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N−CN Bond Cleavage of Cyanamides by a Transition-Metal Complex

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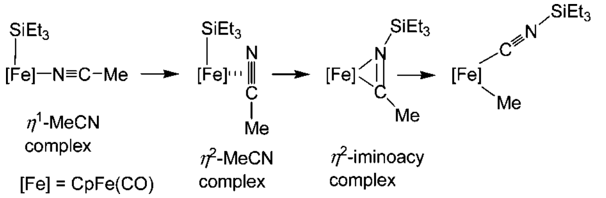
In the last two decades, considerable efforts have been devoted to cleavage of unreactive bonds such as carbon−hydrogen,[1] carbon−carbon,[2] carbon−nitrogen,[3] and carbon−oxygen.[4] Direct cleavage of these bonds provides several advantages in organic syntheses, including atom efficiency, low environmental load, and the potential for unusual chemoselectivity.

Scheme 1. Reaction Pathway of Me−CN Bond Cleavage



We recently reported reactions of C−CN bond cleavage of organonitriles promoted using a silyl−iron complex.[2d] The essence of the reaction mechanism for Me−CN bond cleavage is depicted in Scheme 1. Acetonitrile coordinates to a 16e silyl−iron complex $Cp(CO)Fe(SiEt_3)$ produced from $Cp(CO)_2Fe(SiEt_3)$ (**1**) in a photoreaction to give an η^1-MeCN complex, which is converted into an η^2-MeCN complex. Then, silyl migration from Fe to the nitrile nitrogen atom occurs to form η^2-iminoacyl complex, followed by C−C bond cleavage on the coordination sphere to give a methylsilylisocyanide complex. The η^2-coordination of acetonitrile through C≡N π-bond induces silyl migration, which then causes C−CN bond cleavage. The reaction sequences stimulate us to examine the possibility of R_2N−CN (cyanamide) bond cleavage by a silyl−iron complex because the replacement of the R group in RCN by an NR_2 group yields cyanamide. The R_2N−CN bond is known to be strong and not broken readily. For example, the N−CN bond length in Me(p-C_6H_4Cl)N−CN is reported to be 1.331 Å, which lies just between that of a normal N−C single bond (1.47 Å) and that of an *N*═C double bond (1.27 Å).[5] The von Braun reaction is the only reaction known to date to cleave R_2N−CN bond.[6] However, it requires harsh reaction conditions (strong acid or base conditions). Herein, we describe the first R_2N−CN bond cleavage reaction by a transition-metal complex, isolation of an intermediate, and establishment of a catalytic cycle involving R_2N−CN bond cleavage.

A solution of an equimolar amount of dimethylcyanamide and the silyl−iron complex **1** in toluene was irradiated with a 400-W medium pressure mercury arc lamp (Pyrex filtered) at room temperature for 12 h. The ^{1}H NMR spectrum and the GC analysis of the reaction mixture showed formation of Et_3SiCN. The yield was 51% (entry 1 in Table 1), showing that the Me_2N−CN bond cleavage could be attained at room temperature using a silyl−iron complex.

Results of reactions with other cyanamides are presented in Table 1. Although the yields of Et_3SiCN are less than 50%, these N−CN bonds are cleaved (entries 2−6). The reaction of H_2NCN is noteworthy (entry 6). The H_2N−CN bond has a double bond character because H_2N−CN (cyanamide) is a tautomer of HN═C═NH (carbodiimide). Therefore H_2N−CN bond is stronger than other R_2N−CN. The first H_2N−CN bond cleavage is attainable in our reaction conditions, although the efficiency remains insufficient.

Table 1. Photoreaction of Cyanamides With $Cp(CO)_2Fe(SiEt_3)$[a]

$$R_2N{-}CN + Cp(CO)_2Fe(SiEt_3) \xrightarrow[\text{in toluene}]{h\nu,\ \text{at r.t.}} Et_3SiCN$$

entry	substrates	time (h)	yield (%)[a]
1	Me_2NCN	12	51
2	$^n Hex_2NCN$	12	30
3	*N*-cyanopiperidine	12	41
4	*N*-cyanomorpholine	12	32
5	*N*-cyanopyrrolidine	12	26
6	H_2NCN	12	20[b]
7	$Me_2N(BH_3)CN$	24	14
8	$Me_2N(BF_3)CN$	24	0
9	$C_5H_{10}N(BH_3)CN$	24	18

[a] Yield of Et_3SiCN obtained by GC. [b] In 1,2-dichloroethane.

Cyanamide has a lone pair of electrons on the amino nitrogen in addition to the cyano nitrogen. Coordination of cyanamide to the 16e Fe species, $Cp(CO)Fe(SiEt_3)$, through the amino nitrogen, may reduce the activity of the iron complex toward R_2N−CN bond cleavage. Derivation of cyanamide into the borane adduct at the amino nitrogen, $R_2N(BX_3)CN$ (X = H, F),[7] might engender more effective R_2N−CN bond cleavage because of masking of the lone pair electrons on the amino nitrogen. The results (Table 1, entries 7−9) showed that the introduction of borane into cyanamide did not facilitate R_2N−CN bond cleavage; instead, it reduced the activity, presumably because of steric hindrance.

Reaction sequences resembling those in Scheme 1 are expected for the reaction of **1** with cyanamide. We attempted to isolate the *N*-silylated η^2-amidino iron intermediate, but the reaction of **1** with Me_2NCN was unsuccessful. However, reactions with Me_2NCN of $(C_5R_5)Fe(CO)(py)(SiR'R''_2)$ (py = pyridine), considered as a synthon of a 16e complex $(C_5R_5)Fe(CO)(SiR'R''_2)$,[8] led to isolation of *N*-silylated η^2-amidino iron complexes (Scheme 2). Heating a solution containing **2** and Me_2NCN in benzene at 50 °C for 10 h yielded **3** quantitatively according to the NMR measurements, but the isolation as a solid failed. In contrast, a reaction of **4** with Me_2NCN yielded **5**, which can be isolated as a dark-red powder in 85% yield. The unprecedented η^2-amidino complex was confirmed using X-ray analysis (Scheme 2).[8] The iron takes a distorted three-legged piano-stool structure with an η^2-amidino fragment. The bond distance of N1−C2 (1.327 Å) is shorter than that of a typical N−C single bond (e.g., C3−N1 = 1.455 Å, C4−N1 = 1.458 Å) and is

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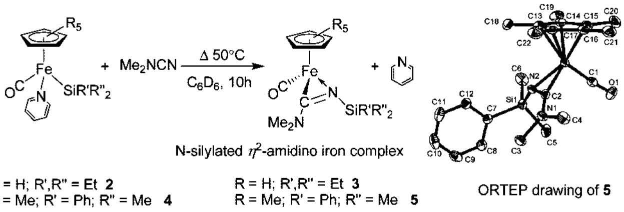
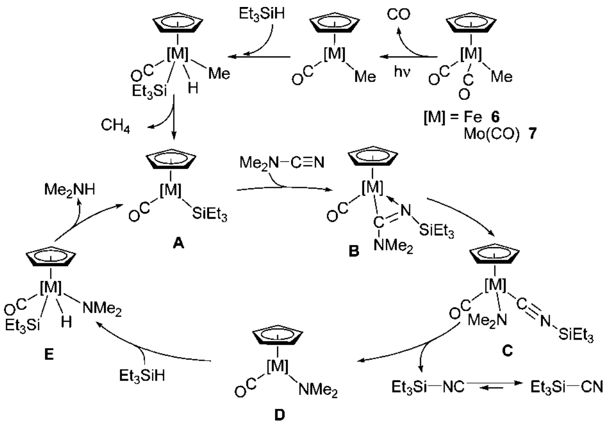
rather similar to that of an *N*=C double bond (e.g., N2−C2 = 1.303 Å). The sum of angles around N1 is 359.9°. These structural characters are consistent with sp^2 hybridization of N1. The C3−N1−C2−N2 fragment is nearly planar with a torsion angle of 2.6(4)°. Both ^1H and ^{13}C NMR spectra show that the structure in a solid state is maintained in solution. Two NCH_3 resonances were observed at room temperature in ^1H and ^{13}C NMR, reflecting that the C2−N1 bond does not rotate freely at room temperature.

Scheme 2. Synthesis of *N*-Silylated η^2-Amidino Iron Complexes



Complexes **3** and **5** were subjected to a thermal reaction. Although **5** produced a small amount of $PhMe_2SiCN$ on heating in toluene at 110 °C for 24 h, **3** gave Et_3SiCN in 62% yield on heating in benzene at 70 °C for 24 h. The results show that an *N*-silylated η^2-amidino complex is an intermediate in the N−CN bond cleavage of cyanamide.

Scheme 3. Proposed Catalytic Cycle



Next, we attempted to extend the stoichiometric R_2N−CN bond cleavage to a catalytic reaction. We envision a catalytic cycle for Fe and Mo complexes shown in Scheme 3 based on that of R−CN bond cleavage.[9] A 16e silyl complex **A** reacts with Me_2NCN to give an *N*-silylated η^2-amidino complex **B**, followed by N−CN bond cleavage to give **C**, and dissociation of silyl isocyanide to give a 16e amido complex **D**. It may react with Et_3SiH to produce **E**, then reductive elimination of Me_2NH regenerates **A** to complete the catalytic cycle. To produce 16e intermediate **A**, $CpMo(CO)_3Me$ (**7**) or $CpFe(CO)_2Me$ (**6**) seem to be good precursors because successive CO dissociation, Et_3Si−H oxidative addition, and CH_4 reductive elimination will give **A**.

Results of reactions of Me_2NCN and Et_3SiH in the presence of a catalytic amount of Fe complex **6** or Mo complex **7** are presented in Table 2. Entry 1 there shows that the Fe complex does not work as a catalyst, whereas the Mo complex does, under photoirradiation conditions (entry 2). The Mo complex shows catalytic activity even under thermal conditions (entries 4−6).

Table 2. Catalytic Cleavage[a] Under Photolysis or Heating

$$Me_2NCN + Et_3SiH \xrightarrow[\text{in toluene}]{\text{cat. } \mathbf{6} \text{ or } \mathbf{7}} Et_3SiCN$$

entry	cat.	[M]:[N]:[Si][b]	conditions	temp/°C	time/h	TON[c]
1	**6**	1:10:10	hν	25	24	0.4
2	**7**	1:10:10	hν	25	24	1.4
3	**6**	1:1:1	Δ	80	12	0
4	**7**	1:1:1	Δ	100	12	0.52
5[d]	**7**	1:10:1000	Δ	100	48	7.9
6[d]	**7**	1:1000:5000	Δ	100	120	32.3

[a] No Me_2N−CN bond cleavage took place in the absence of **6** or **7**. [b] Molar ratio of a transition metal complex, Me_2NCN, and Et_3SiH. [c] Calculated from the isolated Et_3SiCN. The values are based on the concentration of a transition metal complex. [d] In free solvent.

In conclusion, this paper describes the first example of inert N−CN bond cleavage by a transition metal complex. An *N*-silylated η^2-amidino complex can be isolated. It was shown to be an intermediate in the reaction pathway. Catalytic N−CN bond cleavage reaction was also attained using a methyl molybdenum complex. Studies are underway to design transition-metal catalysts to improve activity and to elucidate the reaction mechanism.

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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.

References

(1) See, for example: (a) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731–1770. (b) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698–1712. (c) Naota, T.; Takaya, H.; Murabashi, S. I. *Chem. Rev.* **1998**, *98*, 2599–2660. (d) Zhang, Y.; Li, C.-J. *Angew. Chem., Int. Ed.* **2006**, *45*, 1949–1952. (e) Ma, K.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2006**, *128*, 3303–3312. (f) Kakiuchi, F.; Kan, S.; Igi, K.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **2003**, *125*, 1698–1699. (g) Goosen, L. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3775–3778. (h) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154–162. (i) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083–4091.

(2) See for example: (a) Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610–618. (b) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870–883. (c) Storsberg, J.; Yao, M.-L.; Öcal, N.; De Meijere, A.; Adam, A. E. W.; Kaufmann, D. E. *Chem. Commun.* **2005**, 5665–5666. (d) Nakazawa, H.; Kawasaki, T.; Miyoshi, K.; Suresh, C. H.; Koga, N. *Organometallics* **2004**, *23*, 117–126. (e) Chianese, A. R.; Zeglis, B. M.; Crabtree, R. H. *Chem. Commun.* **2004**, 2176–2177. (f) Terao, Y.; Wakui, H.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2001**, *123*, 10407–10408.

(3) (a) Lei, Y.; Wrobleski, A. D.; Golden, J. E.; Powell, D. R.; Aubé, J. *J. Am. Chem. Soc.* **2005**, *127*, 4552–4553. (b) Fran, L.; Yang, L.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4778–4787. (c) Yao, M.-L.; Adiwidjaja, G.; Kanfmann, D. E. *Angew. Chem., Int. Ed.* **2002**, *41*, 3375–3378. (d) Niklas, N.; Heinemann, F. W.; Hampel, F.; Alsfasser, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 3386–3388.

(4) See for example: (a) Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972–989. (b) Kabalka, G. W.; Yao, M.-L.; Borella, S.; Goins, L. K. *Organometallics* **2007**, *26*, 4112–4114. (c) Szu, P.-h.; He, X.; Zhao, L.; Liu, H.-w. *Angew. Chem., Int. Ed* **2005**, *44*, 6742–6746. (d) Casado, F.; Pisano, L.; Farriol, M.; Gallardo, I.; Marquet, J.; Melloni, G. *J. Org. Chem.* **2000**, *65*, 322–331.

(5) Cunningham, I. D.; Light, M. E.; Hursthouse, M. B. *Acat Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 1833–1835.

(6) Vliet, E. B. *Org Synth.* **1941**, *1*, 201–202.

(7) Syntheses of boran adduct of cyanamide and confirmation of the adduct at the amino nitrogen have been reported: Henneike, H. F.; Drago, R. S. *Inorg. Chem.* **1968**, *7*, 1908–1915.

(8) Selected bond lengths (Å) and angles (deg): C2−N1, 1.327(3); C2−N2, 1.303(2); C3−N1, 1.455(3); C4−N1, 1.458(3); C2−N1−C3, 123.4(2); C2−N1−C4, 119.5(2); C3−N1−C4, 117.0(2); Fe1−C2−N1, 149.40(17); Fe1−C2−N2, 78.31(15); N1−C2−N2, 132.3(3); Fe1−N2-Si1, 134.04(12); Fe1−N2−C2, 63.04(13); Si1−N2−C2, 141.24(19).

(9) (a) Nakazawa, H.; Kamata, K.; Itazaki, M. *Chem. Commun.* **2005**, 4004–4006. (b) Nakazawa, H.; Itazaki, M.; Kamata, K.; Ueda, K. *Chem.−Asian J.* **2007**, *2*, 882–888.

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