Strong bond cleavage promoted by silyl group migration in a coordination sphere

H. Nakazawa
Department of Chemistry, Graduate School of Science,
Osaka City University, Sumiyoshi-ku, Japan

Abstract

C-CN bond cleavage in organonitriles was attained in the photoreaction with $HSiEt_3$ in the presence of a catalytic amount of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$. The reaction sequence was proposed, where silyl migration from Fe to N in the coordinating nitrile is a key step. DFT calculations proposed a silyl migration with small activation energy of 4.0 kcal/mol and subsequent C-CN bond cleavage on the Fe coordination sphere. N-CN bond cleavage in cyanamide (R_2NCN) was also attained by a transition metal catalyst. A catalytic cycle was proposed where a silyl migration from a transition metal to the nitrile nitrogen is involved. An N-silylated η^2-amidino complex was isolated, which was shown to be an intermediate in the catalytic pathway.

Keywords: C-C bond cleavage, C-N bond cleavage, transition metal catalysis, silyl migration.

1 Introduction

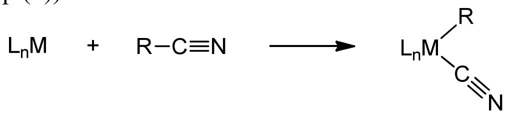
Investigations of selective bond cleavage as well as selective bond formation of chemical compounds is important from the viewpoint of atom efficiency, low environmental load, and sustainable chemistry. Weak bond cleavage is not so difficult, whereas strong bond cleavage with keeping weak bonds intact is quite difficult. Therefore, selective strong bond cleavage is a challenging topic in chemistry. One of the promising ways to overcome the difficulties is using a transition metal catalyst.

As the carbon-carbon bond is relatively unreactive, C-C bond cleavage is an area of considerable current interest [1]. In particular, C-C bond activation in

WIT Transactions on Ecology and the Environment, Vol 154, © 2011 WIT Press
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/CHEM110121

acetonitrile is difficult because it has rather strong C-C bond energy (133 kcal mol^{-1}) compared with alkane C-C bond energy (*ca.* 83 kcal mol^{-1}).

Transition metal complexes have been used to attain C-C bond cleavage of nitrile. They mainly involve Group 10 transition metal triads [2–10]. In addition, one example for Mo [11], Co [12], U [13], and two examples of Cu [14, 15] have been reported. These reactions show stoichiometric C-C bond cleavage. In contrast, a few catalytic reactions involving Ni [16] and Pd [17] complexes have been reported. For these examples, it is proposed or clearly shown that a direct oxidative addition of a C-CN bond toward an electronically unsaturated transition metal fragment takes place to give an alkyl(aryl)-cyano complex (eq. (1)).

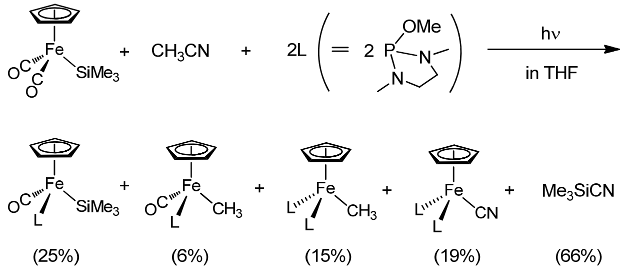


(1)

This article introduces a new reaction pathway for organonitrile C-C bond cleavage where silyl group migration from a transition metal to nitrile nitrogen in the coordination sphere is a key step [18–20]. This article also report silyl assisted N-CN bond cleavage of cyanamide [21].

2 Stoichiometric C-CN bond cleavage of acetonitrile by a silyl-iron complex

Photoreaction with a 400-W medium pressure mercury arc lamp (pyrex filtered) of a THF solution containing CpFe(CO)$_2$(SiMe$_3$), MeCN, and 2 equiv of P(NMeCH$_2$)$_2$(OMe) (L) generated CpFe(CO)L(SiMe$_3$) (25% yield), CpFe(CO)L(Me) (6% yield), CpFeL$_2$(Me) (15% yield), CpFeL$_2$(CN) (19% yield), and Me$_3$SiCN (66% yield) (eq. (2)). When CD$_3$CN was used in place of CH$_3$CN, the corresponding CD$_3$-iron complexes (CpFe(CO)L(CD$_3$) and CpFeL$_2$(CD$_3$)) were obtained. These results obviously show that C-C bond in acetonitrile is cleaved in this reaction. In order to check whether the silyl group on the iron plays an important role to cleave the C-C bond in acetonitrile, CpFe(CO)$_2$Me, CpFe(CO)$_2$(GeMe$_3$), and CpFe(CO)$_2$(SnMe$_3$) were used in place of CpFe(CO)$_2$(SiMe$_3$). No C-CN bond cleavage reaction took place, indicating that the silyl ligand on the iron is inevitable to cleave C-CN bond in acetonitrile [18].



(2)

Similar silyl-assisted nitrile C-C bond cleavage was reported independently by Bergman, Brookhart and co-workers using Rh [22] and Ir [23] complexes. Later, Hashimoto et al. [24] and Tobiso et al. [25] and their co-workers reported this type of silyl-assisted nitrile C-C bond cleavage.

3 Theoretical approach

In order to elucidate the role of a silyl group in the iron complex toward C-C bond activation of acetonitrile, DFT calculations were performed. It is expected that at first the irradiation of the coordinatively saturated CpFe(CO)$_2$(SiMe$_3$) will lead to the dissociation of one CO ligand to form 16e species CpFe(CO)(SiMe$_3$) (**A**). The direct C-C bond oxidative addition of acetonitrile to the 16e species is less likely to happen, because this reaction requires a very high activation barrier of ca. 53 kcal/mol. Several DFT calculations could find a plausible reaction path which is shown in Figure 1 [18].

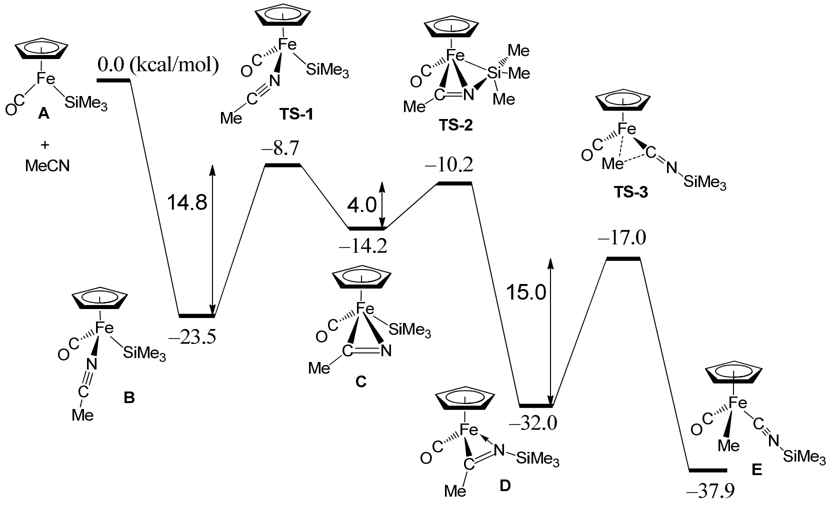


Figure 1: Energy profiles of the reaction of CpFe(CO)(SiMe$_3$) with MeCN (kcal.mol).

The reaction of **A** with MeCN forms **B** with the end-on coordination of acetonitrile with releasing 23.5 kcal/mol. Then, **B** is converted into the CN π-coordinated species **C**. This process takes place through a transition state (**TS-1**) with the activation energy of 14.8 kcal/mol. In **C**, the migration of the silyl group from Fe to nitrile nitrogen is possible. The calculations showed that this requires only a small activation energy of 4.0 kcal/mol (**C** to **TS-2**). From **TS-2**, a somewhat stable imino complex with the coordination of a nitrogen lone pair to the Fe atom, **D**, is formed. If the methyl group of the imino ligand migrates to the iron atom, the methyl iron complex (**E**) could be formed. It has been found that a distortion in **D** that breaks the Fe-N bond leads to the transition state **TS-3**. This process requires an activation energy of 15.0 kcal/mol. The product of this step, **E**, is 5.9 kcal/mol more stable than **D**, which is presumably due to the presence of a strong Fe-C bond.

The reaction profile in Scheme 1 well explains the rupture of the acetonitrile C-C bond by the Fe(II) complex. The highest activation barrier of 15 kcal/mol is well within the reach of a feasible chemical reaction. Once **E** is formed, the formation of CpFe(CO)LMe can be easily achieved by a silylisocyanide/L exchange reaction. The trimethylsilyl isocyanide dissociated from **E** may isomerize to trimethylsilyl cyanide. Theoretical calculation suggests that the cyanide is more stable than the isocyanide. This is in accord with the experimental fact that trimethylsilyl cyanide is thermodynamically more favorable [26].

4 Catalytic C-CN bond cleavage of acetonitrile

In order to establish a catalytic cycle, photoreaction of a THF solution containing an equimolar amount of Et_3SiH and MeCN in the presence of a catalytic amount of $CpFe(CO)_2(SiMe_3)$ (2 mol%) was examined. The main Si-containing product was Et_3SiCN. The yield based on Et_3SiH used was 45% (TON = 23). The results show the C-C bond in MeCN is cleaved catalytically.

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

$$Et_3SiH \quad + \quad H_3C\text{-}CN \xrightarrow[\text{THF, } h\nu]{\text{catalyst}} Et_3SiCN \quad + \quad CH_4$$

Entry	Catalyst	TON[b]
1	$Cp(CO)_2Fe(SiMe_3)$	22.5
2	$Cp(CO)_2Fe(benzyl)$	21.3
3	$Cp(CO)_2FeMe$	36.0
4	$Cp(CO)_2FeCl$	0.6
5	$Cp(CO)_2FeI$	2.0
6	$(C_5MeH_4)(CO)_2FeMe$	32.5
7	$(C_5Me_4H)(CO)_2FeMe$	5.7
8	$(C_5Me_5)(CO)_2FeMe$	4.3
9	$(C_5H_4SiMe_3)(CO)_2FeMe$	26.4
10	$(C_5H_4SiMe_3)(CO)_2FeI$	2.0
11	$(C_5H_4I)(CO)_2FeMe$	12.6
12	$(C_5H_4\{P(O)(OMe)_2\})(CO)_2FeMe$	9.8

[a] Reactions were carried out at room temperature for 24 h under photoirradiation by using catallyst (0.52 mmol), Et_3SiH (26.00 mmol), and THF (5.00 mL) in acetonitrile (13.6 mL, 260.00 mmol). [b] Determined by GC with toluene as internal standard.

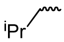
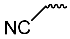
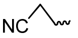
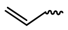
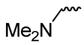
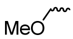
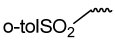
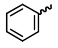
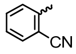
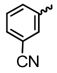
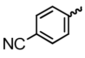
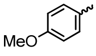
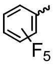
Next, the effect of a ligand at the Fe center on the catalytic activity was examined. For $CpFe(CO)_2R$ the methyl complex showed better activity than the silyl, benzyl, halo complexes. For $(C_5R_5)Fe(CO)_2Me$ introduction of substituents into the Cp ring reduced the catalytic activity. therefore, $CpFe(CO)_2Me$ showed the best catalytic activity among complexes in Table 1. The catalytic activities of the related methyl complexes of Mo and W, $CpM(CO)_3Me$ (M = Mo, W), were sluggish.

5 Catalytic C-CN bond cleavage of organonitriles other than acetonitrile

To see the scope and limitation of catalytic activity of $CpFe(CO)_2Me$ for C–CN bond cleavage, reactions with several organonitriles other than acetonitrile were examined. Table 2 summarizes the results. Propionitrile (EtCN) was converted into Et_3SiCN in 73% yield (TON: 18.2) (Table 2, entry 1). Isobutyronitrile (^{i}PrCN) and malononitrile ($NCCH_2CN$) were poorly converted (Table 2, entries 2, 3). However, succinonitrile ($NCCH_2CH_2CN$) was converted as much as propionitrile (65% yield, TON = 16.3; Table 2, entry 4).

Organonitriles in entries 5-10 were resistant to the C-CN bond cleavage in the reaction conditions (Table 2, entries 5-11). These results indicate that an electron-withdrawing, bulky, or coordination-feasible substituent on a carbon adjacent to the CN group is unfavorable for the C-CN bond cleavage.

Table 2: R-CN bond cleavage reactions of organonitriles.[a]

Entry	1	2	3[b]	4[b]	5	6	7	8	9
R							^{t}Bu	Cl_3C	
TON	18.2	4.2	7.4	16.3	NR	NR	NR	0.3	NR
Entry	10	11	12[c]	13[c]	14[c]	15[c]	16[c]	17[c]	
R									
TON	trace	0.4	12.2	10.5	11.7	11.5	15.2	trace	

[a] Catalyst (0.20 mmol), Et_3SiH (5.00 mmol), THF (0.40 mL), nitrile compound (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.

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 benxonitrile (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 strongly electronegative nature of F.

6 Consideration of catalytic cycle

A plausible catalytic cycle is shown in Figure 2 for the reaction of MeCN with Et_3SiH in the presence of $CpFe(CO)_2Me$ as a catalyst precursor. One CO ligand in the precursor is released by photolysis to give CpFe(CO)Me, which reacts with Et_3SiH to give $CpFe(CO)(Me)(H)(SiEt_3)$. This process seems plausible because oxidative addition of an Si-H bond to a 16e-species of Fe was reported to give, for example, $CpFe(CO)(H)(SiEt_3)_2$ [27]. The subsequent reductive elimination of CH_4 yields $CpFe(CO)(SiEt_3)$. As $SiEt_3Me$ was not observed at all in this system, reductive elimination of CH_4 from $CpFe(CO)Me(H)(SiEt_3)$ seems to precede that of Et_3SiMe. The 16e species thus formed reacts with MeCN to give ultimately $CpFe(CO)(Me)(\eta^1\text{-}CNSiEt_3)$. The reaction sequences have been demonstrated theoretically (Figure 1) [18]. Dissociation of Et_3SiNC generates CpFe(CO)Me to complete the catalytic cycle. The released Et_3SiNC isomerizes to thermodynamically stable Et_3SiCN.

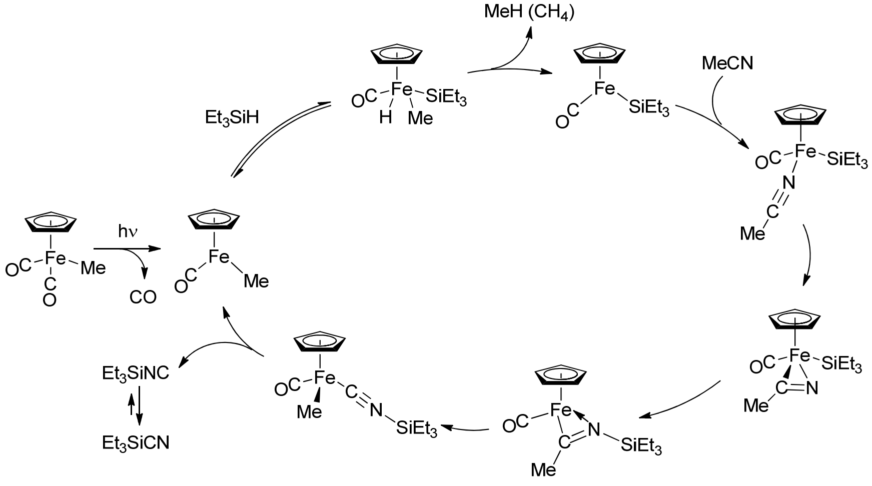


Figure 2: Proposed catalytic cycle.

According to the catalytic cycle shown in Figure 2, $CpFe(CO)(SiEt_3)$ can react with both MeCN and Et_3SiH. The former reaction seems dominant, but the latter is not negligible. If the reaction of $CpFe(CO)(SiEt_3)$ with Et_3SiH is suppressed, the catalytic cycle is expected to work more effectively. Thus the reaction on changing the molar ratio of Et_3SiH and MeCN was examined. Reaction of Et_3SiH with a 10-fold molar excess of MeCN in the presence of 0.83 mol% $CpFe(CO)_2Me$ under photolysis for 24 h at 50°C produced 99% yield of Et_3SiCN base on Et_3SiH (TON: 118). The TON increased with the photoirradiation time (48 h: 156, 96 h: 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 $CpFe(CO)_2Me$. Compared with Pd [17] and Rh [22] systems, this catalytic system is very effective.

7 N-CN bond cleavage of cyanamides

New reaction pattern of C-CN bond cleavage of organonitriles promoted by a silyl-iron complex has been described above. The essence of the reaction mechanism is silyl migration from Fe to the nitrogen in nitrile which is η^2-coordinated through C≡N π-bond. This migration causes C-CN bond cleavage. The replacement of the R group in RCN (organonitrile) by an NR_2 group yields cyanamide described as R_2NCN. Therefore, there is a possibility of N-CN bond cleavage of cyanamide in the reaction with a transition metal complex bearing a silyl ligand.

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) [28]. The von Braun reaction is the only reaction known to date to cleave R_2N-CN bond. However, it requires harsh reaction conditions (strong acid or base conditions). Reactions of cyanamides with a transition metal complex bearing a silyl ligand were examined both in hopes of N-CN bond cleavage and with worrying about coordination of cyanamide to the 16e Fe species, $Cp(CO)Fe(SiEt_3)$, through a lone pair of electrons on the amino nitrogen causing disappearance of the activity of the iron complex toward R_2N-CN bond cleavage.

Table 3: Photoreaction of cyanamides with $CpFe(CO)_2(SiEt_3)$.

$$R_2N\text{-}CN \quad + \quad CpFe(CO)_2(SiEt_3) \xrightarrow[\text{toluene}]{h\nu,\ \text{at r.t.}} Et_3SiCN$$

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

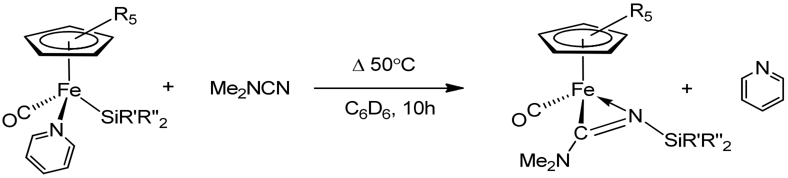
A solution of an equimolar amount of dimethylcyanamide and $CpFe(CO)_2(SiEt_3)$ (**1**) in toluene was photoirradiated at room temperature for 12 h. The ^1H NMR spectrum and the GC analysis of the reaction mixture showed formation of Et_3SiCN. The yield was 51% (Table 3, entry 1), showing that the

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 3. 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 these reaction conditions, although the efficiency remains insufficient.

Derivation of cyanamide into the borane adduct at the amino nitrogen, $R_2N(BX_3)CN$ (X = H, F) [29], might engender more effective R_2N-CN bond cleavage because of masking of the lone pair electrons on the amino nitrogen. The results (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 Figure 2 are expected for the reaction of **1** with cyanamide. Isolation of the N-silylated η^2-amidino iron intermediate was attempted, 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 $(C_5R_5)Fe(CO)(SiR'R''_2)$, led to isolation of N-silylated η^2-amidino iron complexes (eq. (3)). 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 was failed. In contrast, a reaction of **4** with Me_2NCN yielded **5**, which could be isolated as dark-red powders in 85% yield. The unprecedented η^2-amidino complex was confirmed using X-ray analysis (Figure 3). 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 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.



(3)

N-silylated η^2-amidino iron complex

R = H; R',R" = Et **2**
R = Me; R' = Ph; R" = Me **4**

R = H; R',R" = Et **3**
R = Me; R' = Ph; R" = Me **5**

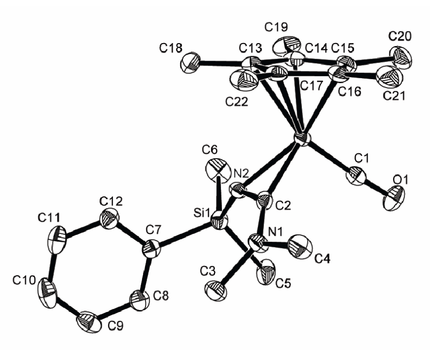


Figure 3: ORTEP drawing of **5**. Selected bond distances (Å) and angles (deg): N1-C2 = 1.327 (3); N2-C2 = 1.303(2); C2-N1-C3 = 123.4(2); C2-N1-C4 = 119.5(2); C3-N1-C4 = 117.0(2).

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.

Table 4: Catalytic cleavage under photolysis or heating.

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

Entry	Cat.	[M]:[N]:[Si][b]	Condition	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_2NCN 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.

Catalytic N-CN bond cleavage of cyanamides has been attempted. Table 4 shows the results of reactions of Me_2NCN and Et_3SiH in the presence of a catalytic amount of $CpFe(CO)_2Me$ or $CpMo(CO)_3Me$. Entry 1 shows that the Fe complex does not work as a catalyst, whereas the Mo complex does under photo-irradiation conditions (Table 4, entry 2). The Mo complex shows catalytic activity even under thermal conditions (Table 4, entries 4-6). These results show the first example of catalytic N-CN bond cleavage of cyanamides by a transition metal complex.

8 Conclusions

It was found that a 16e species bearing a transition metal-silyl bond, such as $CpFe(CO)(SiR_3)$ and $CpMo(CO)_2(SiR_3)$, serves as a real catalyst for C-CN and N-CN bond cleavage in organonitriles and cyanamides, respectively. Silyl migration from a transition metal to the nitrogen of the nitrile group in RCN and R_2NCN coordinating to the transition metal in η^2-fashion leads to the strong C-CN and N-CN bond cleavage.

References

[1] a) Crabtree, R. H., The organometallic chemistry of alkanes. *Chem. Rev.* **85**, pp. 245-269, 1985. b) Rybtchinski, B. & Milstein, D., Metal insertion into C-C bonds in solution. *Angew. Chem., Int. Ed.*, **38**, pp. 870-883, 1999. c) Jun, C.-H., Transition metal-catalyzed carbon-carbon bond activation. *Chem. Soc. Rev.*, **33**, pp. 610-618, 2004.

[2] Burmeister, J. L. & Edwards, L. M., Carbon-carbon bond cleavage via oxidative addition: Reaction of tetrakis(triphenylphosphine)platinum(0) with 1,1,1-tricyanoethane. *J. Chem. Soc. A.*, pp. 1663–1666, 1971.

[3] Gerlach, D. H., Kane, A. R., Parshall, G. W., Jesson, J. P. & Muetterties, E. L., Reactivity of trialkylphosphine complexes of platinum(0). *J. Am. Chem. Soc.*, **93**, pp. 3543–3544, 1971.

[4] Cassar, L., A new nickel-catalyzed synthesis of aromatic nitriles. *J. Organomet. Chem.*, **54**, pp. C57–C58, 1973.

[5] Parshall, G. W., σ-Aryl compounds of nickel, palladium, and platinum. Synthesis and bonding studies. *J. Am. Chem. Soc.*, **96**, pp. 2360–2366, 1974.

[6] Favero, G., Morvillo, A. & Turco, A., Oxidative addition of alkanenitriles to nickel(0) complexes via π-intermediates. *J. Organomet. Chem.*, **241**, pp. 251–257, 1983.

[7] Bianchini, C., Masi, D., Meli, A. & Sabat, M., Reactions of ethyl cyanoformate with $(np_3)Ni$, $(np_3)CoH$ [np_3 = $N(CH_2CH_2PPh_2)_3$], and (triphos)Ni [triphos = $MeC(CH_2PPh_2)_3$]. Crystal structures of the ethoxycarbonyl complexes $[(np_3)Ni(CO_2Et)]BPh_4$ and $(triphos)Ni(CN)(CO_2Et)$. *Organometallics*, **5**, pp. 1670–1675, 1986.

[8] Abla, M. & Yamamoto, T., Oxidative addition of C-CN bond to nickel(0) complex: Synthesis and crystal structures of $Ni(CN)(o\text{-}C_6H_4CN)(bpy)$ and $Ni(CN)(p\text{-}C_6H_4CN)(bpy)$. *J. Organomet. Chem.*, **532**, pp. 267–270, 1997.

[9] a) Brunkan, N. M., Brestensky, D. M. & Jones, W. D., Kinetics, thermodynamics, and effect of BPh_3 on competitive C-C and C-H bond activation reactions in the interconversion of allyl cyanide by [No(dippe)]. *J. Am. Chem. Soc.*, **126**, pp. 3627–3641, 2004. b) Garcia, J. J., Arevalo, A., Brunkan, N. M. & Jones, W. D., Cleavage of carbon-carbon bonds in alkyl cyanides using nickel(0). *Organometallics*, **23**, pp. 3997–4002, 2004.

[10] Liu, Q.-X., Xu, F.-B., Li, Q.-S., Song, H.-B. & Zhang, Z.-Z., Formation of the fluorescent complexes [(carbene)$_2$M^{II}(CN)$_2$] (M = Ni, Pd, Pt) by C-C bond cleavage of CH_3CN. *Organometallics*, **23**, pp. 610–614, 2004.

[11] Churchill, D., Shin, J. H., Hascall, T., Hahn, J. M., Bridgewater, B. M. & Parkin, G., The *ansa* effect in permethylmolybdenocene chemistry: A [Me$_2$Si] *ansa* bridge promotes intermolecular C-H and C-C bond activation. *Organometallics*, **18**, pp. 2403–2406, 1999.

[12] Ozawa, F., Iri, K. & Yamamoto, A., C-CN bond cleavage under mild conditions promoted by electron-rich cobalt complexes. *Chem. Lett.*, pp. 1707–1710, 1982.

[13] Adam, R., Villiers, C., Ephritikhine, M., Lance, M., Nierlich, M. & Vigner, J., Synthesis, structure and oxidative addition reactions of triscyclopentadienyluranium(III) nitrile complexes. *J. Organomet. Chem.*, **445**, pp. 99–106, 1993.

[14] Marlin, D. S., Olmstead, M. M. & Mascharak, P. K., Heterolytic cleavage of the C-C bond of acetonitrile with simple monomeric Cu^{II} complexes: Melding old copper chemistry with new reactivity. *Angew. Chem. Int. Ed.*, **40**, pp. 4752–4754, 2001.

[15] Lu, T., Zhuang, X., Li, Y. & Chen, S., C-C bond cleavage of acetonitrile by a dinuclear copper(II) cryptate. *J. Am. Chem. Soc.*, **126**, pp. 4760–4761, 2004.

[16] a) Penney, J. M. & Miller, J. A., Alkynylation of benzonitriles via nickel catalyzed C-C bond activation. *Tetrahedron Lett.*, **45**, pp. 4989–4992, 2004. b) Chaumonnot, A., Lamy, F., Sabo-Etienne, S., Donnadieu, B., Chaudret, B., Barthelat, J.-C. & Galland, J.-C., Catalytic isomerization of cyanoolefins involved in the adiponitrile process. C-CN bond cleavage and structure of the nickel π-allyl cyanide complex Ni(η^3-1-Me-C_3H_4)(CN)(dppb). *Organometallics*, **23**, pp. 3363–3365, 2004. c) Wilting, J., Müller, C., Hewat, A. C., Ellis, D. D., Tooke, D. M., Spek, A. L. & Vogt, D., Nickel-catalyzed isomerization of 2-methyl-3-butenenitrile. *Organometallics*, **24**, pp. 13–15, 2005. d) Nakao, Y., Yukawa, T., Hirata, Y., Oda, S., Satoh, J. & Hiyama, T., Allylcyanation of alkynes: Regio- and stereoselective access to functionalized di- or trisubstituted acrylonitriles. *J. Am. Chem. Soc.*, **128**, pp. 7116–7117, 2006.

[17] a) Murahashi, S., Naota, T. & Nakajima, N., Palladium-catalyzed decarbonylation of acyl cyanides. *J. Org. Chem.*, **51**, pp. 898–901, 1986. b) Luo, F.-H., Chu, C.-I. & Cheng, C.-H., Nitrile-group transfer from solvents to aryl halides. Novel carbon-carbon bond formation and cleavage mediated by palladium and zinc species. *Organometallics*, **17**, pp. 1025–1030, 1998. c) Nishihara, Y., Inoue, Y., Itazaki, M. & Takagi, K., Palladium-catalyzed cyanoesterification of norbornenes with cyanoformates via the NC-Pd-COOR (R = Me and Et) intermediate. *Org. Lett.*, **7**, pp. 2639–2641, 2005.

[18] Nakazawa, H., Kawasaki, T., Miyoshi, K., Suresh, C. H. & Koga, N., C-C bond cleavage of acetonitrile by a carbonyl iron complex with a silyl ligand. *Organometallics*, **23**, pp. 117–126, 2004.

[19] Nakazawa, H., Kamata, K. & Itazaki, M., Catalytic C-C bond cleavage and C-Si bond formation in reaction of RCN with Et_3SiH promoted by an iron complex. *Chem. Commun.*, pp. 4004–4006, 2005.

[20] Nakazawa, H., Itazaki, M., Kamata, K. & Ueda, K., 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. *Chem. Asian. J.*, **2**, pp. 882-888, 2007.

[21] Fukumoto, K., Oya, T., Itazaki, M. & Nakazawa, H., N-CN bond cleavage of cyanamides by a transition-metal complex. *J. Am. Chem. Soc.*, **131**, pp. 38-39, 2009.

[22] Taw, F. L., Mueller, A. H., Bergman, R. G. & Brookhart, M., A mechanistic investigation of the carbon-carbon bond cleavage of aryl and alkyl cyanides using a cationic Rh(III) silyl complex. *J. Am. Chem. Soc.*, **125**, pp. 9808–9813, 2003.

[23] Klei, S. R., Tilley, T. D. & Bergman, R. G., Stoichiometric and catalytic behavior of cationic silyl and silylene complexes. *Organometallics*, **21**, pp. 4648–4661, 2002.

[24] Hashimoto, H., Matsuda, A. & Tobita, H., Reactions of a silyl(silylene)iron complex with nitriles: Carbon-carbon bond cleavage of nitriles by the transiently generated disilanyliron(II) intermediate. *Organometallics*, **25**, pp. 472–476, 2006.

[25] Tobisu, M., Kita, Y. & Chatani, N., Rh(I)-catalyzed silylation of aryl and alkenyl cyanides involving the cleavage of C-C and Si-Si bonds. *J. Am. Chem. Soc.*, **128**, pp. 8152–8153, 2006.

[26] Seckar, J. A. & Thayer, J. S., Normal-iso rearrangement in cyanotrialkylsilanes. *Inorg. Chem.*, **15**, pp. 501-504, 1976.

[27] Akita, M., Oku, T., Tanaka, M. & Moro-oka, Y., Oxymethylation of alkyliron complex $CpFe(CO)_2R$ with hydrostannane and -silane, leading to RCH_2OH derivatives: related reactions of CpFe(CO)(L)R and CpFe(CO)(L)C(O)R type organoiron complexes and the molecular structure of trans-$CpFe(H)(CO)(SnPh_3)_2$. *Organometallics*, **10**, pp. 3080–3089, 1991.

[28] Cunningham, I. D., Light, M. E. & Hursthouse, M. B., N-(4-chlorophenyl)-N-methylcyanamide. *Acat Cryst. Sect. C, Cryst. Struct. Commun.*, **55**, pp. 1833-1835, 1999.

[29] Henneike, H. F. & Drago, R. S., Comparison of the donor properties of dimethylcyanamide and acetonitriles. *Inorg. Chem.*, **7**, pp. 1908-1915, 1968.