Supporting Information

Scandium Ion-Promoted Reduction of Heterocyclic N=N Double Bond. Hydride Transfer vs Electron Transfer

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Supporting Experimental Section (S1)

**Reaction Procedures and Analysis.** The isolation of the Sc\(^{3+}\)-promoted hydride transfer from AcrH\(_2\) to Ph\(_2\)Tz was performed as follows. Typically, an MeCN solution of AcrH\(_2\) (1.3 \times 10^{-2} \text{ M}, 50 \text{ mL}) was added to the reaction vessel that contained a solution (50 mL) of Ph\(_2\)Tz (1.3 \times 10^{-2} \text{ M}) in the presence of Sc(OTf)\(_3\) (3.5 \times 10^{-2} \text{ M}) under an atmospheric pressure of argon. After the reaction was completed in 30 min, the resulting solution containing the product was evaporated. The residue was dissolved in diethyl ether and washed with deionized water. The organic layer was separated and the solvent was removed from the reaction mixture by distillation at 313 K under vacuum evacuation. The yellowish white solid residue was dried in vacuum. The isolated yield of Ph\(_2\)Tzh\(_2\) was determined to be 88 \%. The elemental analysis of isolated product gave the satisfactory result: Anal. Calcd for C\(_{14}\)H\(_{12}\)N\(_4\)•0.2H\(_2\)O: C, 70.10; H, 5.21; N, 23.36. Found: C, 69.99; H, 4.96; N, 22.98. The \(^1\)H-NMR measurements were performed with a Japan Electron Optics JNM-AL-300 (300 MHz) NMR spectrometer at 300 K. Chemical shifts of \(^1\)H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard (\(\delta = 0\)). \(^1\)H NMR [(CD\(_3\))\(_2\)SO]: \(\delta\) 9.07 (s, 2H), 7.82 (m, 4H), 7.46 (m, 6H).

**Kinetic Measurements.** Kinetic measurements of hydride transfer reactions from AcrH\(_2\) to Ph\(_2\)Tz were performed on a Hewlett Packard 8453 diode array spectrophotometer. Typically, a deaerated MeCN solution of AcrH\(_2\) (2.5 \times 10^{-4} \text{ M}) was added to a quartz cuvette (i.d. 10 mm) containing an MeCN solution of Ph\(_2\)Tz (4.3 \times 10^{-3} \text{ M}) and Sc(OTf)\(_3\) (2.9 \times 10^{-2} - 1.0 \text{ M}), Sc(NTf\(_2\))\(_3\) (1.5 \times 10^{-3} - 8.0 \times 10^{-2} \text{ M}) or Sc[B(C\(_6\)F\(_5\))\(_4\)]\(_3\) (1.5 \times 10^{-5} - 3.4 \times 10^{-4} \text{ M}) by means of a microsyringe under Ar with stirring. Rates of Sc\(^{3+}\)-promoted hydride transfer reactions were monitored by measuring the increase in absorption band at \(\lambda_{\text{max}} = 358 \text{ nm} \ (\varepsilon_{\text{max}} = 1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})\) due to AcrH\(^+\) in MeCN at 298 K in the dark. Measurements of rates of electron transfer reaction from
CoTPP (2.1 × 10^{-6} M) and (AcrH)_2 to Ph₂Tz in the presence and absence of Sc(OTf)₃ (3.7 × 10^{-3} - 4.2 × 10^{-2} M) were performed by using a UNISOKU RSP-601 stopped-flow spectrophotometer equipped with the MOS type highly sensitive photodiode array under deaerated conditions. The rates were monitored by the rise and decay of the absorption band at 434 nm and 412 nm due to CoTPP⁺ and CoTPP in MeCN at 298 K, respectively. All kinetic measurements were carried out under pseudo-first-order conditions where concentrations of Ph₂Tz were maintained at more than 10-fold excess of concentrations of CoTPP at 298 K. Pseudo-first-order rate constants were determined by least-square curve fits using a personal computer. The pseudo-first-order plots were linear for 3 or more half-lives with the correlation coefficient ρ > 0.999.
Figure S1. TOF/MS spectrum for Sc[B(C_6F_5)_4]_3●12H_2O in comparison with the natural isotope abundance pattern (histogram).
Figure S2. Visible spectral changes in the reaction between 3,6-diphenyl-1,2,4,5-tetrazine (Ph$_2$Tz) (4.0 x 10$^{-3}$ M = [Ph$_2$Tz]$_0$) and AcrH$_2$ in deaerated MeCN. Inset: Plot of the absorbance due to Ph$_2$Tz at $\lambda$ = 540 nm vs [AcrH$_2$]/[Ph$_2$Tz]$_0$. 
Figure S3. Time course of the absorption change at $\lambda = 420$ nm due to AcrH$^+$ in the reaction of AcrH$_2$ ($2.5 \times 10^{-4}$ M) with Ph$_2$Tz ($4.4 \times 10^{-3}$ M) in the presence of Sc(OTf)$_3$ (0.4 M) in deaerated MeCN at 298K. Inset: First-order plot.
**Figure S4.** Plot of $k_1$ (s$^{-1}$) vs [Ph$_2$Tz] for the reduction of Ph$_2$Tz by AcrH$_2$ (2.6 x 10$^{-4}$ M) (○) or [AcrD$_2$] = 2.3 x 10$^{-4}$ M (□) in deaerated MeCN at 298K.
Figure S5. Plots of $k_{et}/[\text{Sc(OTf}_3\text{)}]$ vs $[\text{Sc(OTf}_3\text{)}]$ for electron transfer from (a) CoTPP (□, 2.1 x 10^{-6} M) and (b) (AcrH)$_2$ (□, 8.4 x 10^{-5} M) to Ph$_2$Tz in the presence of Sc(OTf)$_3$ in MeCN at 298 K.
Figure S6. Optimized Structure of Ph$_2$Tz$^-$-2H$^+$. 
Figure S7. Visible spectral changes in the reaction between Ph$_2$Tz (3.9 x 10$^{-3}$ M = [Ph$_2$Tz]$_0$) and (AcrH)$_2$ in deaerated MeCN. Inset: Plot of the absorbance due to Ph$_2$Tz at $\lambda$ = 540 nm vs [(AcrH)$_2$]/[Ph$_2$Tz]$_0$. 

$\text{[AcrH$_2$]}/[\text{Ph}_2\text{Tz}]_0$
Figure S8. Plots of $k_{obs}^{-1}$ vs $[\text{Sc}^{3+}]^{-1}$ for the $\text{Sc}^{3+}$-promoted reduction of $\text{Ph}_2\text{Tz}$ by (a) AcrH$_2$ (2.5 x $10^{-4}$ M) and (b) AcrD$_2$ (2.0 x $10^{-4}$ M) in deaerated MeCN at 298 K.