

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

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Received April 18, 2002

Abstract: Hydride transfer from 10-methyl-9,10-dihydroacridine (AcrH₂) to 3,6-diphenyl-1,2,4,5-tetrazine (Ph₂Tz), which contains a N=N double bond, occurs efficiently in the presence of Sc(OTf)₃ (OTf = OSO₂-CF₃) in deaerated acetonitrile (MeCN) at 298 K, whereas no reaction occurs in the absence of Sc³⁺. The observed second-order rate constant (*k*_{obs}) increases with increasing Sc³⁺ concentration to approach a limited value. When AcrH₂ is replaced by the dideuterated compound (AcrD₂), the rate of Sc³⁺-promoted hydride transfer exhibits the same primary kinetic isotope effect (*k*_H/*k*_D = 5.2 ± 0.2), irrespective of Sc³⁺ concentration. Scandium ion also promotes an electron transfer from CoTPP (TPP²⁻ = tetraphenylporphyrin dianion) and 10,10'-dimethyl-9,9'-biacridine [(AcrH)₂] to Ph₂Tz, whereas no electron transfer from CoTPP or (AcrH)₂ to Ph₂Tz occurs in the absence of Sc³⁺. In each case, the observed second-order rate constant of electron transfer (*k*_{et}) shows a first-order dependence on [Sc³⁺] at low concentrations and a second-order dependence at higher concentrations. Such dependence of *k*_{et} on [Sc³⁺] is ascribed to formation of 1:1 and 1:2 complexes between Ph₂Tz^{•-} and Sc³⁺ at the low and high concentrations of Sc³⁺, respectively, which results in acceleration of the rate of electron transfer. The formation of 1:2 complex has been confirmed by the ESR spectrum in which the hyperfine structure is different from that of free Ph₂Tz^{•-}. The 1:2 complex formation results in the saturated kinetic dependence of *k*_{obs} on [Sc³⁺] for the Sc³⁺-promoted hydride transfer, which proceeds via Sc³⁺-promoted electron transfer from AcrH₂ to Ph₂Tz, followed by proton transfer from AcrH₂^{•+} to the 1:1 Ph₂Tz^{•-}-Sc³⁺ complex and the subsequent facile electron transfer from AcrH[•] to Ph₂-TzH[•]. The effects of counteranions on the Sc³⁺-promoted electron transfer and hydride transfer reactions are also reported.

Introduction

Nicotinamide adenine dinucleotide (NADH) is the most important electron source in biological redox reactions, providing a hydride ion that is equivalent to two electrons and a proton. Mechanisms of hydride transfer reactions of NADH analogues with hydride acceptors such as carbonyl compounds and organic cations have been extensively studied chemically¹⁻⁸ or elec-

trochemically.^{9,10} The effects of metal ions on hydride transfer reactions from NADH analogues to substrates have particularly

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attracted considerable interest in relation to the catalytic role of metal ions in the redox reactions of nicotinamide coenzymes in the native enzymatic system.^{1–4,11,12} Metal ions acting as Lewis acids are known to promote electron-transfer reactions, where metal ions bind to the product radical anions produced in the electron-transfer reactions.^{13–16} Both thermal and photochemical redox reactions that would otherwise be unlikely to occur are made possible to proceed efficiently by the catalysis of metal ions on the electron-transfer steps.^{13–16} Among metal ions, rare-earth metal ions have particularly attracted considerable attention as much more effective Lewis acids than divalent metal ions such as Mg^{2+} and Zn^{2+} in various carbon–carbon bond-forming reactions due to the strong affinity to carbonyl oxygen.^{17–19} In particular, scandium ion (Sc^{3+}) has recently been reported to accelerate electron-transfer reduction of *p*-benzoquinone derivatives much more efficiently than any other metal ion, including lanthanide ions.²⁰ The reactions of NADH analogues with *p*-benzoquinone derivatives, which are normally good hydride acceptors, are also accelerated most remarkably by Sc^{3+} .²⁰ In this case, however, efficient [2 + 3] cycloaddition reactions of NADH analogues with *p*-benzoquinone derivatives rather than the hydride transfer reactions occur in the presence of scandium triflate [$Sc(OTf)_3$] in MeCN.²⁰ Moreover, there has so far been no report on the metal ion-promoted hydride transfer from an NADH analogue to hydride acceptors other than carbonyl compounds, which would be difficult to reduce without the metal ion. The effects of counterions on the metal ion-promoted electron transfer or hydride transfer have yet to be examined.

We report herein that hydride transfer from an NADH analogue to 3,6-diphenyl-1,2,4,5-tetrazine (Ph_2Tz), which would otherwise be difficult to reduce,²¹ occurs efficiently in the presence of $Sc(OTf)_3$ ($OTf = OSO_2CF_3$) in MeCN. 1,2,4,5-Tetrazines containing a $N=N$ double bond are valuable electron-deficient 4π components that have been utilized in Diels–Alder reactions with inverse electron demanding, making a large variety of valuable compounds available.^{22–24} The kinetic analysis of the Sc^{3+} -promoted hydride transfer reactions involving kinetic deuterium isotope effects as compared with the authentic electron-transfer reactions provides valuable information for the Sc^{3+} -promoted electron-transfer step and the subsequent proton-transfer step in the overall hydride transfer reaction. The key intermediate for the Sc^{3+} -promoted reduction of Ph_2Tz is found to be the complex formed between the radical anion of Ph_2Tz and Sc^{3+} , which is detected successfully by ESR spectroscopy in this study. The effects of counterions have also been studied to reveal the relation between the electron transfer and the hydride transfer reactions.

Experimental Section

The standard procedures of experiments including product analysis and kinetic measurements are given in the Supporting Information (S1).

Materials. The preparation of 10-methyl-9,10-dihydroacridine ($AcrH_2$) and the dideuterated compound ($AcrD_2$) was described previously.^{4a} The dimeric 1-benzyl-1,4-dihydronicotinamide dimer [$(BNA)_2$] was prepared according to the literature procedure.²⁵ Cobalt(II) tetraphenylporphyrin (CoTPP) was prepared as given in the literature.²⁶ 10,10'-Dimethyl-9,9'-biacridine [$(AcrH)_2$] was prepared by the one-electron reduction of 10-methylacridinium perchlorate by hexamethylditin.²⁷ Scandium triflate [$Sc(OTf)_3$] was prepared by the procedure reported elsewhere.²⁰ Scandium triflate was characterized by ^{13}C NMR in D_2O as compared with the data for $Yb(OTf)_3$.²⁸

1,1,1-Trifluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide, [$Sc(NTf_2)_3$], was obtained commercially from Aldrich. The scandium salt of tetrakis(pentafluorophenyl)borate [$Sc[B(C_6F_5)_4]_3$] was prepared by the following procedure. A powder form of ion-exchange resin (DOWEX 50WX8-200, 0.5 g) obtained from Ardrich was suspended

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in an aqueous solution of $\text{Sc}(\text{OTf})_3$ (1.0 g, 200 mL) and stirred by the magnetic stirrer for 1 day. The isolated Sc^{3+} -exchanged resin was washed with deionized water and dried under vacuum for one night. An aqueous solution of lithium tetrakis(pentafluorophenyl)borate diethyl ether complex (2.9×10^{-2} M, 50 mL) obtained from Tokyo Chemical Industry Co., Ltd. was added dropwise to the glass short column packed with the Sc^{3+} -exchanged resin. The aqueous solution of the scandium borate salt ($\text{Sc}[\text{B}(\text{C}_6\text{F}_5)_4]_3$) trickled down the column and was concentrated by the vacuum evaporation followed by drying under vacuum for one night. The white powder of $\text{Sc}[\text{B}(\text{C}_6\text{F}_5)_4]_3$ with water of crystallization was identified by Shimadzu TOF mass spectrometer, AXIMA-CFR (see Supporting Information S2). Acetonitrile used as a solvent was purified and dried by the standard procedure.²⁹ Acetonitrile- d_3 and dimethyl sulfoxide- d_6 were obtained from EURI SO-TOP, CEA, France.

Electrochemical Measurements. Electrochemical measurements were performed on a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.10 M $n\text{-Bu}_4\text{N}^+\text{ClO}_4^-$ (TBAP) as a supporting electrolyte at 298 K. The platinum working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgNO_3 (0.01 M) reference electrode. The second-harmonic alternating current voltammetry (SHACV)³⁰ measurements of Ph_2Tz in the presence of $\text{Sc}(\text{OTf})_3$ were carried out with a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.10 M TBAP as a supporting electrolyte at 298 K. The E_{red}^0 values (vs Ag/AgNO_3) are converted into those vs SCE by addition of 0.29 V.³¹

ESR Measurements. Ph_2Tz was dissolved in MeCN (1.0×10^{-3} M in 1.0 mL) and purged with argon for 10 min. $\text{Sc}(\text{OTf})_3$ (8.8×10^{-2} M in 1.0 mL) and $\text{Sc}[\text{B}(\text{C}_6\text{F}_5)_4]_3$ (2.0×10^{-1} M in 1.0 mL) were dissolved in deaerated MeCN. The Ph_2Tz solution (200 μL) and Sc^{3+} solution (200 μL) were introduced into the ESR cell (1.8 mm i.d.) containing $(\text{BNA})_2$ (2.0×10^{-2} M) and mixed by bubbling with Ar gas through a syringe with a long needle. The ESR spectra of the $\text{Ph}_2\text{Tz}^{2-}-2\text{Sc}^{3+}$ complex were recorded on a JEOL JES-RE1XE spectrometer under irradiation of a high-pressure mercury lamp (USH-1005D) focusing at the sample cell in the ESR cavity at 298 K. The ESR spectrum of $\text{Ph}_2\text{Tz}^{2-}$ was also measured in the absence of $\text{Sc}(\text{OTf})_3$ under otherwise the same experimental conditions. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (S/N) ratio of the observed spectra under nonsaturating microwave power conditions. The g values were calibrated using an Mn^{2+} marker.

Theoretical Calculations. Density functional calculations were performed on a COMPAQ DS20E computer using the spin-restricted B3LYP functional for the open shell molecule.³² The B3LYP geometry of $\text{Ph}_2\text{Tz}^{2-}-2\text{H}^+$ was determined using the 6-31G(3d,3p) basis set and the Gaussian 98 program.³³ The $\langle S^2 \rangle$ value was determined as 0.761, indicating a good representation of the doublet state.

Results and Discussion

Sc^{3+} -Promoted Hydride Transfer from AcrH_2 to Ph_2Tz . Upon addition of AcrH_2 (1.7×10^{-3} M) to a deaerated MeCN solution of Ph_2Tz (1.7×10^{-3} M) in the presence of $\text{Sc}(\text{OTf})_3$

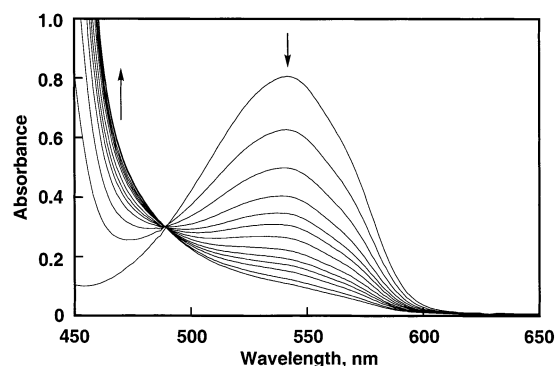
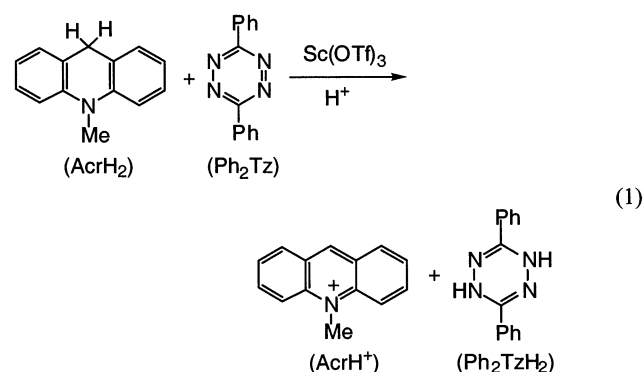


Figure 1. Spectral change in the reaction of AcrH_2 (1.7×10^{-3} M) with Ph_2Tz (1.7×10^{-3} M) in the presence of Sc^{3+} (1.4×10^{-2} M) in deaerated MeCN at 298 K (time interval, 400 s).

(1.4×10^{-2} M), hydride transfer from AcrH_2 to Ph_2Tz occurs efficiently to yield 10-methylacridinium ion (AcrH^+) and dihydrotetrazine (Ph_2TzH_2) in MeCN at 298 K (eq 1, for the



product analysis, see Experimental Section).^{34–37} As the reaction proceeds, the absorption band due to Ph_2Tz ($\lambda_{\text{max}} = 540$ nm) decreases and this is accompanied by the appearance of a new absorption band ($\lambda_{\text{max}} = 358$ nm) due to the formation of AcrH^+ (Figure 1). In the absence of Sc^{3+} , no reaction has occurred between AcrH_2 and Ph_2Tz .

The spectral titration in which the absorbance due to Ph_2Tz at $\lambda = 540$ nm is plotted against $[\text{AcrH}_2]/[\text{Ph}_2\text{Tz}]_0$ (see

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- (34) Formation of Ph_2TzH_2 was confirmed by comparing the ^1H NMR data (see Experimental Section) with the reported values. See: Nagy, J.; Nyitrai, J.; Kolonits, P.; Lempert, K.; Gergely, A.; Párkányi, L.; Kálmán, A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3267. Three positional isomers (1,4-, 1,2-, and 3,6-isomers) are expected to be formed as dihydro-3,6-diphenyl-1,2,4,5-tetrazine on the basis of the ^1H NMR data (see Experimental Section); however, the 1,4-isomer (eqs 1 and 7) is the most likely candidate, since it was calculated to be thermodynamically more stable than the 1,2- and 3,6-isomer by 6.7 and 28.0 kcal mol⁻¹, respectively at the B3LYP/6-31G* level.
- (35) The proton required for formation of Ph_2TzH_2 comes from water contained in MeCN. The acidity of water in the presence of $\text{Sc}(\text{OTf})_3$ in acetonitrile- d_3 increases as compared with that in the absence of $\text{Sc}(\text{OTf})_3$, as indicated by the low-field shift of ^1H NMR signal due to water.
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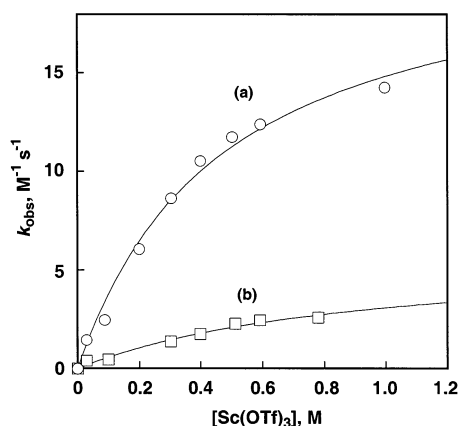


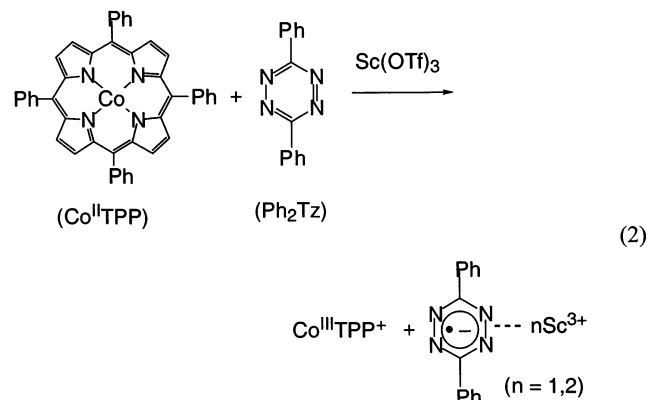
Figure 2. Plots of k_{obs} vs $[\text{Sc}(\text{OTf})_3]$ for reduction of Ph_2Tz by (a) AcrH_2 ($\circ$, 2.5×10^{-4} M) and (b) AcrD_2 ($\square$, 2.0×10^{-4} M) in the presence of $\text{Sc}(\text{OTf})_3$ in deaerated MeCN at 298 K.

Supporting Information S3) confirms the stoichiometry in eq 1, where 1 equiv of AcrH_2 reacts with 1 equiv of Ph_2Tz to yield 1 equiv of AcrH^+ and Ph_2TzH_2 .

The rates of Sc^{3+} -promoted hydride transfer reaction were determined by monitoring the appearance of absorbance due to AcrH^+ ($\lambda_{\text{max}} = 358$ nm, $\epsilon_{\text{max}} = 1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The rates obeyed pseudo-first-order kinetics in the presence of large excess Ph_2Tz and Sc^{3+} relative to the concentration of AcrH_2 (see Supporting Information S5). The pseudo-first-order rate constant (k_1) increases proportionally with Ph_2Tz concentration (see Supporting Information S5). Thus, the rate exhibits a second-order kinetics showing a first-order dependence on each reactant concentration.

The dependence of the observed second-order rate constant (k_{obs}) on $[\text{Sc}^{3+}]$ was examined for the Sc^{3+} -promoted hydride transfer reaction at various concentrations of Sc^{3+} . The k_{obs} value increases with an increase in $[\text{Sc}^{3+}]$ to approach a limited value, as shown in Figure 2a. When AcrH_2 is replaced by the dideuterated compound (AcrD_2), a large kinetic primary isotope effect is observed as shown in Figure 2b.

Sc^{3+} -Promoted Electron-Transfer Reduction of Ph_2Tz . When AcrH_2 is replaced by a one-electron reductant such as CoTPP (TPP^{2-} = tetraphenylporphyrin dianion), electron transfer from CoTPP to Ph_2Tz also occurs efficiently in the presence of $\text{Sc}(\text{OTf})_3$ in MeCN (eq 2), whereas no electron



transfer from CoTPP to Ph_2Tz occurred without $\text{Sc}(\text{OTf})_3$. The electron-transfer rates obeyed a second-order kinetics, showing a first-order dependence on each reactant concentration. The

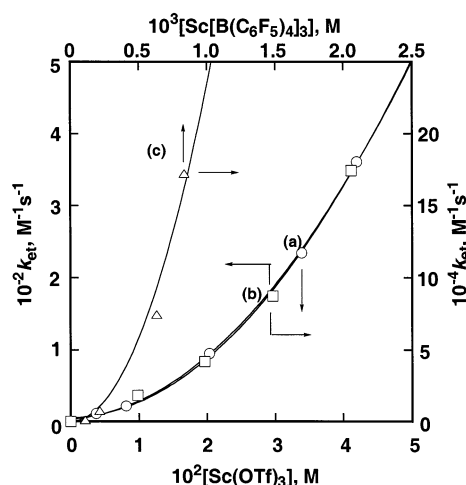


Figure 3. Plots of k_{et} vs $[\text{Sc}(\text{OTf})_3]$ for electron transfer from (a) CoTPP ($\circ$, 2.1×10^{-6} M) and (b) $(\text{AcrH})_2$ ($\square$, 8.4×10^{-5} M) to Ph_2Tz in the presence of $\text{Sc}(\text{OTf})_3$, and (c) for electron transfer from CoTPP ($\triangle$, 2.1×10^{-6} M) to Ph_2Tz in the presence of $\text{Sc}[\text{B}(\text{C}_6\text{F}_5)_4]_3$ in MeCN at 298 K.

dependence of the observed electron-transfer rate constant (k_{et}) on $[\text{Sc}^{3+}]$ was also examined for electron transfer from CoTPP to Ph_2Tz at various concentrations of Sc^{3+} . The results are quite different from those of the hydride transfer reaction, as shown in Figure 3a, where the k_{et} value increases with increasing $[\text{Sc}^{3+}]$ to exhibit a mixture of a first-order and second-order dependence on $[\text{Sc}^{3+}]$ (vide infra).

It was confirmed that there was no interaction between Ph_2Tz and Sc^{3+} , as indicated by the lack of spectral change of Ph_2Tz in the presence of Sc^{3+} .³⁸ In such a case, the acceleration of electron transfer from CoTPP to Ph_2Tz is ascribed to the complexation of Sc^{3+} with $\text{Ph}_2\text{Tz}^{\bullet-}$. The contribution of the second-order dependence of k_{et} on $[\text{Sc}^{3+}]$ in Figure 2a suggests that $\text{Ph}_2\text{Tz}^{\bullet-}$ may form not only a 1:1 complex ($n = 1$ in eq 2) but also a 1:2 complex ($n = 2$ in eq 2) with Sc^{3+} . The complex formation of $\text{Ph}_2\text{Tz}^{\bullet-}$ and Sc^{3+} should result in the positive shift of the one-electron reduction potential of Ph_2Tz (E_{red}), and the Nernst equation may be given by eq 3,

$$E_{\text{red}} = E_{\text{red}}^0 + (2.3RT/F) \log K_1[\text{Sc}^{3+}](1 + K_2[\text{Sc}^{3+}]) \quad (3)$$

where E_{red}^0 is the one-electron reduction potential of Ph_2Tz in the absence of Sc^{3+} , and K_1 and K_2 are the formation constants for the 1:1 and 1:2 complexes between $\text{Ph}_2\text{Tz}^{\bullet-}$ and Sc^{3+} , respectively. Since Sc^{3+} has no effect on the oxidation potential of CoTPP, the free energy change of electron transfer from CoTPP to Ph_2Tz in the presence of Sc^{3+} (ΔG_{et}) can be expressed by eq 4,

$$\Delta G_{\text{et}} = \Delta G_{\text{et}}^0 - (2.3RT) \log(K_1[\text{Sc}^{3+}] + K_1K_2[\text{Sc}^{3+}]^2) \quad (4)$$

where ΔG_{et}^0 is the free energy change in the absence of Sc^{3+} .

Thus, electron transfer from CoTPP to Ph_2Tz becomes more favorable energetically with an increase in concentration of Sc^{3+} . If such a change in the energetics is directly reflected in the

(38) No complex formation between Ph_2Tz and Sc^{3+} in acetonitrile was confirmed by the ^1H and ^{13}C NMR titration. ^1H NMR (CD_3CN) in the absence of $\text{Sc}(\text{OTf})_3$: δ 8.60 (dd, $J = 8.0, 1.5$ Hz, 4H), 7.68 (m, 6H). ^1H NMR (CD_3CN) in the presence of 0.38 M $\text{Sc}(\text{OTf})_3$: δ 8.60 (dd, $J = 8.0, 1.5$ Hz, 4H), 7.68 (m, 6H). ^{13}C NMR (CD_3CN) in the absence of $\text{Sc}(\text{OTf})_3$: δ 128.56 (s), 128.75 (s), 130.11 (s), 130.61 (s), 164.97 (s). ^{13}C NMR (CD_3CN) in the presence of 0.07 M $\text{Sc}(\text{OTf})_3$: δ 128.56 (s), 128.75 (s), 130.11 (s), 130.61 (s), 164.97 (s).

Table 1. Rate Constants (k_0K_1) of Sc^{3+} -Promoted Electron Transfer from CoTPP and $(\text{AcrH})_2$ to Ph_2Tz and the Formation Constants (K_2) of the $\text{Ph}_2\text{Tz}^{\bullet-}-2\text{Sc}^{3+}$ Complexes in Deaerated MeCN at 298 K

electron donor	$k_0K_1,^a \text{ M}^{-2} \text{ s}^{-1}$	$K_2,^a \text{ M}^{-1}$
CoTPP	9.4×10^5	8.2×10
$(\text{AcrH})_2$	1.8×10^3	8.5×10

^a Determined from the dependence of k_{obs} on $[\text{Sc}^{3+}]$ based on eq 6. The experimental error is 10%.

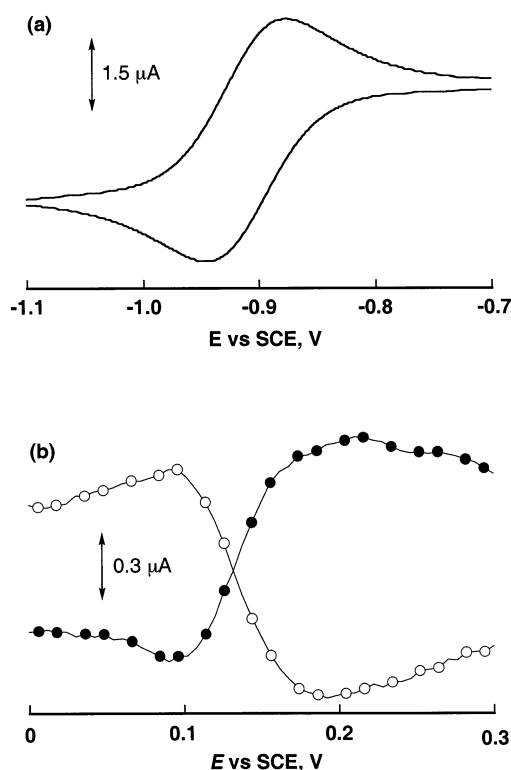


Figure 4. (a) Cyclic voltammogram of Ph_2Tz ($1.0 \times 10^{-3} \text{ M}$) in deaerated MeCN containing 0.10 M TBAP with Pt electrode at 298 K and (b) SHACV of Ph_2Tz ($1.0 \times 10^{-3} \text{ M}$) in the presence of $\text{Sc}(\text{OTf})_3$ ($4.1 \times 10^{-3} \text{ M}$) in deaerated MeCN containing 0.10 M TBAP with Pt electrode at 298 K.

transition state of electron transfer, the dependence of the observed rate constant of electron transfer (k_{et}) on $[\text{Sc}^{3+}]$ is derived from eq 4, as given by eq 5,

$$k_{\text{et}} = k_0K_1([\text{Sc}^{3+}] + K_2[\text{Sc}^{3+}]^2) \quad (5)$$

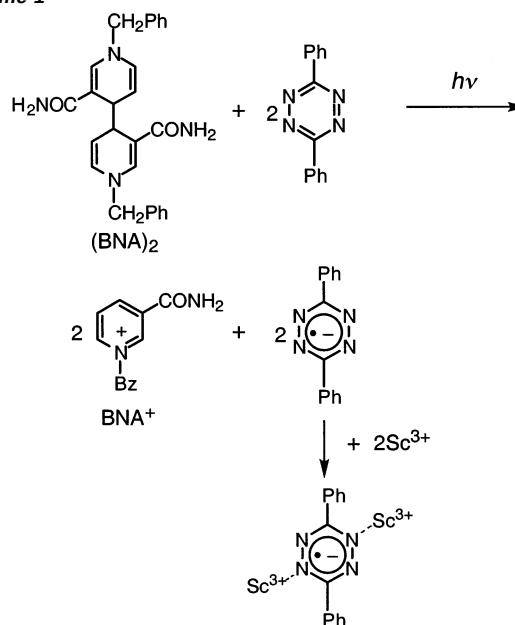
where k_0 is the rate constant in the absence of Sc^{3+} . From eq 5 is derived eq 6,

$$k_{\text{et}}/[\text{Sc}^{3+}] = k_0K_1(1 + K_2[\text{Sc}^{3+}]) \quad (6)$$

the validity of which is confirmed by the linear plot of $k_{\text{et}}/[\text{Sc}^{3+}]$ vs $[\text{Sc}^{3+}]$ for the Sc^{3+} -promoted electron transfer from CoTPP to Ph_2Tz (see Supporting Information S6). From the slope and intercept is obtained the K_2 value which is listed in Table 1 together with the k_0K_1 value. The solid lines in Figure 3 are drawn on the basis of eq 5 with these parameters.

The positive shift of E_{red} caused by the complexation of $\text{Ph}_2\text{Tz}^{\bullet-}$ with Sc^{3+} was verified by the electrochemical measurements. The cyclic voltammogram of Ph_2Tz exhibits a reversible redox wave, as shown in Figure 4a. The one-electron reduction potential of Ph_2Tz is determined from the half-wave potential

Scheme 1



as -0.91 V (vs SCE). The addition of $\text{Sc}(\text{OTf})_3$ ($4.1 \times 10^{-3} \text{ M}$) to an MeCN solution of Ph_2Tz results in a largely positive shift of the one-electron reduction potential ($+1.04 \text{ V}$), as shown in Figure 4b, where the second harmonic ac voltammogram affords the one-electron reduction potential ($+0.13 \text{ V}$).^{39,40}

Detection of the $\text{Ph}_2\text{Tz}^{\bullet-}-2\text{Sc}^{3+}$ Complex. The 1:2 complex formation between $\text{Ph}_2\text{Tz}^{\bullet-}$ and Sc^{3+} has been confirmed by the observation of the ESR spectrum of the $\text{Ph}_2\text{Tz}^{\bullet-}-2\text{Sc}^{3+}$ complex, which is compared with that of $\text{Ph}_2\text{Tz}^{\bullet-}$ (vide infra). The $\text{Ph}_2\text{Tz}^{\bullet-}$ was produced by photoinduced electron transfer from dimeric 1-benzyl-1,4-dihydronicotinamide $[(\text{BNA})_2]$ ⁴¹ to Ph_2Tz in MeCN at 233 K (Scheme 1). The $(\text{BNA})_2$ is known to act as a unique electron donor to produce the radical anions of electron acceptors.⁴² The ESR spectrum of $\text{Ph}_2\text{Tz}^{\bullet-}$ thus obtained under photoirradiation exhibits nine hyperfine lines as shown in Figure 5a, indicating that four nitrogens are equivalent [$a(4\text{N}) = 5.1 \text{ G}$]. The addition of $\text{Sc}(\text{OTf})_3$ ($4.4 \times 10^{-2} \text{ M}$) to the $(\text{BNA})_2$ - Ph_2Tz system results in a drastic change in the hyperfine pattern of $\text{Ph}_2\text{Tz}^{\bullet-}$ due to the complexation with Sc^{3+} (Scheme 1), as shown in Figure 5b. The ESR spectrum is well-reproduced by the computer simulation spectrum with the hfc values of $a(2\text{N}) = 6.6, 5.0 \text{ G}$ and $a(6\text{H}) = 5.0 \text{ G}$ (Figure 5c). The four equivalent nitrogens of $\text{Ph}_2\text{Tz}^{\bullet-}$ are split into two sets of two equivalent nitrogens due to the complexation with two Sc^{3+} ions. The absence of superhyperfine lines due to the scandium nucleus indicates that the interaction between $\text{Ph}_2\text{Tz}^{\bullet-}$ and two Sc^{3+} ions is largely electrostatic rather than covalent. The complexation of $\text{Ph}_2\text{Tz}^{\bullet-}$ with two Sc^{3+} ions

(39) The cyclic voltammogram of Ph_2Tz in the presence of $\text{Sc}(\text{OTf})_3$ shows an irreversible cathodic wave due to the instability of the $\text{Ph}_2\text{Tz}^{\bullet-}-\text{Sc}^{3+}$ complex. Although the one-electron reduction potential determined by SHACV³⁰ may involve uncertainty due to the instability of the $\text{Ph}_2\text{Tz}^{\bullet-}-\text{Sc}^{3+}$ complex, the observed large positive shift as compared to that in the absence of Sc^{3+} is unmistakable.

(40) An even larger positive shift ($+2.02 \text{ V}$) of the reversible one-electron reduction potential of a naphthoquinone derivative, determined by CV, has been reported to be caused by the complexation of the radical anion with Sc^{3+} (7.0 mM) in MeCN. See: Fukuzumi, S.; Okamoto, K.; Imahori, H. *Angew. Chem., Int. Ed.* **2002**, 41, 620. For other examples, see ref 14.

(41) Patz, M.; Kuwahara, Y.; Suenobu, T.; Fukuzumi, S. *Chem. Lett.* **1997**, 567.

(42) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **1998**, 120, 8060.

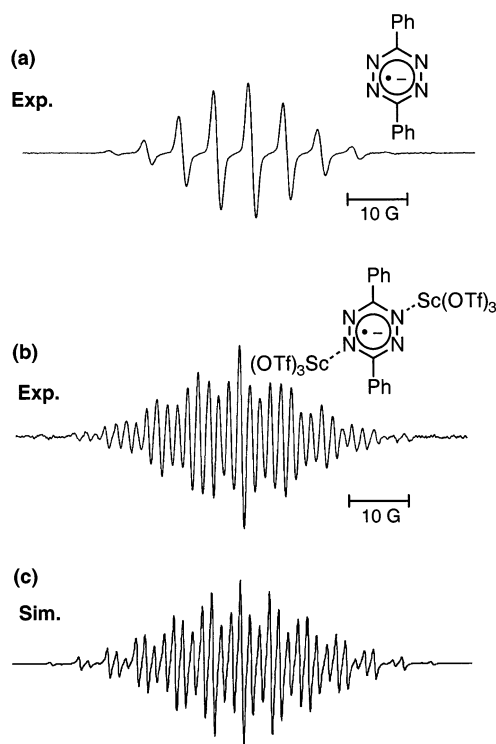
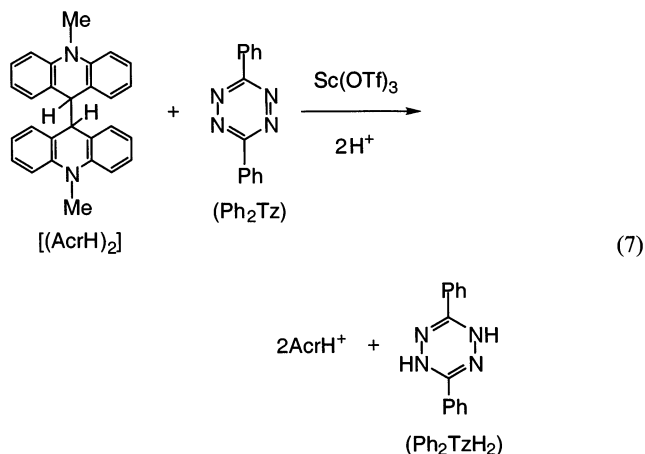


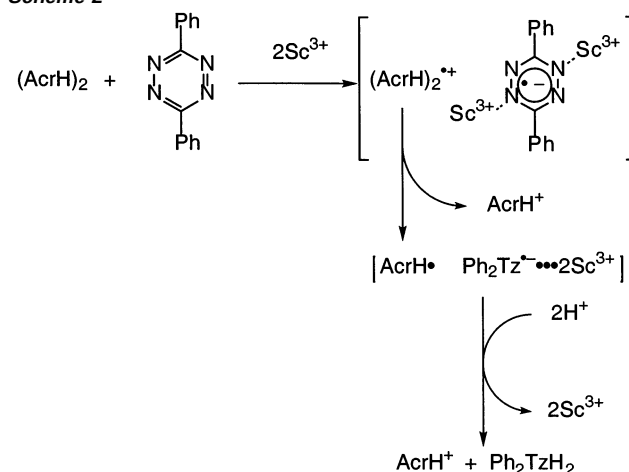
Figure 5. ESR spectra of an MeCN solution containing (BNA)₂ (2.0×10^{-2} M) and Ph₂Tz (5.0×10^{-4} M) in the absence (a) and presence (b) of Sc(OTf)₃ (4.4×10^{-2} M) under irradiation with a high-pressure mercury lamp at 233 K. (c) Computer-simulated spectrum for condition b with $g = 2.0041$, $a(2N^1) = 6.6$ G, $a(2N^2) = 5.0$ G, $a(6H) = 5.0$ G, and $\Delta H_{\text{msl}} = 0.40$ G.

also results in the structural change such that the phenyl group becomes coplanar with the heterocycle ring when the hyperfine lines due to six equivalent protons appear due to the spin delocalization on the phenyl group in the Sc³⁺ complex. Such coplanarity in the Sc³⁺ complex is supported by the B3LYP theoretical calculation of the protonated species Ph₂Tz^{•+}–2H⁺ (see Supporting Information S7).

Electron Transfer vs Hydride Transfer. The acridine dimer, 10,10'-dimethyl-9,9'-biacridine [(AcrH)₂], is known to act as an electron donor, in contrast with the case of the monomer, AcrH₂, which is a hydride donor.^{43,44} Electron transfer from (AcrH)₂ to Ph₂Tz occurs efficiently in the presence of Sc(OTf)₃ in MeCN at 298 K to yield AcrH⁺ and Ph₂TzH₂ (eq 7), which are the same as the products of the Sc³⁺-promoted hydride transfer reaction from AcrH₂ to Ph₂Tz (eq 1).³⁵ The spectral



Scheme 2



titration (see Supporting Information S8) confirms the stoichiometry in eq 7, where 1 equiv of (AcrH)₂ reacts with 1 equiv of Ph₂Tz to yield 2 equiv of AcrH⁺ and Ph₂TzH₂. In this case, the initial Sc³⁺-promoted electron transfer from (AcrH)₂ to Ph₂Tz is followed by the facile C–C bond cleavage to give AcrH⁺ and AcrH[•] (Scheme 2). Since AcrH[•] (E^0_{ox} vs SCE = -0.46 V)^{4e} is much stronger reductant than (AcrH)₂ (E^0_{ox} vs SCE = 0.62 V),⁴³ the rapid electron transfer from AcrH[•] to the Ph₂Tz^{•–}–2Sc³⁺ complex occurs to yield the final products, AcrH⁺ and Ph₂TzH₂ after replacement of Sc³⁺ by H⁺ (Scheme 2).³⁵

The rates of Sc³⁺-promoted electron transfer from (AcrH)₂ to Ph₂Tz were determined by monitoring the appearance of absorbance due to AcrH⁺ as in the case of the hydride transfer from AcrH₂ to Ph₂Tz. However, the dependence of the observed second-order rate constant (k_{et}) on [Sc³⁺] is different from that for the Sc³⁺-promoted hydride transfer reaction in Figure 2a, but it is virtually the same as that for the Sc³⁺-promoted electron transfer from CoTPP to Ph₂Tz (Figure 3a): the k_{et} value increases linearly with [Sc³⁺] to show a first-order dependence on [Sc³⁺] at low concentrations, changing to a second-order dependence at high concentrations (Figure 3b). The same linear plot of $k_{\text{et}}/[\text{Sc}^{3+}]$ vs [Sc³⁺] is applied for the Sc³⁺-promoted electron transfer from (AcrH)₂ to Ph₂Tz to afford the K_2 value as 85 M^{-1} (Figure 4b). This value agrees with the K_2 value (82 M^{-1}) derived from the Sc³⁺-promoted electron transfer from CoTPP to Ph₂Tz (Figure 4a). Such an agreement indicates that the rate-determining step for the two-electron reduction of Ph₂Tz by (AcrH)₂ is indeed the Sc³⁺-promoted electron transfer from (AcrH)₂ to Ph₂Tz (Scheme 2).

The saturated dependence of k_{obs} with respect to [Sc³⁺] for the Sc³⁺-promoted hydride transfer from AcrH₂ to Ph₂Tz (Figure 2a) normally results from the complex formation between Ph₂Tz and Sc³⁺, which enhances the electrophilicity of Ph₂Tz to accelerate the hydride transfer reaction. However, as noted earlier, there was no interaction between Ph₂Tz and Sc³⁺. Only the one-electron reduced species, i.e., Ph₂Tz^{•–}, can form the complex with Sc³⁺ (vide supra). In such a case, the dependence

(43) Fukuzumi, S.; Tokuda, Y. *J. Phys. Chem.* **1992**, *96*, 8409.

(44) The acridine dimer [(AcrH)₂] is employed instead of (BNA)₂, since (AcrH)₂ has no interaction with Sc³⁺, whereas the carbonyl oxygen of [(BNA)₂] forms a complex with Sc³⁺.²⁰ The electron-transfer oxidation mechanism of (AcrH)₂ is similar to that of (BNA)₂, although the oxidation potentials of (AcrH)₂ and AcrH[•] are much higher than those of (BNA)₂ and BNA[•].^{42,43}

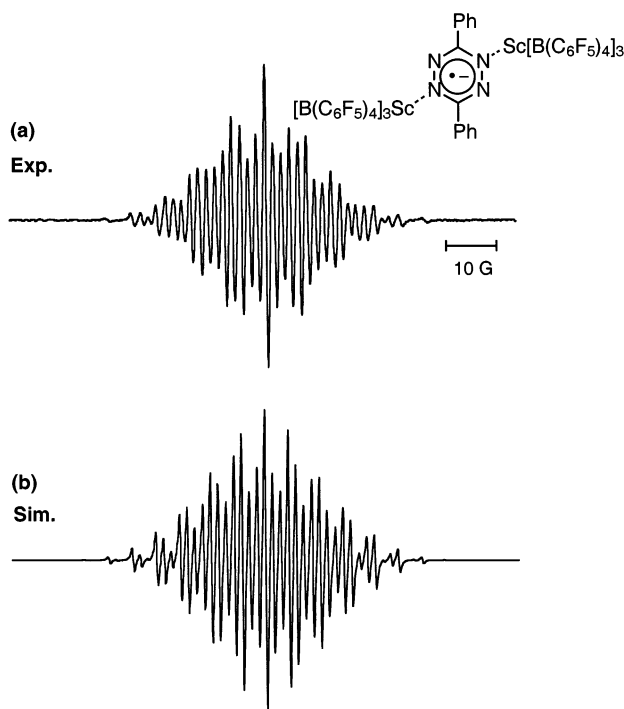


Figure 7. (a) ESR spectrum of an MeCN solution containing (BNA)₂ (2.0×10^{-2} M) and Ph₂Tz (5.0×10^{-4} M) in the presence of Sc[B(C₆F₅)₄]₃ (1.0×10^{-1} M) under irradiation with a high-pressure mercury lamp at 233 K. (b) Computer-simulated spectrum with $g = 2.0039$, $a(2N^1) = 6.1$ G, $a(2N^2) = 4.7$ G, $a(6H) = 4.7$ G, and $\Delta H_{\text{msl}} = 0.40$ G.

to Ph₂Tz. The hydride transfer reaction proceeds via the Sc³⁺-promoted electron transfer from AcrH₂ to Ph₂Tz, followed by

proton transfer and electron transfer. The overall reactivity is regulated by the initial electron transfer and the subsequent proton-transfer processes, in which the formation of a 1:2 complex between Ph₂Tz^{•−} and Sc³⁺ accelerates the electron transfer but decelerates the proton-transfer process. Such accelerating and decelerating effects of Sc³⁺ are controlled by the counterions, which alter the Lewis acidity of Sc³⁺. Thus, the balance between the accelerating effects of Sc³⁺ on the electron-transfer step and the decelerating effects on the subsequent proton-transfer step is of importance to control the overall reactivity of the hydride transfer reaction of NADH analogues.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research Priority Area (Nos. 11228205 and 13031059) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Supporting Experimental Section (S1), TOF/MS spectrum for Sc[B(C₆F₅)₄]₃·12H₂O (S2), UV–vis spectral change in the reaction between Ph₂Tz and AcrH₂ (S3), time course of the absorption change and the first-order plot (S4), plots of pseudo-first-order rate constant vs [Ph₂Tz] (S5), plots of $k_{\text{et}}/[\text{Sc}(\text{OTf})_3]$ vs [Sc(OTf)₃] (S6), optimized structure of Ph₂Tz^{•−}−2H⁺ (S7), UV–vis spectral change in the reaction between Ph₂Tz and (AcrH)₂ (S8), and plots of k_{obs}^{-1} vs [Ph₂Tz]^{−1} (S9). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA026592Y