

Iron-Complex-Catalyzed C–C Bond Cleavage of Organonitriles: Catalytic Metathesis Reaction between H–Si and R–CN Bonds to Afford R–H and Si–CN Bonds

Hiroshi Nakazawa,* Masumi Itazaki, Kouji Kamata, and Kensuke Ueda^[a]

Abstract: The first example of the catalytic C–CN bond cleavage of acetonitrile as well as Si–CN bond formation have been achieved in the photoreaction of MeCN with Et₃SiH promoted by [Cp(CO)₂FeMe]. This catalytic system is applicable to other organonitriles. Several iron complexes [(η⁵-C₅R₅)(CO)₂FeR'] (R₅ = H₅, H₄Me, Me₅, H₄SiMe₃, H₄I, H₄P(O)(OMe)₂; R' = SiMe₃, CH₂Ph, Me, Cl, I) were examined as catalyst, and [Cp(CO)₂FeMe]

was found to be the best precursor. A catalytic reaction cycle was proposed, which involves oxidative addition of Et₃SiH to [Cp(CO)FeMe], reductive elimination of CH₄ from [Cp(CO)FeMe(H)(SiEt₃)], coordination of RCN to [Cp(CO)Fe(SiEt₃)],

Keywords: C–C activation • homogeneous catalysis • metathesis • photolysis • silyliron complexes

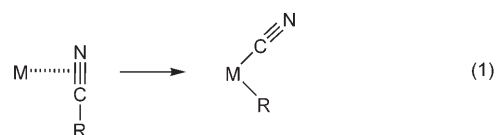
silyl migration from Fe to N in the coordinated RCN, and dissociation of Et₃SiNC from Fe. The reaction with MeCN of [Cp(CO)Fe(py)(SiEt₃)], which was newly prepared and determined by X-ray analysis, and the reaction of Et₃SiH with MeCN in the presence of a catalytic amount of [Cp(CO)Fe(py)(SiEt₃)] showed that the 16-electron species [Cp(CO)Fe(SiEt₃)] is the active species in the catalytic cycle (TON up to 251).

Introduction

C–C bond cleavage is an area of considerable current interest^[1] as the carbon–carbon bond is relatively unreactive. In particular, C–C bond activation in acetonitrile is a challenging topic because the molecule does not contain ring strain and has a larger C–C bond energy (133 kcal mol^{−1}) than the average alkane (≈83 kcal mol^{−1}). The ability to cleave the C–C bond in organonitriles and introduce the CN group into other organic compounds will therefore open up a great opportunity for using organonitriles as a CN source.

Transition-metal complexes have been used to attain C–C bond cleavage of nitriles. They mainly involve Group 10 transition-metal triads.^[2–10] Furthermore, one example each of Mo,^[11] Co,^[12] and U^[13] and two examples of Cu^[14,15] were reported. These reactions show stoichiometric C–C bond cleavage. In contrast, a few catalytic reactions involving Ni^[16] and Pd^[17] complexes were also reported. For these examples, it was proposed or clearly shown that direct oxida-

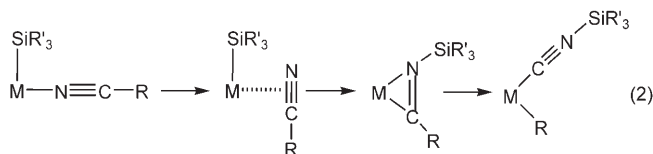
tive addition of the C–CN bond toward an electronically unsaturated transition-metal fragment takes place to give an alkyl(aryl)cyano complex [Eq. (1)].



Another reaction pathway for organonitrile C–C bond cleavage was reported independently by Bergman, Brookhart, and co-workers for Rh^[18] and Ir^[19] complexes and by our group for an Fe complex.^[20] In this mechanism, the silyl ligand on the transition metal plays a crucial role. The nitrile coordinates to the transition metal in an η¹ fashion, which then converts into η², followed by silyl migration to the nitrile nitrogen atom to give an η²-iminoacyl complex and successive C–C bond cleavage on the coordination sphere, thereby yielding an alkyl(aryl)silylsocyanide complex [Eq. (2)].

This silyl-assisted pathway has been demonstrated for a stoichiometric reaction. In this paper, we report the first catalytic C–CN bond cleavage of alkyl and aryl nitriles. A part of this work was reported earlier.^[21] After that communica-

[a] Prof. Dr. H. Nakazawa, Dr. M. Itazaki, K. Kamata, K. Ueda
Department of Chemistry
Graduate School of Science, Osaka City University
Sumiyoshi-ku, Osaka 558-8585 (Japan)
Fax: (+81) 6-6605-2522
E-mail: nakazawa@sci.osaka-cu.ac.jp

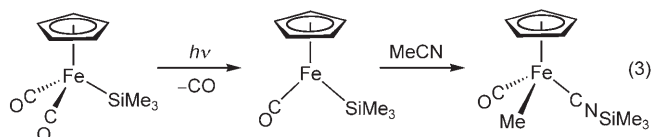


tion, Tobita^[22] and Chatani^[23] and their co-workers reported reactions that involve this type of silyl-assisted nitrile C-C bond cleavage.

Results and Discussion

Catalytic H₃C-CN Bond Cleavage

In our previous report, the theoretical calculation proposed that [Cp(CO)Fe(SiMe₃)] (Cp = cyclopentadienyl) reacts with MeCN to give [Cp(CO)Fe(Me)(CNSiMe₃)] exothermically according to the reaction sequence shown in Equation (2). [Cp(CO)Fe(SiMe₃)] can be generated from [Cp(CO)₂Fe(SiMe₃)] by photolysis [Eq. (3)].^[20] If Me₃SiNC is released from [Cp(CO)Fe(Me)(CNSiMe₃)] and the resulting 16-electron



iron species [Cp(CO)FeMe] is converted into [Cp(CO)Fe(SiMe₃)], then catalytic C-CN bond cleavage would be attained. As oxidative addition of an H-Si bond toward a 16-electron species is well-known, we examined the possibility of introducing a silyl group to an iron center by using a hydrosilane. Photoreaction of MeCN with an equimolar amount of Et₃SiH in the presence of 2 mol % of [Cp(CO)₂Fe(SiMe₃)] was conducted, and formation of Et₃SiCN was confirmed by ¹H and ¹³C NMR spectroscopy and gas chromatography. Immediately after the reaction, both Et₃SiNC and Et₃SiCN were detected, but finally only Et₃SiCN was observed. This observation is consistent with

the report that Et₃SiNC is gradually converted into thermally stable Et₃SiCN.^[24] In the above reaction, Et₃SiCN was formed in 45 % yield from MeCN and Et₃SiH. A small amount of Et₃Si-SiEt₃ was also produced, but SiEt₃Me was not produced at all. The formation of CH₄ was confirmed by the ¹H NMR spectrum of the reaction mixture. These results show the catalytic conversion of MeCN and Et₃SiH into Et₃SiCN and CH₄ by [Cp(CO)₂Fe(SiMe₃)]. The turnover number (TON) was 22.5 (Table 1, entry 1).

Table 1. Catalytic activities of various iron complexes^[a].

Et ₃ SiH + H ₃ C-CN $\xrightarrow[\text{THF, } h\nu]{\text{catalyst}}$ Et ₃ SiCN + CH ₄			
Entry	Catalyst	ν_{CO} [cm ⁻¹] ^[b]	TON ^[c]
1	[Cp(CO) ₂ Fe(SiMe ₃)] (1)	1990, 1931	22.5
2	[Cp(CO) ₂ Fe(benzyl)] (2)	2000, 1947	21.3
3	[Cp(CO) ₂ FeMe] (3)	2006, 1945	36.0
4	[Cp(CO) ₂ FeCl] (4)	2053, 2006	0.6
5	[Cp(CO) ₂ FeI] (5)	2041, 1996	2.0
6	[(C ₅ MeH ₄)(CO) ₂ FeMe] (6)	2002, 1941	32.5
7	[(C ₅ Me ₃ H)(CO) ₂ FeMe] (7)	1988, 1929	5.7
8	[(C ₅ Me ₃)(CO) ₂ FeMe] (8)	1984, 1924	4.3
9	[(C ₅ H ₄ SiMe ₃)(CO) ₂ FeMe] (9)	1992, 1950	26.4
10	[(C ₅ H ₄ SiMe ₃)(CO) ₂ FeI] (10)	2036, 1992	2.0
11	[(C ₅ H ₄ I)(CO) ₂ FeMe] (11)	2012, 1955	12.6
12	[(C ₅ H ₄ {P(O)(OMe) ₂ }(CO) ₂ FeMe] (12)	2016, 1960	9.8

[a] Reactions were carried out at room temperature for 24 h under photoirradiation by using catalyst (0.52 mmol), Et₃SiH (26.00 mmol), and THF (5.00 mL) in acetonitrile (13.6 mL, 260.00 mmol). [b] CH₂Cl₂, 25 °C. [c] Determined by GC with toluene as internal standard.

Next, we examined the effect of the ligand at the Fe center on catalytic activity. The alkyl iron complexes [Cp(CO)₂FeR] (R = benzyl, Me) were used as catalyst. The catalytic activity of the benzyl complex was slightly lower than that of the silyl complex (Table 1, entry 2), whereas the methyl complex was more active (Table 1, entry 3). The halogenoiron complexes [Cp(CO)₂FeX] (X = Cl, I) showed low activities (Table 1, entries 4 and 5). Modification of the Cp ligand in [Cp(CO)₂FeMe] also varied the catalytic activity. As the number of methyl substituents on the Cp ring increased, the catalytic activity decreased (Table 1, entries 6–8). Introduction of SiMe₃, I, and P(O)(OMe)₂ groups resulted in low activity (Table 1, entries 9–12). The electron density of the central Fe is reflected in the CO stretching frequencies in the IR spectra. Figure 1 shows the relationship between TON and the symmetric CO stretching frequency for the complexes in Table 1. With the exception of complex **2**, the data show a sharp, single hump with complex **3** at the top, thus indicating that iron complexes with adequate electron density (ν_{CO} = 1990–2010 cm⁻¹) display high catalytic activity, whereas those with low or high electron density exhibit low activity. As both the processes of oxidative addition and reductive elimination are important in the catalytic cycle, it follows that iron complexes with well-balanced electron densities exhibit high catalytic activity.

The catalytic activities of the related methyl complexes of Mo and W, [Cp(CO)₃MMe] (M = Mo, W), were sluggish.

Abstract in Japanese:

[Cp(CO)₂FeMe] 共存下、MeCNとEt₃SiHに光照射を行うと、触媒的に C-CN 結合切断と Si-CN 結合生成が起こることを見出した。この触媒反応は他の有機ニトリルにも適応可能である。触媒サイクルは [Cp(CO)FeMe] への Et₃Si-H の酸化的付加、CH₄ の還元的脱離により生成した [Cp(CO)Fe(SiEt₃)] へ RCN が配位し、その後シリル基の Fe からニトリル窒素への転位、C-C 結合切断、そして Et₃SiNC の解離により成り立っていることを示した。新たに合成した [Cp(CO)Fe(py)(SiEt₃)] と MeCN との反応、および触媒量の [Cp(CO)Fe(py)(SiEt₃)] 存在下 Et₃SiH と MeCN との反応より、[Cp(CO)Fe(SiEt₃)] が触媒活性種であることを示した。

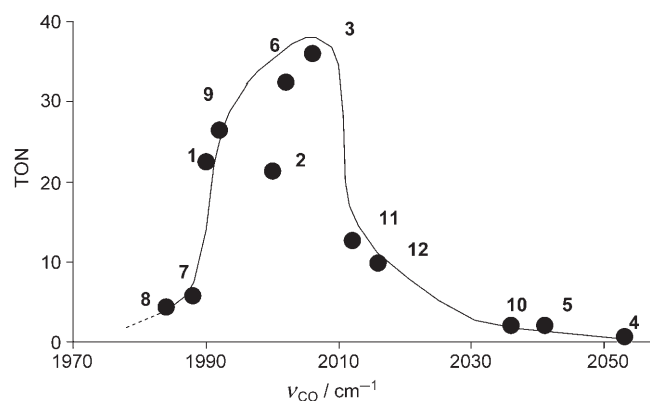


Figure 1. Plot of TON as a function of ν_{CO} (symmetric) for the iron complexes shown in Table 1.

C–CN Bond Cleavage of Organonitriles Other than Acetonitrile

To see the scope and limitations of the catalytic activity of $[\text{Cp}(\text{CO})_2\text{FeMe}]$ (**3**) for C–CN bond cleavage, we examined reactions with several organonitriles other than acetonitrile. Table 2 summarizes the results. Propionitrile (EtCN) was converted into Et_3SiCN in 73 % yield ($\text{TON}=18.2$) (Table 2, entry 1). Isobutyronitrile ($i\text{PrCN}$) and malononitrile (NCCH_2CN) were poorly converted (Table 2, entries 2 and 3). However, succinonitrile ($\text{NCCH}_2\text{CH}_2\text{CN}$) was converted as much as propionitrile (65 % yield, $\text{TON}=16.3$; Table 2, entry 4).

Cyclopropylcyanide ($\text{C}_3\text{H}_5\text{CN}$), allylcyanide ($\text{CH}_2=\text{CHCH}_2\text{CN}$), trimethylacetoneitrile ($t\text{BuCN}$), trichloroacetoneitrile (Cl_3CCN), dimethylaminoacetoneitrile ($\text{Me}_2\text{NCH}_2\text{CN}$), methoxyacetoneitrile (MeOCH_2CN), and *p*-toluenesulfonylacetoneitrile ($\text{MeC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CN}$) were resistant to C–CN bond cleavage under the reaction conditions (Table 2, entries 5–11). These results indicate that an electron-withdrawing, bulky, or coordination-feasible substituent on the carbon atom adjacent to the CN group is unfavorable for C–CN bond cleavage.

For aryl nitriles, the C–CN bonds were cleaved with TONs of about 10 (Table 2, entries 12–15). The TON for phthalonitrile is slightly lower (Table 2, entry 13) than that for benzonitrile, which may be due to the presence of an electron-withdrawing group in the *ortho* position. The TON for *p*-methoxybenzonitrile is slightly higher than for benzonitrile (Table 2, entry 16), which may be due to the electron-releasing OMe group. The C–CN bond was hardly cleaved for pentafluorobenzonitrile (Table 2, entry 17), possibly due to the strongly electronegative nature of F.

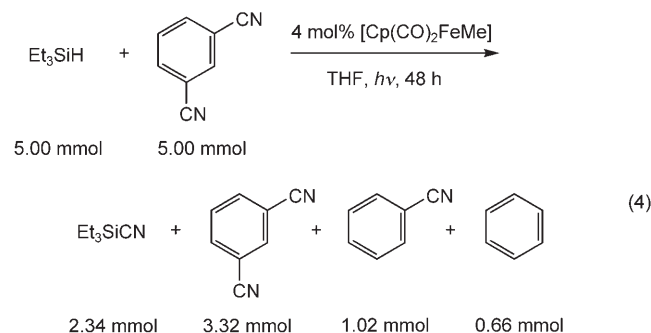
The TONs in Table 2 were obtained based on the amount of Et_3SiCN produced. For Table 2, entries 13–15, Et_3SiCN can be generated from conversion of $\text{C}_6\text{H}_4(\text{CN})_2$ into $\text{C}_6\text{H}_5\text{CN}$, and from subsequent conversion of $\text{C}_6\text{H}_5\text{CN}$ into C_6H_6 . To elucidate the source of Et_3SiCN , every organic product was examined after 48 h irradiation for the case of Table 2, entry 14. The results are shown in Equation (4). Under the reaction conditions, a third of the $\text{C}_6\text{H}_4(\text{CN})_2$ re-

Table 2. C–CN bond-cleavage reactions of organonitriles^[a]

$\text{Et}_3\text{SiH} + \text{R-CN} \xrightarrow[h\nu, 48 \text{ h}]{\text{cat. } [\text{Cp}(\text{CO})_2\text{FeMe}]} \text{Et}_3\text{SiCN} + \text{R-H}$		
Entry	R-CN	TON ^[d]
1	Et-CN	18.2
2	$i\text{Pr-CN}$	4.2
3 ^[b]	$\text{NC-CH}_2\text{-CN}$	7.4
4 ^[b]	$\text{NC-CH}_2\text{-CH}_2\text{-CN}$	16.3
5	Cyclopropyl-CN	no reaction
6	Allyl-CN	no reaction
7	$t\text{Bu-CN}$	no reaction
8	$\text{Cl}_3\text{C-CN}$	0.3
9	$\text{Me}_2\text{N-CH}_2\text{-CN}$	no reaction
10	$\text{MeO-CH}_2\text{-CN}$	trace
11	$\text{Me-C}_6\text{H}_4\text{-SO}_2\text{-CH}_2\text{-CN}$	0.4
12 ^[c]	$\text{C}_6\text{H}_5\text{-CN}$	12.2
13 ^[c]	$\text{C}_6\text{H}_4(\text{CN})_2$ (ortho)	10.5
14 ^[c]	$\text{C}_6\text{H}_4(\text{CN})_2$ (para)	11.7
15 ^[c]	$\text{C}_6\text{H}_3(\text{CN})_3$	11.5
16 ^[c]	$\text{MeO-C}_6\text{H}_4\text{-CN}$	15.2
17 ^[c]	$\text{C}_6\text{F}_5\text{-CN}$	trace

[a] Catalyst (0.20 mmol), Et_3SiH (5.00 mmol), THF (0.40 mL), nitrile (50.00 mmol). [b] Nitrile (2.50 mmol), THF (1.30 mL). [c] Catalyst (0.20 mmol), Et_3SiH (5.00 mmol), THF (8.00 mL), nitrile (5.00 mmol). [d] Determined by GC with toluene as internal standard.

acted, and, interestingly, benzene as well as benzonitrile was produced. The molar ratio of benzene to benzonitrile (1:2) indicates that $\text{C}_6\text{H}_5\text{CN}$ is more reactive than $\text{C}_6\text{H}_4(\text{CN})_2$ for C–CN bond cleavage. This is consistent with the trend mentioned above, that is, that an electron-withdrawing substituent lowers the activity for C–CN bond cleavage.

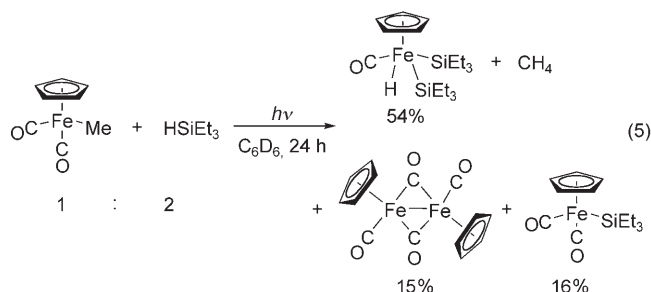


Catalytic Reaction Cycle

A plausible catalytic cycle is shown in Scheme 1 for the reaction of MeCN with Et₃SiH in the presence of [Cp(CO)₂FeMe] as a catalyst precursor. One CO ligand in the precursor is released by photolysis to give [Cp(CO)FeMe], which reacts with Et₃SiH to give [Cp(CO)FeMe(H)(SiEt₃)]. This process seems plausible because oxidative addition of an Si–H bond to a 16-electron species of Fe was reported to give, for example, [Cp(CO)Fe(H)(SiEt₃)₂].^[25] The subsequent reductive elimination of CH₄ yields [Cp(CO)Fe(SiEt₃)]. As SiEt₃Me was not observed at all in this system, reductive elimination of CH₄ from [Cp(CO)FeMe(H)(SiEt₃)] seems to precede that of Et₃SiMe. The 16-electron species thus formed reacts with MeCN to give ultimately [Cp(CO)Fe(Me)(η¹-CNSiEt₃)]. The reaction sequences have been demonstrated theoretically [Eq. (2)].^[20] Dissociation of Et₃SiNC generates [Cp(CO)FeMe] to complete the catalytic cycle. The released Et₃SiNC isomerizes to thermodynamically stable Et₃SiCN. Interruption of the irradiation induced a stop to Et₃SiNC formation. Therefore, we believe that photoirradiation is essential for Et₃SiNC dissociation from [Cp(CO)Fe(Me)(η¹-CNSiEt₃)] as well as CO dissociation from [Cp(CO)₂FeMe].

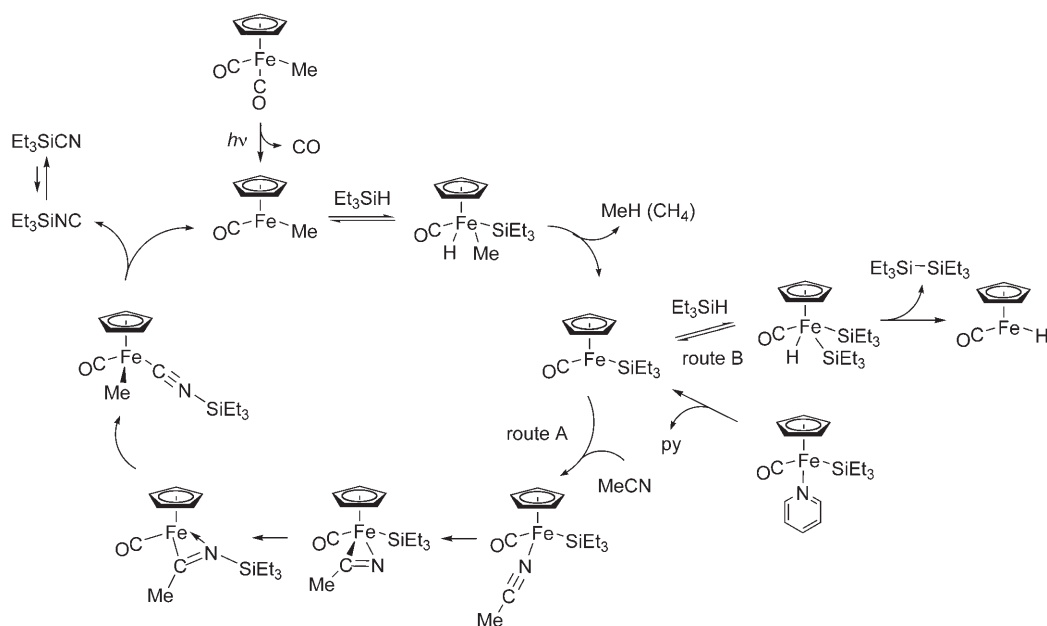
The [Cp(CO)Fe(SiEt₃)] produced in the catalytic cycle is expected to react mainly with MeCN, but it could also react with Et₃SiH present in the solution to give [Cp(CO)Fe(H)(SiEt₃)₂] through Si–H oxidative addition. Et₃Si–SiEt₃ would be formed if the two silyl groups were eliminated reductively from the species. In practice, a small amount of the disilane was observed (see above) in this catalytic system. Photoirradiation was examined with a solution of C₆D₆ containing [Cp(CO)₂FeMe] and Et₃SiH (1:2 molar ratio) but not MeCN. After irradiation for 24 h, the

¹H NMR spectrum exhibited a hydride signal at –14.07 ppm attributable to [Cp(CO)Fe(H)(SiEt₃)₂]^[25] (54% yield by NMR spectroscopy), a signal at 0.15 ppm due to CH₄, and signals due to [[Cp(CO)₂Fe]₂] and [Cp(CO)₂Fe(SiEt₃)] [Eq. (5)]. Therefore, [Cp(CO)Fe(SiEt₃)] can react by either of two routes in the system: route A (reaction with MeCN) and route B (reaction with Et₃SiH).



Exploration of the Active Species

In the catalytic cycle shown in Scheme 1, [Cp(CO)Fe(SiEt₃)] is one of the most important intermediates. However, its isolation and spectroscopic detection are difficult because it is a reactive 16-electron species. Therefore, we planned to trap it by coordination of a weak ligand. Pyridine is a good candidate for this purpose.^[26] The reaction of [Cp(CO)₂Fe(SiEt₃)] with pyridine under photolysis generated [Cp(CO)Fe(SiEt₃)(py)] (**13**) in 89% yield [Eq. (6)]. The structure of **13** was confirmed by single-crystal X-ray diffraction analysis (Figure 2 and Table 3). The iron center is coordinated to a triethylsilyl ligand, a cyclopentadienyl ligand in η⁵ fashion, a terminal CO ligand, and a pyridine molecule to form a typical three-legged piano-stool structure. Structural



Scheme 1. Proposed catalytic cycle.

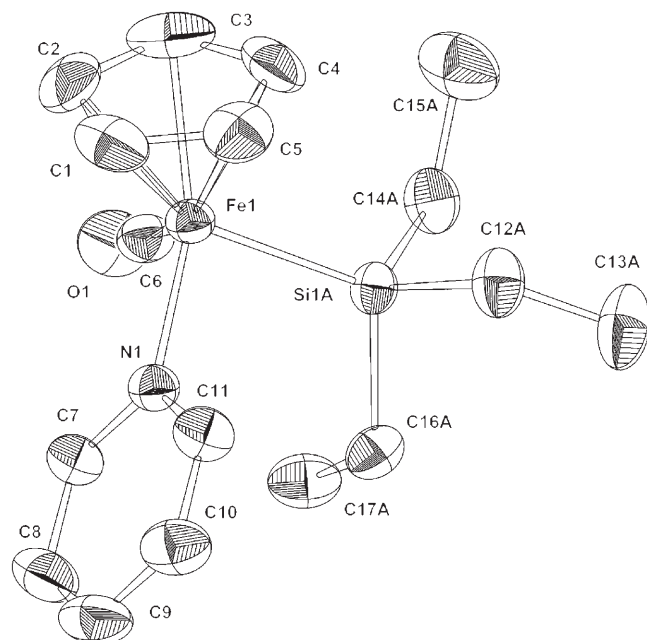
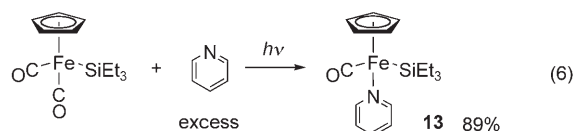


Figure 2. ORTEP drawing of **13** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for simplicity. Selected bond lengths [Å] and angles [°]: Fe1–Si1A=2.303(5), Fe1–Si1B=2.424(17), Fe1–N1=1.9823(17), Fe1–C6=1.719(2), C6–O1=1.167(3); C6–Fe1–N1=97.39(9), C6–Fe1–Si1A=83.24(15), C6–Fe1–Si1B=86.3(4), N1–Fe1–Si1A=89.25(10), N1–Fe1–Si1B=96.4(3).

Table 3. Crystal data and structure refinement for **13**.

Empirical formula	C ₁₇ H ₂₅ NOSiFe
Formula weight	343.32
<i>T</i> [K]	203(2)
Crystal system	monoclinic
Space group	<i>P</i> ₂ /c
<i>a</i> [Å]	13.299(2)
<i>b</i> [Å]	8.3129(13)
<i>c</i> [Å]	15.870(3)
β [°]	93.379(4)
<i>V</i> [Å ³]	1751.5(5)
<i>Z</i>	4
ρ_{calcd} [mg m ⁻³]	1.302
μ [mm ⁻¹]	0.928
<i>F</i> (000)	728
Crystal size [mm ³]	0.34 × 0.34 × 0.14
θ range for data collection [°]	4.08–27.48
Limiting indices	–17 ≤ <i>h</i> ≤ 17 –10 ≤ <i>k</i> ≤ 10 –16 ≤ <i>l</i> ≤ 20
Reflections collected	16273
Independent reflections (<i>R</i> (int))	3969 (0.0310)
Completeness to $\theta = 27.48^\circ$ [%]	98.6
Goodness-of-fit on <i>F</i> ²	1.149
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> 1 = 0.0451, <i>wR</i> 2 = 0.0983
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0503, <i>wR</i> 2 = 0.1008
Largest diff. peak, hole [e Å ⁻³]	0.382, –0.316

disorder was observed in the SiEt₃ group. The Fe–N bond (1.9823(17) Å) is shorter than that in the previously reported [(η^5 -C₅Me₅)(CO)Fe(SiMe₂NPh₂)(py)] (Fe–N 1.991(1) Å).^[27]

To examine the activity of the pyridine complex, **13** was dissolved in MeCN, and the amount of Et₃SiCN produced was determined with time under various conditions [Eq. (7)]. The results are shown in Figure 3. It was found

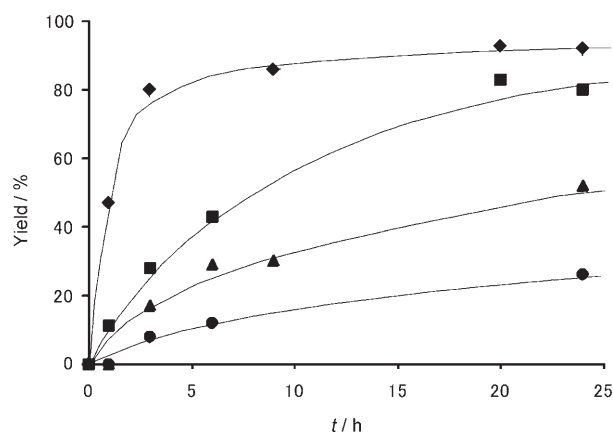
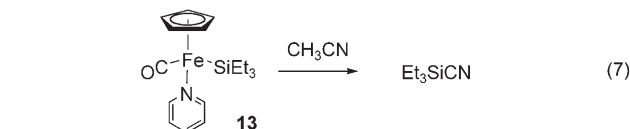
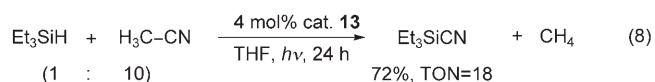


Figure 3. Plot of yield of Et₃SiCN as a function of time for the reaction of **13** with CH₃CN. Conditions: *hν*, 25°C (◆), 80°C (■), 50°C (▲), 25°C (●).

that **13** reacts with MeCN to give Et₃SiCN, and the reaction proceeds faster with increasing temperature. Photolysis was most effective for producing Et₃SiCN, which implies that dissociation of pyridine may require photoenergy.^[28] The catalytic activity of **13** was also examined. Photoreaction of a solution of THF containing 4 mol % of **13**, Et₃SiH, and MeCN gave Et₃SiCN in 72% yield (TON=18) [Eq. (8)], thus showing that **13** serves as a catalyst. These results strongly suggest that [Cp(CO)Fe(SiEt₃)] is an active species in the catalytic cycle.



Optimization of Reaction Conditions

According to the catalytic cycle shown in Scheme 1, [Cp(CO)Fe(SiEt₃)] can react with both MeCN and Et₃SiH. The former reaction seems dominant, but the latter is not negligible. If the reaction of [Cp(CO)Fe(SiEt₃)] with Et₃SiH is suppressed, the catalytic cycle is expected to work more

effectively. Thus, we attempted the reaction with a change in the molar ratio of Et_3SiH and MeCN . Reaction of Et_3SiH with a 10-fold molar excess of MeCN in the presence of 0.83 mol % $[\text{Cp}(\text{CO})_2\text{FeMe}]$ under photolysis for 24 h at 50°C produced Et_3SiCN in 99% yield based on Et_3SiH ($\text{TON}=118$). The TON increased with photoirradiation time (48 h: $\text{TON}=156$; 96 h: $\text{TON}=197$). The highest TON (251) was obtained when Et_3SiH and a 10-fold molar excess of MeCN were photolyzed for 1 week at 50°C in the presence of 0.2 mol % of $[\text{Cp}(\text{CO})_2\text{FeMe}]$. Compared with $\text{Pd}^{[17]}$ and $\text{Rh}^{[18]}$ systems, our catalytic system is very effective.

Conclusions

We have established a new catalytic system involving C–CN bond cleavage of organonitriles promoted by a silyliron complex. In this system, Et_3SiH and C–CN are converted into C–H and Et_3SiCN . In other words, a metathesis reaction between H–Si and C–CN bonds catalytically takes place to afford C–H and Si–CN bonds. This reaction is unprecedented in terms of 1) catalytic acetonitrile C–C bond cleavage, 2) transition-metal catalysts other than Ni for organonitrile C–CN bond activation, and 3) catalytic silylcyanide formation derived from organonitriles. The findings open up a great opportunity to use organonitriles as a CN source.^[29]

Experimental Section

General Methods

All manipulations were carried out with standard Schlenk techniques under nitrogen atmosphere. $[(\text{C}_5\text{R}_5)(\text{CO})_2\text{FeMe}]$ ($\text{C}_5\text{R}_5 = \text{C}_5\text{H}_5$,^[30] $\text{C}_5\text{H}_4\text{Me}$,^[31] C_5HMe_2 ,^[32] C_5Me_5 ,^[33] $\text{C}_5\text{H}_4(\text{SiMe}_3)$,^[34] $\text{C}_5\text{H}_4[\text{P}(\text{O})(\text{OMe})_2]$,^[35] $\text{C}_5\text{H}_4\text{I}$,^[36]), $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeX}]$ ($\text{X} = \text{Cl}$,^[37] I ,^[38] CH_2Ph ,^[39] SiMe_3 ,^[40]), and $[\text{Cp}(\text{CO})_2\text{Fe}(\text{SiEt}_3)]$ ^[41] were prepared according to literature methods. Acetonitrile and THF were distilled from sodium and benzophenone prior to use and stored under nitrogen. The other chemicals were commercially available. NMR spectra (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$) were recorded on a JEOL EX-400 spectrometer. The residual peaks of the solvent were used as the reference for ^1H NMR spectra ($[\text{D}_6]\text{benzene}$: $\delta = 7.15$ ppm). For $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, solvent signals were used as the chemical-shift reference. Peak positions of the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum were referenced to external tetramethylsilane ($\delta = 0$ ppm). GC analysis was performed on a Shimadzu GC 14B equipped with an Rtx-1701 column (30 m \times 0.25 mm, detector=FID, 250°C) with helium gas as carrier. All yields and TONs were determined by GC with toluene as internal standard.

Syntheses

General method for catalytic C–CN bond cleavage: In a typical reaction, a solution of triethylsilane (15.00 mmol, 2.4 mL), acetonitrile (150.00 mmol, 7.86 mL), and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{Me})]$ (0.83 mol %, 0.13 mmol, 24 mg) in THF (2.1 mL) was irradiated with a 400-W medium-pressure mercury arc lamp at 50°C for 24 h under nitrogen atmosphere. After irradiation, toluene (0.20 mmol, 21.2 μL) was added to the reaction mixture. The resulting solution was subjected to GC (99% yield base on Et_3SiH , $\text{TON}=118$).

Reaction of $[\text{Cp}(\text{CO})_2\text{FeMe}]$ with triethylsilane in an NMR tube: Et_3SiH (0.288 mmol, 46.0 μL) and triphenylmethane (0.132 mmol, 32.3 mg) as internal standard were added to a solution of $[\text{Cp}(\text{CO})_2\text{FeMe}]$ (0.132 mmol, 25.4 mg) in C_6D_6 (0.5 mL) in an NMR sample tube. The

NMR tube was sealed and photolyzed for 24 h at room temperature. The products were $[\text{Cp}(\text{CO})\text{FeH}(\text{SiEt}_3)_2]$ (54%), CH_4 ($\delta = 0.15$ ppm), $[\text{Cp}(\text{CO})_2\text{Fe}]$ (15%), and $[\text{Cp}(\text{CO})_2\text{Fe}(\text{SiEt}_3)]$ (16%). $[\text{Cp}(\text{CO})\text{FeH}(\text{SiEt}_3)_2]$: ^1H NMR (400 MHz, C_6D_6): $\delta = -14.07$ (s, 1H, FeH), 0.89–0.98 (m, 12H, CH_2), 1.13 (t, $J_{\text{HH}} = 7.6$ Hz, 18H, CH_3), 5.23 ppm (s, 5H, C_5H_5).

13: A solution of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{SiEt}_3)]$ (2.19 mmol, 641 mg) and pyridine (6.68 mmol, 540 μL) in benzene (10 mL) was subjected to irradiation. After 1 h, pyridine (4.95 mmol, 400 μL) was added to the reaction mixture. Irradiation was continued for several hours. Removal of volatile materials under reduced pressure led to the formation of a dark-red oil, which was dissolved in hexane (2 mL). After the solution was cooled at -20°C for 9 h, the resulting dark-red crystals were filtered off and dried in vacuo to give **13** (1.95 mmol, 669 mg, 89%). ^1H NMR (400 MHz, C_6D_6): $\delta = 0.92$ –1.06 (m, 6H, SiCH_2CH_3), 1.19 (t, $J_{\text{HH}} = 8.0$ Hz, 9H, SiCH_2CH_3), 4.21 (s, 5H, Cp), 5.86 (t, $J_{\text{HH}} = 7.2$ Hz, 2H, *m*-py), 6.40 (t, $J_{\text{HH}} = 7.2$ Hz, 1H, *p*-py), 8.47 ppm (d, $J_{\text{HH}} = 5.6$ Hz, 2H, *o*-py); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 10.2$ (CH_2), 11.0 (CH_3), 81.7 (Cp), 122.9 (py), 133.4 (py), 133.5 (py), 157.7 (py), 157.7 (py), 223.5 ppm (CO); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.3 MHz, C_6D_6): $\delta = 50.2$ ppm; elemental analysis: calcd (%) for $\text{C}_{17}\text{H}_{25}\text{NOSiFe}$: C 59.47, H 7.34, N 4.08%; found: C 59.04, H 7.13, N 4.06%.

X-ray Diffraction Structure Analysis of 13

A crystal of **13** suitable for X-ray diffraction study was mounted in a glass capillary. Data for **13** were collected at -70°C on a Rigaku AFC-7/ Mercury CCD area-detector diffractometer equipped with monochromatized MoK_α radiation. Calculations for **13** were performed with the CrystalClear software package of Molecular Structure Corporation. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculation without further refinement of the parameters. Relevant crystal data are listed in Table 3, together with refinement details. CCDC-622512 (**13**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/data_request.cif.

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