Electronic supplementary information (ESI) of

Catalytic C-C Bond Cleavage and C-Si Bond Formation in Reaction of RCN with Et$_3$SiH Promoted by an Iron Complex

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All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. (C$_5$R$_5$)(CO)$_2$FeMe (C$_5$R$_5$ = C$_5$H$_5$, C$_5$H$_4$Me, C$_5$HMe$_4$, C$_5$Me$_5$, C$_5$H$_4$(SiMe$_3$), Indenyl)(CO)$_2$FeMe, and (C$_5$H$_5$)(CO)$_2$FeX (X = Cl, I, CH$_2$Ph, H) were prepared according to the literature methods. Acetonitrile and THF were distilled from sodium and benzophenone prior to use. The other chemicals were commercially available. NMR spectra ($^1$H, $^{13}$C{${^1}$H}) were recorded on JEOL EX-400 spectrometer. Residual peaks of solvent were used as the reference for $^1$H NMR ($\delta$, ppm: chloroform-d$_3$, 7.24; benzene-d$_6$, 7.15). For $^{13}$C{${^1}$H} NMR, solvent signals were used as the chemical shift reference. GC analysis was performed on a Shimadzu GC 14B equipped with a Rtx-1701 column (30 m x 0.25 mm, detector = FID, 250 °C) with helium gas as carrier. All yields and TONs were determined by GC using toluene as an internal standard.

General method for catalytic H$_3$C-CN bond cleavage:

A solution of triethylsilane (15.00 mmol, 2.4 mL), acetonitrile (150.00 mmol, 7.86 mL), and Cp(CO)$_2$Fe(Me) (0.83 mol%, 0.125 mmol, 24 mg) in THF (2.1 mL) was irradiated with a 400 W medium pressure mercury arc lamp at 50°C for 24 h in nitrogen atmosphere. After irradiation, toluene (0.2 mmol, 21.2 µL) was added into the reaction mixture. The resulting materials were not purified and were analyzed directly by GC (Yield: 99% / Et$_3$SiH, TON: 118).
General method for catalytic aryl(C)-CN bond cleavage:

A solution of triethylsilane (11.40 mmol, 1.8 mL), isophthalonitrile (11.40 mmol, 1.46 g), and Cp(CO)₂Fe(Me) (5.0 mol%, 0.57 mmol, 110 mg) in benzene (20 mL) was irradiated with a 400 W medium pressure mercury arc lamp at room temperature for 24 h in nitrogen atmosphere. After irradiation, toluene (0.57 mmol, 60 µL) was added into the reaction mixtures. The resulting materials were analyzed directly by GC (Yield: 51% / Et₃SiH, TON: 10.2).

References
3. (C₅HMe₄)(CO)₂FeMe was prepared according to the analogous method¹² using 1,2,3,4-tetramethyl-1,3-cyclopentadiene.