Intermolecular Electron-Transfer Reactions Involving Hydrazines

Stephen F. Nelsen,*,[†] Ling-Jen Chen,[†] Michael T. Ramm,[†] Gilbert T. Voy,[†] Douglas R. Powell,[†] Molly A. Accola,[‡] Troy R. Seehafer,[‡] Jobiah J. Sabelko,[‡] and Jack R. Pladziewicz^{*,‡}

S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706-1396, and the Department of Chemistry, University of Wisconsin, Eau Claire, Wisconsin 54702

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The self-exchange electron-transfer (ET) rate constant k_{22} for 1,2,3,4,5-pentamethylferrocene was determined by NMR line broadening to be $8.5(\pm 0.8) \times 10^6$ M⁻¹ s⁻¹ (25 °C, CD₃CN/0.09 M Et₄NBF₄) and k_{11} for the bis-N,N-bicyclic hydrazine, 9,9'-bi-9-azabicyclo[3.3.1]nonane, to be 8.7(0.5) \times 10³ $M^{-1} s^{-1} (25 °C, CH_2Cl_2)$. These self-exchange rate constants are used to analyze cross reactions of these molecules with hydrazines, ferrocenes, and tetramethyl-p-phenylenediamine (TMPD) using Marcus theory. Cross-reaction rate constants for eight reactions are reported. Included are six cross-reactions between methylferrocenes and four cyclic hydrazines, one hydrazine, hydrazinereaction, and the reduction of \mathbf{TMPD}^+ by a cyclic hydrazine. These are the first cross-reaction rate constants reported for hydrazine-hydrazine and hydrazine-TMPD⁺ ET reactions. The crossreaction rate constants are used to test the application of Marcus theory to hydrazine ET reactions and to extract estimates of hydrazine self-exchange ET rate constants in systems for which direct measurement is presently impossible.

Introduction

The Marcus cross-relation¹ estimates rate constants for electron transfer (ET) between different species 1 and 2 by using the equilibrium constant K_{12} of (1) and the

$$[\mathbf{1}]^{\circ} + [\mathbf{2}]^{\bullet +} \stackrel{K_{12}}{\underbrace{\longleftrightarrow}} [\mathbf{1}]^{\bullet +} + [\mathbf{2}]^{\circ}$$
(1)

average of the intrinsic barriers (2), which, when used with the rate expression (3) for the effect of ΔG° for (1)

$$\lambda_{12} = (\lambda_{11} + \lambda_{22})/2$$
 (2)

$$k = Z_{12} \exp(-[\Delta G^{\circ} + \lambda_{12}]^2 / 4\lambda_{12} RT)$$
 (3)

on the effective barrier, produces (4) as the expression for the cross rate constant where k_{12} (calc). These expres-

$$k_{12}(\text{calc}) = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$
 (4)

$$\ln f_{12} = (\ln K_{12})^2 / 4 \ln(k_{11} k_{22} / Z_{12}^2)$$
 (5)

sions clearly work rather well for many inorganic reactions.² We recently examined these relationships for ET between bis-N,N'-bicyclic (sesquibicyclic) tetraalkylhydrazines 22/u22 and 21/u22 and substituted ferrocenes $Cp_{2}^{*}Fe$, $Cp^{*}CpFe$, and $Cp_{2}^{'}Fe^{3}$. In abbreviating these



structures we use the number of carbons connecting the

bridgehead carbons on each side of the dinitrogen bridge common to both rings of the hydrazines, with **u** designating an unsaturated bridge and Cp*, Cp', and Cp pentamethyl, monomethyl, and unsubstituted cyclopentadienyl ligands, so that the compound designations convey easily



remembered structural information. The self-ET rate constants, k_{11} , for the hydrazines were measured by slow exchange region NMR,³ and k_{22} for ferrocene derivative self-exchange have been studied by fast exchange region NMR. We used data from Weaver and co-workers for Cp_2Fe and Cp_2Fe^4 and interpolated k_{22} for the other two ferrocenes. k_{12} values were measured by stoppedflow spectrophotometry, monitoring the absorption of the ferrocenium species. The hydrazine k_{11} and ferrocene k_{22} values are very different, $k_{22}(Cp_{2}Fe)/k_{11}(21/u22) = 1.3$ \times 104, probably largely as a result of their very different Marcus inner sphere vertical ET barriers,² λ_{in} , which are argued to be approximately 2 kcal/mol for ferrocenes⁴ and measured at 37.6 kcal/mol for an N,N'-bis-bicyclic hydrazine using a dimeric compound (see below). For the hydrazine–ferrocene reactions reported,³ k_{12} (obs) is within a factor of 4 of that calculated, k_{12} (calc), using (4) with the traditional $Z_{12} = 1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ and self-exchange rate constants from NMR measurements. This agreement is comparable to the best-behaved inorganic systems.²

In the present work we determined k_{22} for **Cp*CpFe**^{0/+}, finding it to be significantly lower than the extrapolated value previously employed. This is important because this ferrocene has a reduction potential ideally suited to reactions with many organic molecules of interest, and

[†] UW–Madison. ‡ UW–Eau Claire.

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Table 1. Rate Constant Data for Cp*CpFe^{0/+} Mixtures in Acetonitrile Containing 90 mM Et₄NBF₄ at 25 °C

	ring hydrogen signal ^a					methyl signal ^b					
no.	C _{tot} , mM	$v_{\rm DP}, {\rm Hz}$	χ_P , 10^{-3}	C _P , mM	$W_{\rm DP}$, Hz	$k_{ m ex}{}^c imes 10^{-6}$	$v_{\rm DP},{\rm Hz}$	χ_P , 10^{-3}	<i>C</i> _P , mM	$W_{\rm DP}$, Hz	$k_{ m ex}^{c} imes 10^{-6}$
1	77.1	930.4	3.09	0.24	4.10	6.34	440.8	2.95	0.23	8.21	7.72
2	73.3	940.5	5.19	0.38	6.54	7.05	418.9	5.06	0.37	13.61	8.50
3	69.9	951.0	7.36	0.51	8.91	7.86	397.6	7.10	0.50	19.40	8.62
4	66.8	960.2	9.27	0.62	11.51	7.65	376.0	9.17	0.61	26.22	8.46
5	63.9	1115	11.57	0.74	13.77	8.68	355.3	11.15	0.71	30.99	9.11

 $^{a} W_{D} = 0.2_{6}, W_{P} = 644 \pm 40 \text{ Hz. } \nu_{D} = 915.4, \nu_{P} = 5\ 749 \pm 10, \Delta\nu = 4834 \pm 10 \text{ Hz.} \ ^{b} W_{D} = 0.4_{7}, W_{P} = 413 \pm 20 \text{ Hz. } \nu_{D} = 471.6, \nu_{P} = -9\ 962 \pm 10, \Delta\nu = 10\ 440 \pm 10 \text{ Hz.} \ ^{c} M^{-1} \text{ s}^{-1}.$

knowing k_{22} allows greater confidence in analysis of reactions that utilize it or its radical cation. We have also considerably widened the range of structural variation of the compounds used, including hydrazines which have lone pair—lone pair dihedral angle θ values of 180° and near 120°, as well as the radical cation of the aromatic diamine tetramethyl-*p*-phenylenediamine, **TMPD**, which significantly extends the k_{22} range for the oxidants used. This is of significance because it allows a more rigorous test of (2)–(5).

Results

Self-Exchange Rate Constants. We determined k_{22} for **Cp*CpFe**^{0/+} using fast exchange region NMR. The rate constant for fast exchange region NMR line broadening kinetics is given by (6),^{4b,5} where γ_D and γ_P are the

$$k_{\rm ex} = 4\pi \chi_{\rm D} \chi_{\rm P} (\Delta \nu)^2 / [(W_{\rm DP} - \chi_{\rm D} W_{\rm D} - \chi_{\rm P} W_{\rm P}) C_{\rm tot}] \qquad (6)$$

mole fractions of the diamagnetic and paramagnetic species D and P respectively, $\Delta \nu = |\nu_D - \nu_P|$ (hertz) is the chemical shift difference between the NMR signals of D and P, W_D and W_P are the NMR line widths at halfheight in hertz for these species, W_{DP} is the linewidth for the D,P mixture, and C_{tot} is the sum of the concentrations of D and P. Only small amounts of the paramagnetic species can be added, and χ_P was determined using (7).^{4b} Table 1 summarizes our results for **Cp*CpFe**^{0/+}.

$$\chi_{\rm P} = (\nu_{\rm DP} - \nu_{\rm D}) / \Delta \nu \tag{7}$$

Four determinations of the chemical shifts and line widths for Cp*CpFe⁺BF₄⁻ between 0.03 and 0.12 M in acetonitrile gave the values and ranges for $W_{\rm P}$ and $v_{\rm P}$ quoted at the bottom of Table 1, without a clear trend with concentration (signal-to-noise is a problem for small concentrations of Cp*CpFe⁺, more serious for the broader and less intense ring hydrogen signal). Cp*CpFe^{0/+} mixtures have two DP signals (ring and methyl hydrogens) which should produce the same $\chi_{\rm P}$ and $k_{\rm ex}$ values. Slightly different values are produced using (6) and (7), presumably reflecting experimental errors. The k_{ex} values are quite insensitive (\pm (0.01 \times 10⁶) M⁻¹ s⁻¹) to the observed uncertainty in $\nu_{\rm P}$ and vary by $\leq \pm (0.08 \times$ 10⁶) $M^{-1} s^{-1}$ ($\leq \pm 1\%$) and by $\pm (0.5-0.7)$ ($\leq \pm 8\%$) for those in $W_{\rm P}$ (Me) and $W_{\rm P}$ (ring), respectively. The ring hydrogen signal is seen from Table 1 to produce slightly smaller $k_{\rm ex}$ values than the methyl hydrogen signal, and there is drift to higher k_{ex} values at higher C_P (and hence W_{DP}) in both data sets, but less for the methyl signal. The plot of k_{ex} vs W_{DP} shown in Figure 1 suggests that the assumptions involved in deriving (6) are not fulfilled at the lower concentrations studied. Equation 6 assumes



Figure 1. Plot of k_{ex} vs NMR linewidth for mixtures of **Cp*CpFe**⁰ and **Cp*CpFe**⁺. The circles are for ring and the squares for methyl hydrogen signals.

that exchange between the radical and diamagnetic forms is rapid compared to the difference in the NMR frequency and also that electron spin relaxation is faster than the hyperfine frequency in the radical, so that the spin exchange is a two-site problem.⁵ Heisenberg spin exchange between the radicals can make electron spin relaxation fast enough so that (6) holds, its rate depends upon radical concentration,⁶ and the hyperfine frequencies are different for the methyl and ring hydrogen signals. The methyl and ring hydrogen signals give different k_{ex} values at low concentration and hence low $W_{\rm P}$, indicating that spin exchange between the radicals may not be rapid enough for (6) to hold. We suggest that the higher, limiting k_{ex} values measured at higher W_{DP} are likely to be correct and evaluate $k_{ex}(CD_3CN, 25 \text{ °C})$ for $Cp*CpFe^{0/+}$ as 8.5(±0.8) \times 10⁶ M⁻¹ s⁻¹ from these data.

Hydrazines have far smaller self-exchange rate constants than ferrocenes, but some may be studied in the slow exchange NMR region. Measurement of k_{11} for **33N**)₂^{0/+} proved difficult for solubility reasons. Neutral



33N)₂ was too insoluble in acetonitrile, dimethylformamide, or nitromethane to allow observation of slow exchange region NMR kinetics, which requires a large excess of neutral over radical cation. Its solubility is higher in methylene chloride, and $k_{11}(25 \text{ °C}, \text{CD}_2\text{Cl}_2)$ was determined to be 8.7(0.5) × 10³ M⁻¹ s⁻¹. Solvent effect studies on k_{11} have been carried out for **22/u220**/+ and

⁽⁵⁾ Chen, M.-S.; De Roos, J. B.; Wahl, A. C. J. Phys. Chem. 1973, 77, 2163.

⁽⁶⁾ Hausser, K. H.; Bunner, H.; Joachims, J. C. Mol. Phys. 1966, 10, 233.

			v		
reaction	$\Delta G^{\circ \ a}$	$10^{-5}k_{12},^{b}$ M ⁻¹ s ⁻¹	$k_{11}(calc),^{c}$ M ⁻¹ s ⁻¹	ΔG^{\sharp}_{11} (calc), ^c kcal/mol	Z_{12} , effect ^d
1. Cp′ ₂ Fe ⁺ ,22/tBuMe ⁰	-3.9	3.2(±0.3)	22	15.6	+0.15, -0.08
2. Cp*CpFe ⁺ ,22/tBuMe ⁰	-0.3	0.23(±0.02)	36	15.3	< 0.01
3. TMPD ⁺ ,22/tBuMe ⁰	-0.2	$1.1(\pm 0.1)$	5.6	16.4	< 0.01
4. Cp*CpFe ⁺ ,22/tBuiPr ⁰	-5.2	8.1(±0.8)	23	15.6	+0.26, -0.12
5. Cp*2Fe ⁺ ,22/tBuiPr ⁰	+0.2	$0.14(\pm 0.03)$	9.6	16.1	< 0.01
6. Cp*CpFe ⁺ ,22/iPr ₂ 0	-1.0^{e}	$0.59(\pm 0.06)$	75^{e}	14.9^{e}	< 0.07
<i>6a.</i> Čp*ČpFe⁺,22/iPr₂⁰	$-5.4^{ m e}$	0.59(±0.06)	<i>0.08</i> ^e	<i>18.9</i> ^{e 2}	
7. Cp*CpFe ⁺ ,33N) ₂ ⁰	-3.1	$11(\pm 1)$	990	13.4	+0.14, -0.06
8. 21/21 ⁺ ,33N) ₂ ⁰	-0.5	0.0209^{f}	109	14.7	< 0.02

^{*a*} Unit, kcal/mol, using data from Table 3. ^{*b*} At 25 °C in acetonitrile, $\mu = 0.1$ M. ^{*c*} For the neutral in each reactant pair, calculated from k_{12} and (4), using data from Table 3 and $Z_{12} = 1 \times 10^{11}$ M⁻¹ s⁻¹. ^{*d*} Fractional change in k_{11} (calc) using $Z_{12} = 1 \times 10^9$ M⁻¹ s⁻¹ (positive number) and $Z_{12} = 1 \times 10^{13}$ M⁻¹ s⁻¹ (negative number). ^{*e*} For $E^{\circ}(22/i\mathbf{Pr}_2) = +0.08$ V. The numbers in italics (*6a*) use E° of -0.11 (see text for why this was done). ^{*f*} (±0.0005).

21/u22^{0/+},⁷ giving k_{11} (CD₃CN)/ k_{11} (CD₂Cl₂, 25 °C) ratios of 0.20₅ and 0.19₉. Our best estimate for k_{11} (CD₃CN, 25 °C) for **33N**)₂^{0/+} is therefore 20% that in CD₂Cl₂, or 2.2 × 10³.

Stopped-Flow k_{12} **Measurements.** The one-electron oxidations of three 2,3-diazabicyclo[2.2.2]octane derivatives with unlinked 2,3-dialkyl substituents, abbreviated **22/RR'**, have been examined by reacting them with three



ferroceniums and with **TMPD**⁺ (Table 2, Reactions 1–6). The one-electron oxidation of $33N)_2^0$ has been studied using **Cp*CpFe**⁺ and **21/21**⁺ as oxidants, monitoring



disappearance of **Cp*CpFe**⁺ (reaction 7) and formation of **33N**)₂⁺ (reaction 8). All eight reactions are observed to obey second-order rate laws at 25 °C, $\mu = 0.10$ in acetonitrile, and the observed second-order rate constants, k_{12} , are listed in Table 2, and for convenience, the formal potentials and self-ET rate constants necessary for analysis are collected in Table 3.

Discussion

 k_{22} for Cp*CpFe^{0/+}. Because of its convenient formal potential, $E^{\circ\prime}$, Cp*CpFe^{0/+} was employed as an oxidant for many of the compounds studied, making experimental determination of its k_{22} value especially important for interpretation of the stopped-flow studies. Weaver and co-workers found a significant effect of the presence of added electrolyte for Cp₂Fe^{0/+} but little dependence of k_{22} upon ionic strength in the region of 0.1 M total BF₄⁻ concentration.^{4b} Hunt and co-workers report larger

Table 3. Formal Potentials and Self-ET Rate Constants

couple	<i>E</i> ⁰, <i>ª</i> V vs SCE	$k_{11}(\text{NMR}), {}^{b}$ M ⁻¹ s ⁻¹	$\Delta G^{\ddagger}_{11}(\text{NMR}),$ kcal/mol					
	Н	lydrazines						
22/u22 ^{0/+}	-0.24_{1}	$12.1(\pm 1) \times 10^{3}$	11.89 ± 0.05					
21/u22 ^{0/+}	$+0.05_{8}$	$2.29(\pm .10) \times 10^{3}$	12.87 ± 0.02					
22/tBuMe ^{0/+}	+0.11	(too slow)						
22/tBuiPr ^{0/+}	-0.10	(too slow)						
33N) ₂ 0/+	-0.01	$2.17 imes10^3$ c	12.9					
21/21 ^{0/+}	+0.01	$18.5(\pm0.5) imes10^3~d$	11.63 ± 0.02					
	Ferroc	ene Derivatives						
Cp* ₂ Fe ^{0/+}	-0.10_{9}	$2.9 imes10^7$	7.27					
Cp*CpFe ^{0/+}	$+0.12_{4}$	$8.5 imes10^6$	8.00					
Cp' ₂ Fe ^{0/+}	$+0.28_{1}$	$8.3 imes10^6$	8.01					
Cp ₂ Fe ^{0/+}	$+0.39_{5}$	$8.1 imes 10^6$	8.02					
	Aromatic Amine							
TMPD ^{0/+}	+0.12	$1.4_6 imes10^{9}$ d	4.95					

^{*a*} In acetonitrile containing 0.1 M nBu₄NClO₄ at 25 °C. ^{*b*} In acetonitrile at 25 °C, without supporting electrolyte for the hydrazines and with 0.09 M Et₄NBF₄ for **Cp*CpFe**. ^{*c*} From ref 10. ^{*c*} Estimated from the rate constant in CD₂Cl₂ (see text). ^{*d*} Extrapolated to 25 °C from the activation parameters reported in ref 19.

decreases in k_{22} with **Cp₂Fe**⁺ concentration increases in the absence of added electrolyte.⁸ The measured value for $k_{22}(\mathbf{Cp}^*\mathbf{CpFe^{0/+}})$ is 57% of that used previously,³ which was interpolated from the values measured by Weaver and co-workers for $Cp_2Fe^{0/+}$ and $Cp_2Fe^{0/+}$. Weaver and co-workers pointed out that k_{22} values for metallocenes do not correlate with E° for these compounds,⁴ so perhaps we should not be surprised that our interpolation between the k_{22} values for ferrocene and decamethylferrocene was not very successful for **Cp*CpFe**. They attribute the substantial decrease in k_{22} between cobaltacenes and ferrocenes to smaller electronic matrix coupling elements V (which is equal to half the energy separation between the ground state and excited state surfaces at the electron transfer transition state, and is called H_{12} by Weaver and co-workers and J or H_{ab} by others²) in the iron systems, caused by greater localization of the odd electron at the metal.^{4a} They also evaluate "closest approach" V° values of 0.2 and 0.1 kcal/ mol for $Cp_2^*Fe^{0/+}$ and $Cp_2Fe^{0/+}$, respectively, using a solvent friction-electron tunneling model. Because the steric effect of methylation would only seem capable of lowering π,π overlap at the transition state, methyl substitution presumably would have to be increasing odd electron density in methylated (**Cp***) rings relative to the unmethylated (**Cp**) rings, to account for the increase in k_{22} for **Cp***₂**Fe** and larger *V* value. The NMR spectra of

^{(7) (}a) Nelsen, S. F.; Wang, Y. J. Org. Chem. **1994**, 59, 1655. (b) **22/u23**^{0/+} was also studied, ^{5a} giving $k_{11}(CD_3CN)/k_{11}(CD_2Cl_2, 25 °C) = 0.284$. Analysis of the rate constants for the **22/u23**^{0/+} system was only consistent with a ~30% smaller ΔG^*_{out} than for the other two compounds, which is not consistent with the small changes in molecular size. We concluded that this system has a problem, most likely cation stability, because **22/u23⁺** is noticably less stable in the presence of the neutral hydrazine than are the other two, and that the solvent rate ratio is likely to be not as reliable.

⁽⁸⁾ Kirchner, K.; Dang, S.-Q.; Stebler, M.; Dodgen, H. W.; Wherland, S.; Hunt, J. P. *Inorg. Chem.* **1989**, *28*, 3604.

Table 4. Comparison of Ring Carbon π Spin Densities for Methylated and Unmethylated Ferrocenium Rings^a

compound	$\delta_{\mathrm{P}}(\mathrm{C}H)$	$\delta_{\rm P}({\rm C}H_3)$	$\rho_{\rm C}^{\pi}(C{\rm H})$	$\rho_{\rm C}^{\pi}(C{ m Me})$	$\Sigma \rho_{\rm C}^{\pi}$
$\begin{array}{c} Cp_2Fe^+\\ Cp^*CpFe^+\\ Cp^*_2Fe^+ \end{array}$	+28.67 + 19.36	$-41.73 \\ -38.44$	$-0.017 \\ -0.011$	$-0.021 \\ -0.019$	$-0.17 \\ -0.16 \\ -0.19$

^{*a*} From NMR data in CD₃CN at 25 °C, using $a(H)/\delta_P = 73.27$ G/ppm^{10a} and the simple McConnell relationships.^{10b}

the ferrocene cations bear directly upon this question, because the π spin density at the ring carbons, $\rho_{\rm C}^{\pi}$, can be calculated from the ESR splitting constants a(H), which are available from the paramagnetic shifts.⁹ $\rho_{\rm C}^{\pi}$ values using chemical shifts from Weaver and coworkers^{4a} for Cp*₂Fe⁺ and Cp₂Fe^{+ 10} and data from Table 1 for **Cp*CpFe**⁺ are compared in Table 4. The total π spin density at the ring carbons is similar for all three compounds, and although the **Cp*** ring has almost twice the spin density as the **Cp** ring for **Cp*CpFe**⁺, ρ_{C}^{π} is only 7% higher for the **Cp**^{*} ring of **Cp**^{*}₂**Fe**⁺ than for the **Cp** ring of $\mathbf{Cp}_{2}\mathbf{Fe}^{+}$. We conclude that there is not a correlation between k_{22} and $\rho_{\rm C}^{\pi}$ for these ferrocenes. We do not know why k_{22} for **Cp*CpFe**^{0/+} is closer to that of **Cp₂Fe**^{0/+} than of $\tilde{\mathbf{Cp}}_{\mathbf{2}}^*\mathbf{Fe}^{0/+}$, but the differences are rather small, and more than one factor might contribute.

Cross Rate Studies. The cross relations (2)-(5)traditionally used for analysis of ET reactions between two different species assume that the rate constants will be controlled by the ET barrier ($\lambda_{12} + \Delta G^{\circ}$), that λ_{12} will be given by (2), and that the same preexponential factor $(Z_{12} \text{ in } (3))$ may be used for all cases. More modern ET theory² has emphasized that ET reactions will have different preexponential factors depending upon whether they are adiabatic or diabatic (nonadiabatic). The preexponential factor for adiabatic reactions is approximately $\nu_n = ch \nu_{in} [\lambda_{in}/(\lambda_{out} + \lambda_{in})]^{1/2}$ in a semiclassical model where single solvent and inner sphere barrier crossing frequencies are assumed,² where hv_{in} is the frequency (in cm⁻¹) of the nuclear vibration which leads to crossing the activated complex configuration. The preexponential factor for diabatic reactions is controlled by the electronic coupling frequency v_{el} , which is approximately given by $(1.5 \times 10^{14})[V^2/\lambda^{1/2}]$ at 25 °C.² Intermolecular self-ET has been argued to be diabatic because of small V values for all three compound types studied here, hydrazines,⁷ ferrocenes,⁴ and TMPD.¹¹ With the large range in structure for the compounds employed, substantial variations in hv_{in} certainly occur. Ferrocenes have effective $hv_{\rm in}$ estimated at under 400 cm⁻¹, hydrazines doubtless have several effective hv_{in} values but are believed to have intermediate frequencies active for ET, and TMPD has larger, aromatic stretching frequencies involved (Grampp and Jaenicke estimated *hv*_{in} at 1668 cm⁻¹).¹¹ Tunneling effects also appear in the preexponential factor and

depend upon $hv_{\rm in}$, so different Z_{ii} values might be expected to occur for different compound types. It is therefore important to consider what Z_{ii} values might be expected for self-ET reactions of the compound types studied here, as well as how large the effects of different Z_{12} values for cross-reactions between different compound types might be on the k_{11} values calculated using (4) with the traditional Z_{12} value of 1×10^{11} M⁻¹ s⁻¹.

 Z_{ii} estimates for self-ET reactions can be obtained using Hush theory,¹² from the transition energies E_{op} for dimeric radical cations **1–4**. Marcus and Sutin define



 $E_{\rm op}$ as λ for such symmetrical "intervalence" compounds,^{2a} although the solvent reorganization contribution to λ , $\lambda_{\rm out}$, can obviously be different for the self-ET transition state and the dimeric species. Table 5 summarizes Z_{ii} value estimations from the $E_{\rm op}$ data. The solvent dependence of $E_{\rm op}$ for **1** gives a 9.0 kcal/mol $\lambda_{\rm out}$ (CH₃CN),¹³ which is close to the 10 kcal/mol estimated from solvent dependence of k_{11} for self-ET of sesquibicyclic hydrazines^{5a} and we employ 46–49 kcal/mol as a reasonable range for λ for **22/22**^{0/+} (the bicyclic rings of neutral **22/22** may be slightly more twisted than those of **1**, which may raise λ somewhat). **2**¹⁴ is included despite the fact that k_{11} for



22/tBuMe has not been experimentally determined. Using a k_{11} value range derived from the cross rate studies in this work, we determine that a Z_{11} value similar to those for the sesquibicyclic hydrazines apply to **22/tBuMe** as well. Determination of Z_{ii} for **3** uses the λ_{out} estimate from the solvent dependence of E_{op} .¹⁵ We agree with Weaver and co-workers that λ_{out} for **3** should be reasonably close to that for **Cp₂Fe^{0/+}**, but not on the partitioning of λ_{out} and λ_{in} for these systems.^{15b} **4** is not as good a model for **TMPD** as the other dimeric cases

^{(9) (}a) For a recent paper on obtaining *a*(H) from NMR data, see: Petillo, P. A.; De Felippis, J.; Nelsen, S. F. *J. Org. Chem.* **1991**, *56*, 6496. (b) $a(H_{\alpha}) \cong Q_{H\rho}c\pi$, $a(H_{\beta}) \cong Q_{Me}\langle \cos^2 \theta \rangle_{Pc}\pi$, where $\langle \cos^2 \theta \rangle = 0.5$ for a methyl group. We employed $Q_{H} = -23$ and $Q_{Me} = +54.^{8c}$ (c) Fischer, H. *Free Radicals*, Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 19, p 435.

Vol. 2, Chapter 19, p 435. (10) (a) Fritz, H. P.; Keller, H. T.; Schwarzhaus, K. E. J. Organomet. *Chem.* **1967**, 7, 105. (b) Rettig, M. F.; Drago, R. S. J. Am. Chem. Soc. **1969**, 91, 1361, report a(H) = +0.183 for **6**⁺ using the above data.^{8a} which we do not understand because both the paramagnetic shift and the $\rho_{C\pi}$ Fritz and co-workers report correspond to a(H) = +0.338 G.

^{(11) (}a) Grampp, G.; Jaenicke, W. Ber. Bunsenges. Phys. Chem. **1991**, 95, 904. (b) Grampp and Jaenicke^{9a} suggest V to be as small as 0.1-0.02 kcal/mol for **TMPD**, but we have argued on the basis of optical studies of the **4** radical cation that their V was significantly underestimated because of underestimation of λ_{in} .¹⁴

⁽¹²⁾ For a review, see: Hush, N. S. Coord. Chem. Rev. 1985, 64, 135.

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Table 5. Z_{ii} Values for Self-ET (25 °C, CH₃CN) Estimated from E_{op} Values of Dimeric Compounds and k_{ii} for Self-ET

dimer'+	E _{op} , kcal/mol	λ _{out} (est), kcal/mol	monomer	k_{ii} , $\mathrm{M}^{-1}~\mathrm{s}^{-1}$	λ(est), kcal/mol	$Z_{ii}(ext{est}) imes 10^{-11}$
1ª 2 ^b	46.6 52.2	9 9	22/22 22/tBuMe	$\begin{array}{c} 7\times10^2\\ 20{-}36\ ^{\rm b}\end{array}$	$46-49 \\ 52-54$	2-7 0.7-3
3^{c} 4^{d}	21.4 29.7	11 unknown	Cp₂Fe TMPD	$\begin{array}{c} 8.1\times10^6\\ 1.5\times10^9\end{array}$	$\substack{20-22\\20-25}$	0.4 - 0.9 70 - 600

^{*a*} Reference 13. ^{*b*} Reference 14. The k_{11} range uses k_{11} (calc) values from Table II. ^{*c*} Reference 15. Reference 16.

are for their monomers, both because the charge-bearing units are less similar (AM1 calculations suggest that λ_{in} might be 2.4 kcal/mol less for **TMPD** itself than for the six-membered-ring-containing **4**)¹⁶ and because the λ_{out} values are expected to be greater for the extended geometry of **4** than for the π -overlapping geometry argued for the **TMPD**^{0/+} transition state;¹¹ we include a wider range for the λ_{22} estimate for **TMPD** than for the other compounds for these reasons. It should be noted that our estimate (based both on the E_{op} for **4** and more recent theoretical estimates of λ_{in} for **TMPD**) is larger than that employed by Grampp and Jaenicke.¹¹ We conclude from the information in Table 5 that 10^{11} M⁻¹ s⁻¹ is a reasonable estimate of the effective Z_{ii} for both hydrazines and ferrocenes, but that it is larger for **TMPD**.

We note that a $k_{11}(\text{calc})$ value obtained from an observed k_{12} and an experimental k_{22} value using (2)–(5) is quite insensitive to the Z_{12} value employed unless K_{12} is large. The effect of using Z_{12} of 10^9-10^{13} M⁻¹ s⁻¹ on $k_{11}(\text{calc})$ for our data is shown in Table 2, last column (and Table 6, see below), where it can be seen that it only becomes significant when ΔG° becomes more negative than about -2 kcal/mol and never exceeds a 50% change in $k_{11}(\text{calc})$ for any of our data. We conclude that k_{12} values are not expected to be influenced significantly compared to experimental error by rather wide variations in the effective preexponential factor for the cross ET reaction and that the use of (2)–(5) for estimation of k_{11} is reasonable, even for compounds of very different structure.

The lower experimental k_{22} value for **Cp*CpFe**^{0/+} has caused us to revise our estimate of k_{22} for **Cp'₂Fe**^{0/+} to between those of **Cp*CpFe**^{0/+} and **Cp₂Fe**^{0/+}. Our new estimate for **Cp'₂Fe**^{0/+} is the same as the experimental value reported by Wahl and co-workers (although their number was measured at about 3 mM cation concentration in the absence of added electrolyte).¹⁷ Consequently, we have recalculated the previously reported³ selfexchange rate constants k_{11} (calc), see Table 6. It may be noted that k_{11} (NMR) is now rather close to k_{11} (calc) for the reactions of **Cp'₂Fe**⁺ and **Cp*CpFe**⁺ with **21**/ **u22**⁰, k_{11} (NMR)/k₁₁(calc) ratios of 1.4 and 2.0, respectively, but that the reactions involving $\mathbf{Cp}^*{}_{2}\mathbf{Fe}$ (entries 1 and 4) give substantially lower $k_{11}(\text{calc})$, ratios 9 and 16, respectively. We do not know why the use of $\mathbf{Cp}^*{}_{2}\mathbf{Fe}$ gives smaller $k_{11}(\text{calc})$ values than the other ferrocenes, but note that smaller k_{12} when $\mathbf{Cp}^*{}_{2}\mathbf{Fe}$ is employed than with $\mathbf{Cp}^*\mathbf{CpFe}$ is also observed for the other reaction studied, Table 2, reaction 5. It seems possible that the smaller k_{12} than expected might result from a steric effect: methyls block approach to the ferrocene iron on both sides of $\mathbf{Cp}^*{}_{2}\mathbf{Fe}$. However, if the methyl groups present steric hindrance to electron transfer, it is not apparent in the self-exchange rate constants because $\mathbf{Cp}^*{}_{2}\mathbf{Fe}$ has the largest k_{22} of the ferrocenes used.⁴

Relatively few hydrazines have isolable radical cations, making preparation of solutions with accurately known radical cation concentrations difficult, and because most hydrazine radical cations decompose in the presence of excess neutral compound, accurate measurement of k_{11} by dynamic NMR broadening is often impossible. Significant line broadening of the neutral species NMR by the radical cation is not observed when k_{11} is below about 300 $M^{-1}\ s^{-1}.$ We hoped to use cross rate constant measurements to estimate k_{11} for **22/RR**' hydrazines in this work. These compounds have θ near 120°, and as a result, k_{11} values which are too small to measure by NMR line broadening. The **22/tBuMe** and **22/tBuiPr** k_{11} (calc) values obtained using ferrocenes (Table 2, entries 1, 2, and 4, 5, respectively) show good internal agreement, especially when the smaller values produced using **Cp** $*_{2}$ **Fe**, noted above, are considered. The k_{11} (calc) values are also consistent with our inability to observe NMR line broadening for 22/tBuiPr^{0/+} and 22/Pr₂^{0/+} mixtures,¹⁸ an increase expected in λ_{in} for these $\theta \ {\sim} 120^\circ$ compounds compared to $\theta \sim 0$ hydrazines, and the increase in E_{op} for **2** compared to **1** (ΔG^{\dagger}_{11} (calc) for **22/tBuMe**^{0/+} is 2.0 and 1.7 kcal/mol higher than $\Delta G^{\ddagger}_{11}(\text{NMR})$ for **22/22**^{0/+} using the two ferrocenes, while $\Delta E_{op}/4$ for **2** and **1** is 1.4 kcal/ mol). Only a slightly smaller k_{11} (calc) value is obtained from the Cp*CpFe⁺,22/tBuiPr⁰ reaction than from the Cp*CpFe⁺,22/tBuMe⁰ reaction, indicating that the effect of additional steric hindrance at the nitrogens when the bulkier iPr group is present is small.

The Cp*CpFe⁺,22/iPr₂⁰ reaction (entry 6) is of particular interest because of the anomalous CV at a platinum electrode for $22/iPr_2^{0/+}$, where the oxidation and reduction peaks have a large separation.¹⁸ We argued that this behavior is caused by isopropyl group gearing effects which produce the radical cation in an unstable isopropyl group rotamer, which rapidly isomerizes to the more stable form on the CV time scale, so that the conformations of the neutral form which is oxidized and the radical cation which is reduced are different. A significant part of our argument was that the heterogeneous rate constant for electron exchange, $k_{\rm s}$, should be similar for compounds as similar as 22/RR'. Independent measurement of solution ET kinetics involving these compounds is important because a direct relationship is predicted between homogeneous and heterogeneous ET barriers.² The E° value for **22/iPr₂^{0/+}** is in question because of the large oxidation and reduction potential peak separation observed at a Pt electrode. The gearing hypothesis would make the midpoint of the oxidation and reduction CV curves different from E° , which is a relative measure of the free energy difference between relaxed

^{(15) (}a) McMannis, G. E.; Gochev, A.; Nielson, R. M.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 7733. (b) Although the E_{op} vs solvent polarity parameter γ plots for the radical cations of **Cp₂Fe** values linked by zero, one, and two acetylenes (**3** is linked by one acetylene) all extrapolate to similar values at $\gamma = 0$ (11.4, 10.1, and 10.2 kcal/mol respectively), Weaver and co-workers specifically reject assuming this is λ_{in} for **Cp₂Fe**^{0/+}, because they believe this number to be $\langle 2.0 \text{ kcal/}$ mol on theoretical grounds. Although we agree that the enthalpy contribution to λ_{in} should be small, it is not as obvious that λ_{in} is that small. Use of Weaver and co-worker's interpretation requires a λ_{out} of about 20 kcal/mol for **Cp₂Fe**^{0/+}, which which we believe is too large, considering the similar size of **Cp₂Fe**, sesquibicyclic hydrazines, and **TMPD**.

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Table 6. Bis-N,N'-bicyclic Hydrazine, Substituted Ferrocene Cross Rate Studies^a

reaction	$\Delta G^{\circ \ b}$	$10^{-5}k_{12}$, ^c M ⁻¹ s ⁻¹	$k_{11}(ext{calc})^d\ (\Delta G^{\ddagger}_{11})^e$	$k_{11}(NMR)/k_{11}(calc)^{f}$	Z_{12} effect ^g
1. Cp* ₂ Fe ⁺ ,22/u22 ⁰	-3.0	$23(\pm 2)$	1410 (<i>13.2</i>)	8.6 (1.3)	$\begin{array}{c} +0.19, \ -0.07 \\ +0.44, \ -0.16 \\ +0.03, \ -0.02 \\ +0.26, \ -0.10 \end{array}$
2. Cp' ₂ Fe ⁺ ,21/u22 ⁰	-5.1	$63(\pm 1.3)$	1630 (<i>13.1</i>)	1.2 (0.2)	
3. Cp*CpFe ⁺ ,21/u22 ⁰	-1.5	$3.5(\pm 0.5)$	1170 (<i>13.3</i>)	2.0 (0.4)	
4. 21/u22 ⁺ ,Cp* ₂ Fe ⁰	-3.9	$13.5(\pm 2.3)$	143 (<i>14.5</i>) ^h	16.0 (1.6) ^h	

^{*a*} Data of ref 3 reanalyzed using the data of Table 3. ^{*b*} kcal/mol. ^{*c*} At 25 °C in acetonitrile, $\mu = 0.1$ M. ^{*d*} In M⁻¹ s⁻¹ for the hydrazine, calculated from k_{12} and (4), using the data of Table 3 and $Z_{12} = 1 \times 10^{11}$ M⁻¹ s⁻¹. ^{*e*} In kcal/mol. ^{*f*} The number in parentheses is ΔG^{+}_{11} (calc) $- \Delta G^{+}_{11}$ (NMR), kcal/mol. ^{*g*} Fractional change in k_{11} (calc) using $Z_{12} = 1 \times 10^9$ M⁻¹ s⁻¹ (positive number) and $Z_{12} = 1 \times 10^{13}$ M⁻¹ s⁻¹ (negative number). ^{*b*} Calculated for the hydrazine.

cation and neutral. As shown in Table 2, if the true E° were the +0.08 V value which fit the time dependence of the CV experiments assuming gearing, k_{11} (calc) is similar for the three Cp*CpFe⁺,22/RR'⁰ reactions studied (Table 2, reactions 2, 4, 6: k_{11} (calc) for **22/iPr**₂ is 2.1 times that of 22/tBuMe and 3.3 times that of 22/tBuiPr), while if E° were the -0.11 value which also fit the CV experiments assuming "direct" oxidation with no gearing but a small k_s value for $22/iPr_2^{0/+}$, k_{11} (calc) for $22iPr_2$ would be 1/450th that of 22/tBuMe (Table 2, entry 6a). The latter interpretation appears unreasonable given the small k_{11} (calc) change between **22/tBuMe** and **22/ tBuiPr**; k_{11} for **22/RR'**^{0/+} is rather clearly not as sensitive to steric effects as the "direct oxidation" hypothesis would require. The difference between the pathways is clearer in the cross rate study than in the CV study because heterogeneous ET halves the barrier compared to homogeneous ET, making the difference between the two mechanistic interpretations of the CV data smaller.

We used the aromatic amine radical cation **TMPD**⁺ as the oxidant for 22/tBuMe⁰ in Table 2, reaction 3. This considerably extends both the range of structure of the oxidant and the range of k_{22} values examined. Grampp and Jaenicke determined $k_{22}(25 \text{ °C}, \text{ acetonitrile})$ for $\textbf{TMPD}^{0\!/\!+}$ to be $1.46\times10^9\,M^{-1}\,s^{-1}$ by fast exchange region ESR studies,¹⁹ which is 172 times faster than that for $Cp*CpFe^{0/+}$, and as noted above, Z_{22} appears to be significantly larger than for hydrazines and ferrocenes. The k_{11} (calc) ratio for **Cp*CpFe**⁺ vs **TMPD**⁺ oxidation of 22/tBuMe⁰ (Table 2, reactions 2 and 3) is 6.4, which is significantly poorer agreement than is seen using Cp'₂Fe and Cp*CpFe. We believe that seeing as small a deviation as observed from the behavior predicted by (4) for compounds with structures and electron transfer properties as different as TMPD and 22/tBuMe (k₁₁ ratio 4×10^7) is notable confirmation of its utility.

The $k_{11}(\text{calc})$ value from the **33N**)₂⁰, **Cp*****CpFe**⁺ reaction (990 M⁻¹ s⁻¹, Table 2, reaction 7) and the value of 2170 M⁻¹ s⁻¹ estimated from NMR line broadening experiments in CH₂Cl₂ give a $k_{11}(\text{NMR})/k_{11}(\text{calc})$ ratio of 2.2, corresponding to $\Delta\Delta G^{\dagger}_{11}(\text{calc})$ of 0.5 kcal/mol. This is not much higher than the $\Delta\Delta G^{\dagger}_{11}(\text{calc})$ values of 0.2 and 0.4 kcal/mol obtained for **21/u22** using **Cp'_2Fe^+** and **CpCp*Fe**⁺ (Table 6) and demonstrates that the special conformational restrictions of bis(N,N'-bicyclic) structures are not necessary for simple cross rate theory to provide useful estimates of k_{11} for hydrazines. Information on ET rate constants for the structurally similar but conformationally more complex bis-N,N-bicyclic $\theta = 180^{\circ}$ hydrazine **32N**)₂ which are independent of both the NMR and stopped-flow methods are available from the studies



of Cunkle.²⁰ The *syn* and *anti* NN bond rotational isomers of 32N₂⁺ have different oxidation potentials and

$$syn^{0} + anti^{+} \stackrel{k_{2}}{\underset{k_{-2}}{\longrightarrow}} syn^{+} + anti^{0}$$
 (8)

UV spectra, so their mixtures can be analyzed by both CV wave size and UV spectrophotometry. The secondorder rate constants for the exchange reaction (8), called k_2 and k_{-2} previously,²⁰ were found to affect both the CV curve for its oxidation (because they allow conversion of syn^+ to the more stable $anti^+$ by (8) so that the relative size of the oxidation waves of syn^+ and $anti^+$ depends upon scan rate) and the rate of isomerization of photochemically enriched *syn*⁺ mixtures to *anti*⁺ by addition of neutral compound. Best fit to the CV curves as a function of scan rate at 22 °C gave $k_2 = 260 \text{ M}^{-1} \text{ s}^{-1}$, k_{-2} = 4500 $M^{-1}\,s^{-1}\!,$ while that to the UV spectrophotometry isomerization data at 11 °C (where thermal conversion of syn^+ to $anti^+$ is negligible) gave $k_2 = 105 \text{ M}^{-1} \text{ s}^{-1}$, k_{-2} = 2000 M⁻¹ s⁻¹. Assuming that self-ET for $syn^{o/+}$ and *ant*^{**p**/+} have the same rate constant (which seems plausible to us), cross rate theory gives k_{11} (calc) for **32N**)₂ = 1110 M⁻¹ s⁻¹ at 22 °C ($\Delta G^{\ddagger}_{11} = 13.1_6$ kcal/mol) from the CV experiment, while it is 470 M⁻¹ s⁻¹ at 11 °C (ΔG^{\ddagger}_{11} = 13.1₃ kcal/mol) from the spectrophotometric experiment. Although measured by very different types of experiments, these k_{11} values are in rather good agreement both with each other and with the k_{11} value estimated by NMR line broadening and ferrocenium oxidation for 33N)2. Whether similar k_{11} values are expected for **32N**₂ and **33N**)₂, however, requires consideration of whether the internal geometry reorganization values (λ_{in}) are similar for these two compounds, especially since changing bicyclic ring size by one carbon leads to significant rate differences for sesquibicyclic compounds. Semiempirical calculations do not do a good enough job on these compounds to make consideration of calculated values of λ_{in} fruitful. Although **33N**)₂⁺ was the first hydrazine radical cation isolated,^{21a} the crystal structure originally obtained of its PF6⁻ salt^{21b} had undetected disorder which made the nitrogens come out planar and significantly underestimated the NN bond length. This result unfortunately clouded our understanding of the geometry change upon electron loss from hydrazines until a non-

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 Table 7.
 Comparison of Neutral and Radical Cation

 X-ray Geometries at Nitrogen

	•	-	
33N) ₂	neutral ^a	rad.cat. ^b	difference
<i>d</i> (NN), Å	1.505(3)	1.357(4)	-0.148 (9.8%)
α (CNN), deg	109.2, 108.1	118.7, 118.9	
α (CNC), deg	106.7(1)	111.4(2)	
α_{av} , c deg	108.0	116.3(3)	+8
$\theta,^d \deg$	180	180	
32N)2	е	e, f	
d(NN), Å	1.469(2)	1.323(4)	-0.146 (9.9%)
α (CNN), deg	111.1(1)	120.7(1)	
	111.2(1)	120.7(1)	
α (CNC), deg	101.3(1)	105.5(2)	
α_{av} , c deg	107.9(1)	115.6(2)	+7.7
$\theta,^d \deg$	180	180	

^{*a*} From ref 21. ^{*b*} From this work, for the TsO⁻ salt. Data quoted are for the nondisordered cation unit, **a**. ^{*c*} Average of the three bond angles at nitrogen. ^{*d*} Lone pair, lone pair twist angle. ^{*e*} From ref 20. Both oxidation states are in the conformation shown as the structure **32N**₂. ^{*f*} For the NO₃⁻·H₂O salt.



Figure 2. Thermal ellipsoid drawing of the nondisordered cation unit (a) of $33N)_2$.

disordered structure of 32N)₂⁺TsO⁻ was obtained, which demonstrated that its nitrogens are significantly pyramidal.²⁰ We have now obtained the structure of 33N)2⁺TsO⁻ in an effort to find out how much the geometry reorganizations upon electron removal differ for these two $\theta = 180^{\circ}$ hydrazines. **33N**)₂⁺TsO⁻ crystals have two different half-molecules of cation per anion; one cation (b) was badly disordered, fit in the solution of the structure with a complex model having three different nearly superimposed **b** units, and is not considered further. The other half-cation unit (a) was not disordered and provides usable geometric information (see Table 7 and Figure 2). As can be seen from Table 7, the NN bond length changes upon electron removal from 32N)₂ and 33N)₂ are within experimental error of being the same, and the changes in pyramidality are comparable, so that similar λ_{in} values and hence k_{11} values are expected.

Another reason for interest in using **33N**)₂ as a reactant in cross rate studies is that it provides the opportunity to study hydrazine–hydrazine ET reactions. **33N**)₂⁺ has $\lambda_{max} = 340$ nm,²² significantly longer wavelength absorption than most other hydrazine radical

cations,²³ which allowed measurement k_{12} for its oxidation by **21/21**⁺ by following the increase in absorption at 340 nm (Table 2, reaction 8). The k_{11} (calc) value for **33N**)₂ obtained from the hydrazine–hydrazine reaction is a factor of 9.1 smaller than that from the hydrazine–ferrocene reaction and 20-fold smaller than k_{11} (NMR).

Conclusions

Wide ranges in Z_{12} values are not expected to affect the k_{11} (calc) values obtained from cross rate theory, especially when K_{12} is small. All of the reactions examined for which both k_{ii} values are independently known from NMR studies have given smaller k_{12} (and hence smaller k_{11} (calc) values) than predicted by (4). The deviations observed for di- and pentamethylferrocenehydrazine reactions are rather small, and cross rate studies of these reactions produce k_{11} (calc) values when analyzed using (4) which are usefully close to the k_{11} (NMR) values. In this work the $\theta = 180^{\circ}$ hydrazine **33N)**₂ was found to give a k_{11} (calc) value comparably close to k_{11} (NMR) of the $\theta = 0^{\circ}$ hydrazines previously studied and also close to that estimated completely independently of both cross rate and NMR studies from isomerization of **32N**)₂⁺ isomers involving electron transfer. The **33N**)₂ and **32N**)₂ systems were shown to have similar λ values by X-ray crystallographic studies, establishing comparable geometry reorganizations upon electron loss. k_{11} values were estimated for the $\theta \sim 120^{\circ}$ hydrazines 22/ **RR**', which have k_{11} values too small to measure by any other method reported, and that obtained for 22/iPr2 was shown to be consistent with its unusual heterogeneous ET behavior.

The degree of structural similarity between the components of an ET reaction does not allow accurate prediction of how well (4) works. Anomalously low k_{11} (calc) values are produced when **Cp***₂**Fe** is employed as a reactant, for unknown reasons. The ratio of k_{11} (calc) values for 21/u22 using Cp*CpFe and Cp*2Fe as the other component is 8.2, which is larger than the 6.4 observed for reaction of 22/tBuMe with Cp*CpFe⁺ and **TMPD**⁺, despite the extreme difference in ET parameters for the latter three components. Conversely, the hydrazine-hydrazine reaction (Table 2, reaction 8) gives a significantly smaller k_{11} (calc) than does the hydrazinepentamethylferrocene case (reaction 7). More hydrazine-hydrazine and hydrazine-TMPD reactions will have to be studied before we can tell whether the behavior observed in these cases has any generality.

Experimental Section

NMR Line Broadening for Cp*CpFe^{0/+}. Air-free mixtures of neutral and cation in base-washed glassware proved stable enough to allow experiments in NMR tubes closed by septa. Aliquots of a solution of **Cp*CpFe**⁺**BF**₄⁻ in acetonitrile containing 0.09 M tetraethylammonium fluoroborate were added to a solution of **Cp*CpFe**⁰ in the same solvent, and NMR data were recorded on a Brucker 250 MHz spectrometer at 25 °C. The data are summarized in Table 1.

NMR Line Broadening for 33N)₂^{0/+}. A solution of **33N)**₂ (20.2 mg, 0.813 mM) in 400 μ L of CD₂Cl₂ (0.203₃ M) was treated with aliquots of a solution of **33N)**₂⁺**PF**₆^{-8b}(7.0 mg, 0.178 mmol) in 700 μ L of CD₂Cl₂ (0.0254 M). Spectra were recorded at 25.5 °C (determined using a methanol thermom-

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eter²²) on a Brucker 250 MHz spectrometer. Amounts of exchange line broadening were assigned by fitting the observed spectrum to that without cation after adding various amounts of broadening.^{3,10} Pairs listing the volume, μL , of cation solution added and in parentheses dynamic broadening (Hz): 15 (3.0), 30 (5.0), 50 (8.2), 80 (11.8), 120 (16.0), 160 (20.0), 210 (24.0). These data give $k_{ex} = 8450 \text{ M}^{-1} \text{ s}^{-1}$. A separate run at 25.5 °C using 0.180 neutral and 0.020 M cation solution gave the following: 15 (2.6), 30 (4.2), 50 (6.4), 80 (8.8), 120 (11.8), 160 (14.6), 210 (17.6), 260 (20.2); k_{ex} 8000 M⁻¹ s⁻¹. A variable temperature run with a solution 0.144 M in 33N)20 and 0.0066 M in **33N**)₂+**PF**₆⁻ gave temperature, °C, paramagnetic broadening (Hz) in parentheses, k_{ex} (M⁻¹ s⁻¹) values in brackets: 25.5 (18.5) [8900], 6.4₅ (9.0) [4300], 11.1 (10.7) [5100], 15.9 (12.4) [5900], 20.6 (15.2) [7300], 25.2 (18.2) [8700], 30.0 (22.0) [10500]; $k_{\text{ex}}(25 \text{ °C}) 8700$, $\Delta H^{\ddagger} = 5.8 \pm 0.4 \text{ kcal/mol}$, $\Delta S^{\ddagger} = -21$ \pm 1.3 cal deg⁻¹ mol⁻¹. We estimate approximately a 5% error in $k_{\rm ex}(25 \ ^{\circ}{\rm C})$

Stopped-Flow Kinetics. HPLC or spectrophotometric grade solvents (Aldrich or Baker) were used for all kinetic measurements. Tetrabutylammonium perchlorate (Baker or Kodak), used to maintain ionic strength, was recrystallized from 50/50 volume percent water/ethanol. Hydrazine solutions were prepared by weighing ca. 5 mg samples of the neutral hydrazine, or the tetrafluoroborate salt of its conjugate acid, to the nearest 0.05 mg using a Mettler microbalance. These samples were transferred to a Coy oxygen-free glovebox and dissolved in deoxygenated solvents to which sufficient standardized sodium hydroxide solution had been added to ensure complete conversion of the hydrazine to its neutral, conjugate base form. These solutions were typically 1 mM in NaOH and 0.5% in water. TMPD (Aldrich) was oxidized to TMPD⁺ with NOPF₆ and crystallized as its tetrafluoroborate salt. TMPD⁺ solutions were prepared by dissolving weighed samples of **TMPD**[**BF**₄] in acetonitrile containing tetrabutylammonium perchlorate. Ferrocenium hexafluorophosphate salts were prepared by literature methods from their ferrocenes.²⁵ 1,1-Dimethylferrocene (Alfa Inorganics) was recrystallized from ethanol, decamethylferrocene (Strem Chemical) was sublimed, and 1,2,3,4,5-pentamethylferrocene was prepared by a modification of the method of King²⁶ for the preparation of decamethylferrocene in which a mixture of equal amounts of LiC_5H_5 and $LiC_5(CH_3)_5$ was used in place of $LiC_5(CH_3)_5$. Ferrocenium hexafluorophosphate solutions were also prepared in an inert atmosphere and their concentrations determined by spectrophotometric analysis ($Cp_{2}Fe^{+}$, $\epsilon_{778} = 540$ M^{-1} cm⁻¹, $\hat{C}p'_{2}F\hat{e}^{+}$, $\epsilon_{650} = 332 M^{-1}$ cm⁻¹, $\hat{C}p^{*}CpFe^{+}$, $\epsilon_{740} =$ 360 $M^{-1}\ cm^{-1}$). All solutions were prepared immediately before use, and Cp*CpFe⁺ solutions were prepared under slightly acidic (ca. 1×10^{-5} M HCl) conditions because its neutral or basic acetonitrile solutions decompose slowly.

Reactant solutions were transferred under an inert atmosphere of nitrogen to a Durrum Model D-110 stopped-flow spectrophotometer interfaced to a 386 computer with On-Line-Instrument-Systems (OLIS) stopped-flow data acquisition and analysis software. Reactions between all hydrazines and ferrocenes were monitored by observing the absorbance decrease that accompanies reduction of the ferrocenium to the ferrocene between 280 and 320 nm; reaction between 21/21⁺ and 33N)₂ was monitored by observing the absorbance increase at 340 nm due to oxidation of the neutral hydrazine; the oxidation of 22/tBuMe by TMPD⁺ was monitored by observing the reduction of TMPD⁺ absorption at 614 nm. Typically three replicate measurements were made on each pair of reactant solutions, and the observed absorbance changes were fitted to the appropriate integrated rate equation using OLIS fitting routines. All reactions were studied under pseudo-firstorder concentration conditions with the neutral typically in 10-fold or greater stoichiometric excess of the radical cation. Each reaction was studied by varying the concentration of the neutral over as wide a range as possible, typically at least a factor of 10, and obtaining the second-order rate constant from a linear regression of a plot of the observed pseudo-first-order rate constants versus the neutral concentration. The reported uncertainties reflect the uncertainty of this fit.

Crystal Structure of 33N)₂+TsO⁻.²⁸ Neutral 33N)₂²¹ (0.303 g, 1.22 mmol) was suspended in acetonitrile and cooled to 0 °C, and a solution of silver tosylate (0.339 g, 1.21 mmol) in 20 mL of acetonitrile was added by syringe over 2 min. After stirring 45 min at 0 °C, filtration through Celite, and concentration to one-forth of the initial volume, 30 mL of ether was layered on top, and the product was collected after 1 day. Recrystallization from acetonitrile (~5 mL) followed by carefully layering 30 mL of ether on top in a Schlenck tube gave 0.420 g (82%) of 33N)₂+TsO⁻ as dark yellow crystals, dec 203-204 °C. The structure was determined at 113(2) K using a $0.4 \times 0.2 \times 0.1$ mm crystal, on a Siemens P3f diffractometer using graphite-monochromated Cu K α radiation ($\lambda = 1.541$ 78 Å), Wyckoff scan type, θ range 2.00 to 57.00°. The solution of the structure with direct methods used program SHELXS-86 and the refinement used SHELXL-93, which refines on F^2 values.²⁷ **33N**)₂⁺**TsO**⁻ ($C_{16}H_{28}N_2 + C_7H_7O_3S$, fw 419.59) crystals are monoclinic, space group $P2_1/c$, unit cell dimensions a = 9.4267(8), b = 12.5296(13), and c = 17.777(2) Å, $\beta = 90.104(9)^{\circ}$, volume 2099.7(4) Å³, Z = 4, density(calc) = 1.327 mg/m^3 , absorption coefficient = 1.327 mm⁻¹, F(000) = 908. Reflections collected = 3814, independent reflections 2822[R(int) = 0.0379], data = 2822, restraints = 0, parameters = 294, goodness-of-fit on $F^2 = 1.042$, final R indices R1/wR2 = 0.0483/0.1170, *R* indices (all data) R1/wR2 = 0.0639, 0.1277, extinction coefficient 0.0022(2), largest difference peak/hole = 0.337/-0.315 e A⁻³. The structure consists of two half-cations per anion. One of the half cations (a) is well behaved, but the other (b) is disordered. Three orientations of the disordered half were located, with occupancies 0.379(9), 0.334(9), and 0.287(7), and the disordered nitrogens and carbons were refined with isotropic thermal parameters. Nearly 300 geometry restraints were used in initial refinements to get the disordered groups to behave in a chemically reasonable manner. After the restrained refinements converged, the restraints were removed for the final refinement. We have little faith in the postions of the disordered site atoms and do not consider these data here. The methyl of the tosylate anion was also disordered and modeled with six 0.5 occupancy hydrogens.

Cyclic voltammetry experiments have been previously described. $^{\rm 18}$

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⁽²⁸⁾ The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.