

F-CN Bond Cleavage by Silyl Iron Complex. Electronic Effect of the Group or Atom Attached to Cyano Group. A DFT Theoretical Study

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1. Introduction:

Cleavage of strong bonds in some ligands will give new species which are important in organic syntheses. There are a number of experimental and theoretical works focusing on cleavage of these unreactive bonds, especially E-CN (E = C, N, O) bonds in the presence of iron or molybdenum silyl complexes in cases of E = N and O by Nakazawa et al.¹⁻⁴ The idea behind using transition metals is that the metal attaching to the ligand through its special part will affect the electronic properties of the strong bond and that the silyl group will facilitate this cleavage. As a matter of fact, in the case of CH₃-CN, a new species which contains CN and CH₃ ligands are formed¹ while in the cases of cyanamides and cyanates, Et₃SiCN is formed, to demonstrate the E-CN bond cleavage.^{2,3} The N-CN bond is difficult to be broken; because, for example, in the case of H₂NCN, the lone pair of electrons on amino N atom strengthens this bond (because of its tautomerization to HN=C=NH), and it is even stronger than CH₃-CN bond.^{2,4} N-silylated η²-amidino iron complex was isolated and identified by x-ray crystallography in the case of cyanamides and its heating lead also to the formation of Et₃SiCN.² Accordingly, Nakazawa et al. suggested the mechanism shown in Scheme in the cases of cyanamides as well as cyanates. It was found that the low activation energy for the silyl group migration from Fe to N_{CN} is attributed to the hypervalent character of Si atom and the charges on the Si and N atoms.

In this theoretical study, continuing to our study for the cleavage of E-CN bond in the presence of silyl iron complex; (i) the cleavage of F-CN will be studied according to Scheme to show if they are similar to those in the cases of E = C, N, and O; and (ii) the effect of the group attached to CN on the reaction mechanism will be studied in detail.

2. Computational methods:

Density functional theory (DFT) calculations were performed to verify the feasibility of the reaction mechanism suggested in Scheme. The optimized structures of intermediates and transition states and the profiles for potential energy corrected with zero-point energy (ZPE) and the Gibbs free energy for the studied mechanism are shown in Figure. Unless explicitly stated otherwise, the ZPE-corrected potential energies are used in the discussion.

3. Results and Discussion:

As shown in Figure, searching for a minimum for the complex of FCN with complex **1**, leads to the end-on (η¹-) complex, **2d**. **2d** is more stable than **1** and FCN by 16.9 kcal/mol. This is because the strong coordination of FCN to **1** via the lone pair of electrons on the N_{CN} atom. The end-on complex, **2d**, isomerizes to the side-on (η²-) complex, **3d**, via the TS_{2d-3d}. The activation energy for this step is 13.2 kcal/mol. The vibrational mode with an imaginary frequency at TS_{2d-3d} is the Fe...C_{CN} bond distance stretching. Accordingly, this bond distance shortens during the reaction from 3.054 Å in **2d** to 2.745 Å in TS_{2d-3d}, and the Fe-C_{CN} bond forms in **3d** with a bond length of 1.882 Å. The next step is the migration of the silyl group from Fe to N_{CN} which transforms **3d** to **4d** via TS_{3d-4d}. The activation energy of 0.6 kcal/mol for this step is relatively small. The vibrational mode with an imaginary frequency at TS_{3d-4d} is the N...Si bond distance stretching. Accordingly, during the reaction this bond distance shortens from 2.695 Å in **3d** to 2.329 Å in TS_{3d-4d} and then the N-Si bond forms in **4d** with a bond distance of 1.746 Å. This small activation energy is because of a large exothermicity of -32.6 kcal/mol, the hypervalent character of Si atom, and the strong electrostatic interaction between the positively charged Si and negatively charged N atoms as stated previously. The Mulliken charges on the Si and N atoms in **3d** are +0.923 and -0.296, respectively. Therefore, the Si atom may be strongly attracted by the N atom to form a strong bond. In the next step, it is expected that **5d** having the Fe-C-F three-membered ring, similar to **5**'s in the cases of H₂NCN, Me₂NCN and MeOCN, is formed. In fact, **5d** does not form from **4d** but instead **4d** is directly transformed to **6d** via TS_{4d-6d}. The activation energy for this step is 15.9 kcal/mol and it is the rate-determining step. The vibrational mode with an imaginary frequency is the combination of cleavage of Fe-N bond and formation of Fe-F bond. Accordingly, the Fe-N bond is elongated from 2.123 Å in **4d** to 2.890 Å in TS_{4d-6d} and then to 3.006 Å in **6d**. On the other hand, the Fe-F bond shortens from 3.082 Å in

4d to 2.773 Å in **TS_{4d-6d}** and eventually to 1.854 Å in **6d**. This reaction coordinate at **TS_{4d-6d}** is similar to those at the TSs for **4**→**5** with E=C, N, and O, to suggest that neither **5d** nor **TS_{5d-6d}** exists. This is ascribed to the large stability of **6d**; it is 23.5 kcal/mol more stable than **4d** in contrast to the reactions with E=C, N, and O in which **6a** and **6c** are more stable than **4a** and **4c** by only 5.9 and 7.9 kcal/mol, respectively, and **6b** and **6b'** are less stable than **4b** and **4b'** by 5.9 and 10.1 kcal/mol, respectively.

In conclusion, the reaction mechanism with E = F is similar to those in cases of E = C, N, and O. The activation energies for the rate-determining steps are 28.9, 29.9, 28.0, 19.1, and 15.9 kcal/mol in the cases of ER_n = CH₃, H₂N, Me₂N, MeO, and F, respectively. Those for MeO and F are much lower than the others; while in the rate-determining step with ER_n = CH₃, H₂N, and Me₂N the structures of ER_n groups must change drastically, the lone pair of electrons on the O and F atoms can easily interact with the Fe atom.⁴ The large exothermicity in the case of ER_n = F makes a contribution to the lower activation energy.

Scheme. Proposed Scheme for E-CN bond cleavage in the presence of iron silyl complex.

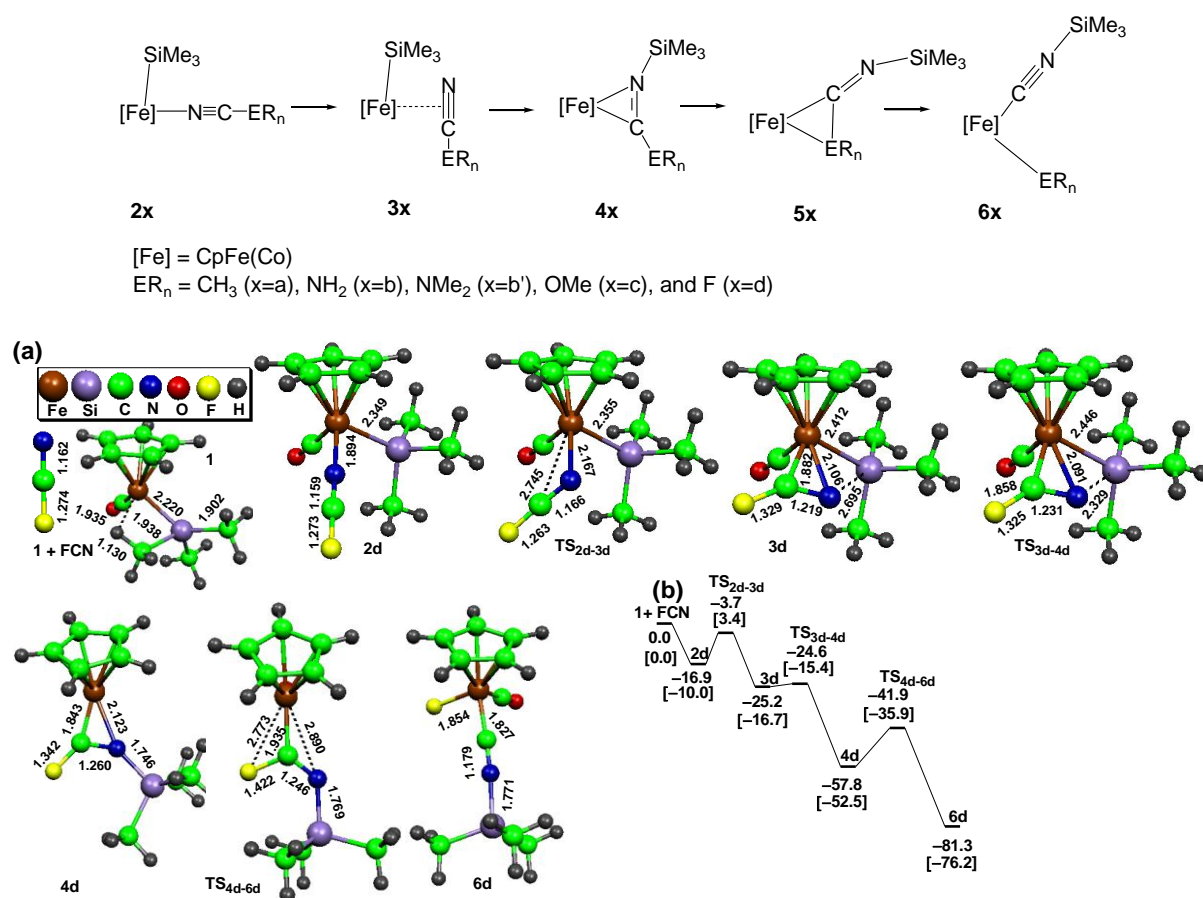


Figure. The (a) optimized structures and (b) the energy profile for the cleavage of F-CN bond in the presence of iron silyl complex. All bonds are in Å. All energies are ZPE-corrected and relative to CpFe(CO)SiMe₃, **1**, and F-CN. Energies in parenthesis are free energies relative to **1** and F-CN.

References:

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