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Catalytic C-C Bond Cleavage and C-Si Bond Formation in Reaction of RCN with Et₃SiH Promoted by an Iron Complex

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All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. (C₅R₅)(CO)₂FeMe (C₅R₅ = C₅H₅,¹ C₅H₄Me,² C₅HMe₄,³ C₅Me₅,⁴ C₅H₄(SiMe₃),⁵ C₅H₄{P(O)(OMe)₂}⁶), (Indenyl)(CO)₂FeMe,⁷ and (C₅H₅)(CO)₂FeX (X = Cl,⁸ I,⁹ CH₂Ph,¹⁰ H¹¹) 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 (¹H, ¹³C{¹H}) were recorded on JEOL EX-400 spectrometer. Residual peaks of solvent were used as the reference for ¹H NMR (δ, ppm: chloroform-*d*₃, 7.24; benzene-*d*₆, 7.15). For ¹³C{¹H} 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 H₃C-CN bond cleavage:

A solution of triethylsilane (15.00 mmol, 2.4 mL), acetonitrile (150.00 mmol, 7.86 mL), and Cp(CO)₂Fe(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% / Et₃SiH, 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 μ L) was added into the reaction mixtures. The resulting materials were analyzed directly by GC (Yield: 51% / Et₃SiH, TON: 10.2).

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