si), 53.4 (s, SiCH<sub>2</sub>CH<sub>3</sub>). **4**; <sup>1</sup>HNMR (δ, C<sub>6</sub>D<sub>6</sub>): -0.16 (s, 3H, *t*-BuMe<sub>2</sub>Si), -0.11 (s, 3H, t-BuMe<sub>2</sub>Si), 0.81 (s, 9H, t-Bu), 1.49 (s, 15H,  $C_5Me_5$ , 7.22 (m, 9H, Ph), 7.96 (m, 6H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ ,  $C_6D_6$ : -6.1 (s, t-BuMe<sub>2</sub>Si), 9.5 (s,  $C_5Me_5$ ), 16.4 (s, Me<sub>3</sub>CSi), 25.5 (s, Me<sub>3</sub>CSi), 92.1 (s, C<sub>5</sub>Me<sub>5</sub>), 127.2 (s, Ph), 136.6 (s, Ph), 137.0 (s, Ph), 143.4 (s, CN), 145.6 (s, Ph), 223.2 (s, CO). <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): -4.2 (s, *t*-BuMe<sub>2</sub>Si), 40.7 (s, SiPh<sub>3</sub>).

**Photoreaction of 2 with Et<sub>3</sub>SiH.** A solution of complex **2** (22.3 mg, 46.0  $\mu$ mol, 1.0 equiv) in 500  $\mu$ L of benzene- $d_6$  was treated with Et<sub>3</sub>SiH (14.7  $\mu$ L, 92.0  $\mu$ mol, 2.0 equiv) under nitrogen and photoirradiated at 25 °C. After 96 h of photo-irradiation, the solution changed color from brown to yellow, and <sup>1</sup>H NMR spectroscopy revealed the formation of Et<sub>3</sub>SiCN and *t*-BuMe<sub>2</sub>SiH in 58% yield based on the amount of complex **2** used.

**Computational Methods.** Molecular geometries were optimized at the density functional theory level using the M06 functional with 6-311+G(d,p) basis functions using the Gaussian09 program.<sup>34–36</sup> Normal coordinate analysis was performed for all stationary points to characterize the equilibrium structures and intermediates (the Hessian matrix has positive eigenvalues for equilibrium structures and one negative value for each TS). Calculations of intrinsic reaction coordinates near the TS followed by geometry optimization were performed for all reactions to confirm the connectivity of the TSs.<sup>37</sup> Unscaled vibrational frequencies were used to calculate zero-point-energy (ZPE) correction to the total energies. The

Gibbs free energies were also calculated at a temperature of 298.15 K and a pressure of 1.00 atm. Unless otherwise explicitly stated, the ZPE-corrected potential energies are used in the discussion.

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