

Catalytic C–C bond cleavage and C–Si bond formation in the reaction of RCN with Et₃SiH promoted by an iron complex†

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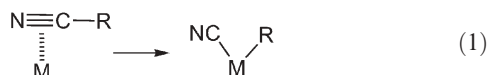
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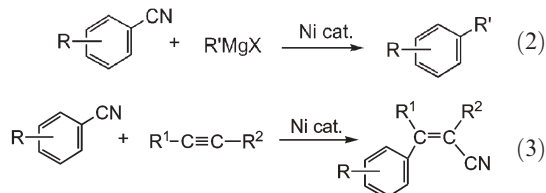
Catalytic C–C bond cleavage of acetonitrile and C–Si bond formation have been attained in the photoreaction of MeCN with Et₃SiH in the presence of an iron complex, Cp(CO)₂FeMe. This catalytic system can be applied for aryl nitrile C–C bond cleavage.

Carbon–carbon bond cleavage is a challenging topic. Especially, C–C bond activation in acetonitrile, being the most common and widely used organonitrile, is of great interest because its bond energy (133 kcal mol⁻¹) is much greater than those of alkanes (ca. 83 kcal mol⁻¹). Acetonitrile has been used in the organometallic chemistry field as a solvent and also as a weak ligand towards a very reactive transition metal fragment, indicating that acetonitrile is resistant to C–C bond cleavage.

Some transition metal complexes have been reported to cleave the C–C bond of nitriles. They mainly involve Group 10 transition metal triads.^{1–9} In addition, one example for Mo,¹⁰ Co,¹¹ U,¹² and two examples of Cu^{13,14} have been reported. In some cases, a mechanism for nitrile C–C bond cleavage has been proposed; η²-nitrile coordination and successive oxidative addition of the C–C bond towards a transition metal center to give an alkyl(aryl)–cyano complex (eqn. (1)).

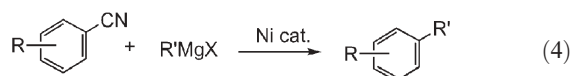


Most nitrile C–C bond cleavages are stoichiometric reactions. Only a few catalytic reactions have been reported. Miller *et al.* demonstrated nickel-catalyzed cross coupling of Grignard reagents with aryl nitriles *via* cleavage of the C–CN bond (eqn. (2)).¹⁵ Hiyama *et al.* reported nickel-catalyzed arylocyanation of alkynes *via* oxidative addition of the C–CN bond to the Ni(0), alkyne insertion into the Ni–CN bond, and then reductive elimination to give an arylocyanation product (eqn. (3)).¹⁶ The Sabo-Etienne and Vogt groups have independently reported nickel-catalyzed isomerization of 2-methyl-3-butenitrile to 3-pentenitrile (eqn. (4)).^{17,18}

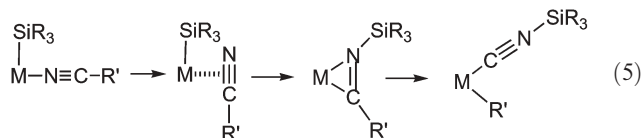


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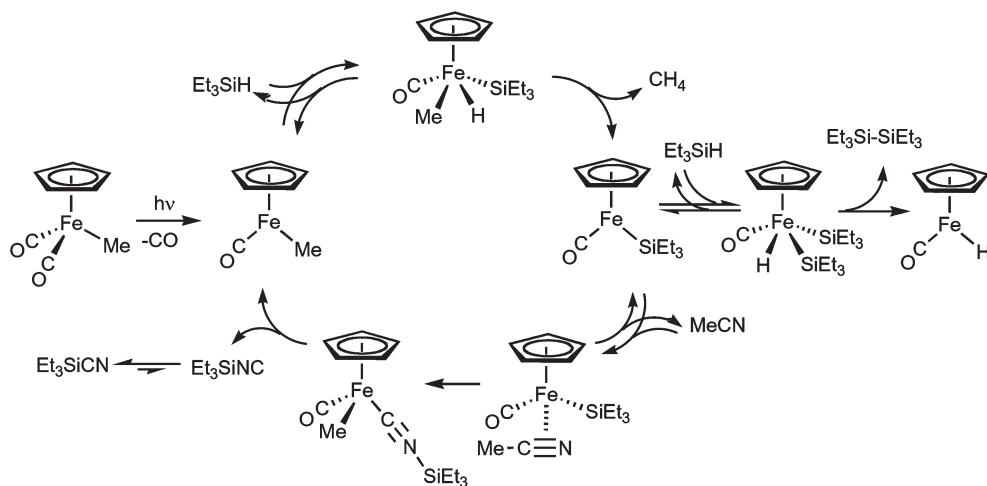
Recently, Bergman and coworkers,¹⁹ and our group²⁰ independently reported new reaction pathways for nitrile C–C bond cleavage that respectively use silyl containing Rh and Fe complexes. In both cases, a silyl group on a transition metal plays a crucial role. Nitrile coordinates to the transition metal in an η¹-fashion and it is then converted into the η²-fashion, followed by silyl migration to the nitrile nitrogen to give an η²-iminoacyl complex and successive C–C bond cleavage on the coordination sphere, thereby yielding an alkyl(aryl)–silylisocyanide complex (eqn. (5)). This reaction is stoichiometric. Herein, we report the first catalytic C–C bond cleavage in nitrile promoted by a transition metal complex other than Ni. This report also involves the first catalytic Si–NC bond and subsequent Si–CN bond formation in which the CN group comes from organonitrile.



Photoreaction of Cp(CO)₂Fe(SiMe₃) with MeCN in THF gives metal-free Me₃SiNC, which is then converted into thermodynamically stable Me₃SiCN.²⁰ Supplying the reaction system with silyl source is necessary to apply this stoichiometric reaction to the catalytic system. Of the many silyl compounds examined, we found that Et₃SiH was a good silyl group source. A THF solution containing equimolar amounts of Et₃SiH and MeCN in the presence of a catalytic amount of Cp(CO)₂Fe(SiMe₃) (2 mol%) was photolyzed for 24 h at room temperature. The main Si-containing product was Et₃SiCN. The yield based on Et₃SiH used

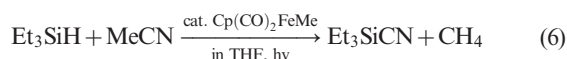
Table 1 Catalytic aryl–CN bond cleavage reaction

	$\text{Et}_3\text{SiH} + \begin{array}{c} \text{X} \\ \\ \text{C}_6\text{H}_4-\text{CN} \end{array} \xrightarrow[\text{in THF, } h\nu]{\text{cat. Cp(CO)}_2\text{FeMe}} \text{Et}_3\text{SiCN} + \begin{array}{c} \text{X} \\ \\ \text{C}_6\text{H}_5 \end{array}$			
Reactant				
Product				
TON	9.8	8.6	10.2	10.1



Scheme 1 Proposed catalytic cycle.

was 45% (TON = 23). The results show the C–C bond in MeCN is cleaved catalytically. Seeking a more effective catalyst, we examined the reaction in identical conditions for many iron complexes, such as $(C_5R_5)(CO)_2FeMe$ ($C_5R_5 = C_5H_5, C_5H_4Me, C_5HMe_4, C_5Me_5, C_5H_4(SiMe_3), C_5H_4\{P(O)(OMe)_2\}$), (Indenyl)- $(CO)_2FeMe$, and $(C_5H_5)(CO)_2FeX$ ($X = Cl, I, CH_2Ph, H$). Consequently, we found that $Cp(CO)_2FeMe$ is an effective catalyst. That reaction is shown in eqn. (6). The yield of Et_3SiCN was 72% and the TON is 36. Other organic products in this reaction were CH_4 and a small amount of $Et_3Si-SiEt_3$.



The catalytic system found for acetonitrile C–C bond cleavage was next applied to a catalytic arylcyanide C–C bond cleavage. The results in Table 1 show that $Cp(CO)_2FeMe$ can also serve as a catalyst for aryl–CN bond cleavage. The main product for dicyanobenzene was cyanobenzene in the reaction condition. The TONs were about 10 in all cases; they were similar to those reported for Ni-catalyzed aryl cyanation of alkynes reported by Hiyama *et al.*¹⁶

We propose the catalytic cycle shown in Scheme 1 for reaction with MeCN. One CO ligand in $Cp(CO)_2FeMe$ is released by photolysis to give $Cp(CO)FeMe$, which reacts with Et_3SiH to give $Cp(CO)FeMe(H)(SiEt_3)$. The successive reductive elimination of CH_4 yields $Cp(CO)Fe(SiEt_3)$. Then MeCN reacts with the 16e species to give $Cp(CO)Fe(SiEt_3)(\eta^2-NCMe)$, which is converted into $Cp(CO)Fe(Me)(\eta^1-CNSiEt_3)$ according to eqn. (5). Dissociation of Et_3SiNC reproduces $Cp(CO)FeMe$ to complete the catalytic cycle. The released Et_3SiNC isomerizes to Et_3SiCN .

$Cp(CO)Fe(SiEt_3)$ produced in the catalytic cycle is expected to react mainly with MeCN, but it may also react with Et_3SiH that is present in solution to give $Cp(CO)FeH(SiEt_3)_2$. $Et_3Si-SiEt_3$ may be formed, if the two silyl groups are eliminated reductively from the species. A small amount of the disilane was observed (see above). The reaction with MeCN may become dominant, and the catalytic cycle is expected to work more effectively if the reaction of $Cp(CO)Fe(SiEt_3)$ with Et_3SiH is suppressed. Thus we attempted

the reaction on changing 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% $Cp(CO)_2FeMe$ under photolysis for 24 h at 50 °C produced 99% yield of Et_3SiCN base on Et_3SiH (TON = 118). The highest TON (156) was obtained when Et_3SiH and a 10-fold molar excess of MeCN were photolyzed for 48 h at 50 °C in the presence of 0.30 mol% of $Cp(CO)_2FeMe$.

In summary, we have established a new catalytic system involving C–C bond cleavage in organonitrile. Furthermore, it initially involves Si–NC and finally Si–CN bond formation. This report is unprecedented in terms of (i) catalytic acetonitrile C–C bond cleavage, (ii) a transition metal catalyst other than Ni for organonitrile C–C bond activation, and (iii) catalytic silylcyanide formation where the cyano group stems from organonitrile. Efforts for expansion of this scope and elucidation of the detailed mechanism are now under way in our laboratory.

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