

## N-CN Bond Cleavage of Cyanamides by a Transition-metal Complex

Kozo Fukumoto, Tsukuru Oya, Masumi Itazaki, and Hiroshi Nakazawa\*

*Department of Chemistry, Graduate School of Science, Osaka City  
University,*

*Sumiyoshi-ku, Osaka 558-8585, Japan*

### Supporting Information

**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 metal. These were stored under nitrogen atmosphere. Me<sub>2</sub>NCN and H<sub>2</sub>NCN were commercially available. Photo-irradiation was performed with a 400 W medium-pressure mercury arc lamp at room temperature under nitrogen atmosphere. NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si) were recorded on a JEOL EX-400 spectrometer. The residual peaks of the solvent were used as the reference for <sup>1</sup>H NMR spectra. For <sup>13</sup>C NMR spectra, solvent signals were used as the chemical-shift reference. Peak positions of the <sup>29</sup>Si NMR spectra were referenced to external tetramethylsilane ( $\delta = 0$  ppm).

**Preparation of cyanamides:** Di-*n*-hexylcyanamide, N-cyanopiperidine, N-cyanomorpholine, and N-cyanopyrrolidine were synthesized according to the literature methods<sup>1</sup>. Secondary amine (10.0 mmol) was added to 20 mL of anhydrous ether at room temperature with stirring and the mixture was cooled to 0 °C. To the solution was added dropwise over 30 min 20 mL of anhydrous ether containing cyanogen bromide (5.0 mmol, 0.530 g). Then, the reaction mixture was allowed to warm to room temperature, and was stirred for 2 h. Precipitates of ammonium chloride formed were removed by filtration, and the filtrate was concentrated under reduced pressure to a small volume, which was distilled to give the desired cyanamide. The spectroscopic data (<sup>1</sup>H and <sup>13</sup>C NMR and IR data) were identical with those in the literatures.

**Photoreaction of cyanamides with 1:** In a typical reaction, a solution of dimethylcyanamide (0.0787 mmol, 6.57  $\mu$ L) and Cp(CO)<sub>2</sub>Fe(SiEt<sub>3</sub>) (0.0787 mmol, 23.0 mg) in toluene (0.31 mL, 0.25 M solution) was photo-irradiated. After removal of volatile materials at 3000 Pa, the residue was dissolved in a small amount of pentane and loaded on a silica-gel column, and eluted with pentane to isolate triethylsilyl cyanide.

**Preparation of  $\text{Cp}^*(\text{CO})(\text{py})\text{Fe}(\text{SiMe}_2\text{Ph})$  (py = pyridine) (**4**):** Complex **4** was prepared in a manner similar to that for  $\text{Cp}(\text{CO})(\text{py})\text{Fe}(\text{SiEt}_3)$ .<sup>2</sup> A solution of  $\text{Cp}^*(\text{CO})_2\text{Fe}(\text{SiMe}_2\text{Ph})$  (2.21 mmol, 844 mg) and pyridine (11.0 mmol, 0.893 mL) in toluene (10 mL) was subjected to photo-irradiation for several hours. Removal of volatile materials under reduced pressure led to the formation of a dark-red solid, which was washed three times with hexane at  $-78^\circ\text{C}$ . Pure crystals of **4** were obtained by recrystallization with hexane at  $-20^\circ\text{C}$  (1.66 mmol, 721 mg, 75 %).  $^1\text{H}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 0.72 (s, 3H,  $\text{SiCH}_3$ ), 0.63 (s, 3H,  $\text{SiCH}_3$ ), 1.42 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 5.96 (s, 1H,  $p\text{-NC}_5\text{H}_5$ ), 6.46 (s, 2H,  $m\text{-NC}_5\text{H}_5$ ), 7.23-7.80 (m, 5H, Ph), 8.31 (s, 2H,  $o\text{-NC}_5\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 2.7 (s,  $\text{SiCH}_3$ ), 3.6 (s,  $\text{SiCH}_3$ ), 10.0 (s,  $\text{C}_5\text{Me}_5$ ), 90.4 (s,  $\text{C}_5\text{Me}_5$ ), 123.2 (s,  $p\text{-NC}_5\text{H}_5$ ), 126.7 (s, Ph), 127.1 (s, Ph), 133.2 (s,  $m\text{-NC}_5\text{H}_5$ ), 134.1 (s, Ph), 150.5 (s,  $o\text{-NC}_5\text{H}_5$ ), 156.6 (s, Ph), 223.4 (s, CO).  $^{29}\text{Si}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 34.5 (s). IR ( $\text{cm}^{-1}$ , in  $\text{C}_6\text{D}_6$ ):  $\nu(\text{CO})$ : 1874.

**Synthesis of N-silylated  $\eta^2$ -amidino complexes **3** and **5**:** Complex **2** (1.37 mmol, 592 mg) was treated with  $\text{Me}_2\text{NCN}$  (1.37 mmol, 0.114 mL) in toluene at  $50^\circ\text{C}$  for 10 h. Removal of volatile materials under reduced pressure led to the formation of the corresponding N-silylated  $\eta^2$ -amidino complex **3** as a dark-red oil in 100 %  $^1\text{H}$  NMR yield. In a similar way, the N-silylated  $\eta^2$ -amidino complex **5** was obtained as orange powders which were purified by washing with pentane at  $-78^\circ\text{C}$  (1.16 mmol, 492 mg, 85 %). **3**:  $^1\text{H}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 0.64 (q, 6H,  $\text{SiCH}_2\text{CH}_3$ ,  $J_{\text{HH}} = 75.9$  Hz), 0.95 (t, 9H,  $\text{SiCH}_2\text{CH}_3$ ,  $J_{\text{HH}} = 75.9$  Hz), 2.49 (s, 3H,  $\text{NCH}_3$ ), 3.20 (s, 3H,  $\text{NCH}_3$ ), 4.36 (s, 5H, Cp).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 7.1 (s,  $\text{SiCH}_2\text{CH}_3$ ), 7.7 (s,  $\text{SiCH}_2\text{CH}_3$ ), 39.1 (s,  $\text{NCH}_3$ ), 42.8 (s,  $\text{NCH}_3$ ), 79.5 (s, Cp), 194.8 (s,  $\text{NCN}$ ), 219.5 (s, CO).  $^{29}\text{Si}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 7.1 (s). IR ( $\text{cm}^{-1}$ , in toluene):  $\nu(\text{CO})$ : 1902. **5**:  $^1\text{H}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 0.32 (s, 3H,  $\text{SiCH}_3$ ), 0.47 (s, 3H,  $\text{SiCH}_3$ ), 1.72 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 2.37 (s, 3H,  $\text{NCH}_3$ ), 3.05 (s, 3H,  $\text{NCH}_3$ ), 7.22-7.60 (m, 5H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 0.9 (s,  $\text{SiCH}_3$ ), 3.1 (s,  $\text{SiCH}_3$ ), 10.9 (s,  $\text{C}_5\text{Me}_5$ ), 39.6 (s,  $\text{NCH}_3$ ), 42.4 (s,  $\text{NCH}_3$ ), 89.9 (s,  $\text{C}_5\text{Me}_5$ ), 128.6 (s, Ph), 129.2 (s, Ph), 133.8 (s, Ph), 141.1 (s, Ph), 204.0 (s,  $\text{NCN}$ ), 220.6 (s, CO).  $^{29}\text{Si}$  NMR ( $\delta$ , in  $\text{C}_6\text{D}_6$ ): 35.4 (s). IR ( $\text{cm}^{-1}$ , in toluene):  $\nu(\text{CO})$ : 1884.

**Photoreaction of dimethylcyanamide with triethylsilane in the presence of **6** or **7**:** A solution containing methylcomplex **6** or **7** (0.0150 mmol), dimethylcyanamide (0.150 mmol, 12.5  $\mu\text{L}$ ) and triethylsilane (0.150 mmol, 24.0  $\mu\text{L}$ ) in toluene (3.0 mL) was photo-irradiated. After removal of volatile materials at 3000 Pa, the residue was dissolved in a small amount of pentane and was charged on a silica-gel column to isolate

triethylsilyl cyanide.

**Thermal reaction of dimethylcyanamide with triethylsilane in the presence of **6** or **7**:**

In stoichiometric reactions, a solution containing methylcomplex **6** or **7** (0.0150 mmol), dimethylcyanamide ( 0.0150 mmol, 12.5  $\mu$ L) and triethylsilane (0.0150 mmol, 24.0  $\mu$ L) in toluene ( 3.0 mL) was heated under nitrogen atmosphere. Then, triethylsilylcyanide formed was isolated in the similar manner described above. The catalytic activity of **6** and **7** was also examined.

**X-ray Crystal structure determination of **5**:** Dark-red crystals of **5** suitable for an X-ray diffraction study were obtained through crystallization from pentane. The single crystal was mounted in a glass capillary. Data for **5** were collected at -70  $^{\circ}$ C on Rigaku/MSM Mercury CCD area-detector diffractometer equipped with monochromated MoK $\alpha$  radiation. Calculations for **5** were performed with the teXane crystallographic software package of Molecular Structure Corporation. Crystal Data: C<sub>22</sub>H<sub>32</sub>FeN<sub>2</sub>OSi, *M* = 424.44, orange plate, 0.18  $\times$  0.10  $\times$  0.06 mm<sup>3</sup>, monoclinic, space group P2<sub>1</sub>/c (No. 14), *a* = 12.2300(12) Å, *b* = 9.0822(8) Å, *c* = 20.872(2) Å,  $\beta$  = 103.847(5) $^{\circ}$ , *V* = 2251.0(4) Å<sup>3</sup>, *Z* = 4,  $\mu$ (MoK $\alpha$ ) = 7.358 cm<sup>-1</sup>, *D*<sub>calc</sub> = 1.252 g/cm<sup>3</sup>, 16617 reflections collected, 5062 (*I* > 3 $\sigma$ *I*) unique reflections were used in all calculations, number of variables = 373, *R* = 0.0680, *R*<sub>w</sub> = 0.1077, and goodness of fit = 1.116.

**Table S1** Crystal data and structure refinement for **5**.

	<b>5</b>
Empirical formula	C <sub>22</sub> H <sub>32</sub> FeN <sub>2</sub> OSi
Formula weight	424.44
Crystal system	Monoclinic
Crystal size(mm <sup>3</sup> )	0.18 $\times$ 0.10 $\times$ 0.06
Space group	P2 <sub>1</sub> /c (No. 14)
<i>a</i> , Å	12.2300(12)
<i>b</i> , Å	9.0822(8)
<i>c</i> , Å	20.872(2)

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$\beta$ , deg	103.847(5)
$V$ , Å <sup>3</sup>	2251.0(4)
$Z$	4
$\mu$ , cm <sup>-1</sup>	7.358
$F(000)$	904.00
$D_{\text{calcd}}$ , g cm <sup>-1</sup>	1.252
No. of unique reflections	16617
No. of used reflections	5062
No. of variables	373
$^aR$	0.0502
$^bR_w$	0.1077
<i>Goodness-of-fit</i>	1.116

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$$^aR = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|.$$

$$^bR_w = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma wFo^2]^{0.5}$$

$$\text{Weighting scheme } [\sigma(F_o)^2]^{-1}$$

**Table S2** Selected bond distances (Å), bond angles (°), and torsion angles (°) for **5**.

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Fe(1)–N(2)	2.043(2)
Fe(1)–C(1)	1.732(2)
Fe(1)–C(2)	1.859(2)
Si (1)–N(2)	1.7181(18)
Si(1)–C(5)	1.866(3)
Si(1)–C(6)	1.847(3)
Si(1)–C(7)	1.880(2)
O(1)–C(1)	1.167(3)

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N(1)–C(2)	1.327(3)
N(1)–C(3)	1.455(3)
N(1)–C(4)	1.458(3)
N(2)–C(2)	1.303(2)
N(2)–Fe(1)–C(1)	100.34(10)
N(2)–Fe(1)–C(2)	38.65(8)
C(1)–Fe(1)–C(2)	94.65(12)
C(3)–N(1)–C(4)	117.0(2)
Fe(1)–N(2)–Si(1)	134.04(12)
Fe(1)–N(2)–C(2)	63.04(13)
Si(1)–N(2)–C(2)	141.24(19)
Fe(1)–C(1)–O(1)	175.0(2)
Fe(1)–C(2)–N(1)	149.40(17)
Fe(1)–C(2)–N(2)	78.31(15)
N(1)–C(2)–N(2)	132.3(2)
C(1)–Fe(1)–N(2)–Si(1)	-51.99(19)
C(1)–Fe(1)–N(2)–C(2)	84.48(16)
N(2)–Fe(1)–C(2)–N(1)	178.3(4)
C(2)–Fe(1)–N(2)–Si(1)	-136.5(2)
C(1)–Fe(1)–C(2)–N(1)	77.5(3)
C(1)–Fe(1)–C(2)–N(2)	-100.75(14)
C(2)–Fe(1)–C(1)–O(1)	-127(2)
C(5)–Si(1)–N(2)–Fe(1)	70.9(2)

C(5)–Si(1)–N(2)–C(2)	-30.4(3)
C(6)–Si(1)–N(2)–Fe(1)	-49.9(2)
C(6)–Si(1)–N(2)–C(2)	-151.3(3)
C(7)–Si(1)–N(2)–Fe(1)	-168.91(15)
C(7)–Si(1)–N(2)–C(2)	89.7(3)
C(3)–N(1)–C(2)–Fe(1)	-175.1(2)
C(3)–N(1)–C(2)–N(2)	2.6(4)
C(4)–N(1)–C(2)–Fe(1)	1.2(4)
C(4)–N(1)–C(2)–N(2)	179.0(2)
Fe(1)–N(2)–C(2)–N(1)	-178.8(3)
Si(1)–N(2)–C(2)–Fe(1)	127.7(2)
Si(1)–N(2)–C(2)–N(1)	-51.1(4)

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## References

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- (2) Nakazawa, H.; Itazaki, M.; Kamata, K.; Ueda, K. *Chem. Asian. J.* **2007**, *2*, 882-888.