

modeling of the form⁻ ligands with the (NHCHNH)⁻ systems is a satisfactory approximation.

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Supplementary Material Available: Full listings of bond distances, bond angles, and anisotropic displacement parameters for Mo₂(form)₄ and Mo₂(form)₄PF₆ (4 pages); listings of observed and calculated structure factors for the complexes (10 pages). Ordering information is given on any current masthead page.

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Electron Self-Exchange of Hexakis(2,6-diisopropylphenyl isocyanide)chromium(0,I) in Dichloromethane

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The rate of electron self-exchange between chromium hexakis(2,6-diisopropylphenyl isocyanide) (Cr(CNdipp)₆) and Cr(CNdipp)₆BF₄ has been measured as a function of reactant concentration and temperature, -89 to +22 °C, in CD₂Cl₂, by ¹H NMR line broadening. The temperature dependence yields an enthalpy of activation of 1.5 ± 0.2 kcal/mol and an entropy of activation of -15.6 ± 0.6 cal/(mol K). These extrapolate to a rate constant of 1.8 × 10⁸ M⁻¹ s⁻¹ at 25 °C, one of the highest electron self-exchange rate constants known.

Introduction

Outer-sphere electron-transfer reactions have been the subject of extensive experimental and theoretical study.¹⁻³ Electron self-exchange reactions have been of particular interest for theoretical treatment because they have an equilibrium constant which is by definition unity. As part of our ongoing effort to study nonaqueous electron transfer by transition-metal complexes, we have chosen the chromium(0,I) hexakis(2,6-diisopropyl phenyl isocyanide), Cr(CNdipp)₆^{0/+}, system for detailed study. Several features of this class of complexes make them appealing for study. They are substitution inert in three oxidation states, (Cr(0,I,II)), crystal structures are known for the four oxidation states of Cr(CNC₆H₅)₆^{0/+2+/3+}, a variety of symmetrical complexes can be synthesized that have adequate stability and solubility in nonaqueous solvents over a large temperature range, and the electron self-exchange process can be followed directly by ¹H NMR line broadening. The reactivity of the system studied here can be compared to that of the isoelectronic manganese(I,II) hexakis(isocyanide) electron self-exchange reactions studied previously.⁴⁻⁶ Furthermore, in the Cr(CNdipp)₆^{0/+} reaction there is no Coulombic repulsion between the reactants in forming the precursor complex. This work sets the reference point for further studies in which the Cr(CNdipp)₆^{+2/+} exchange is being studied along with that of other aryl isocyanide ligands.

Experimental Section

The ligand 2,6-diisopropylphenyl isocyanide (CNdipp) was prepared from the corresponding aniline (Aldrich) by utilizing dichlorocarbene generated by a phase-transfer method.⁷ The hexakis(2,6-diisopropylphenyl isocyanide)chromium(0) complex, Cr(CNdipp)₆, was synthesized from Cr₂(CH₃CO₂)₄(H₂O)₂ by a standard method⁸ and recrystallized from a dichloromethane-hexane mixture under nitrogen to give bright red crystals. Anal. Calcd: C, 79.70; H, 8.74; N, 7.15. Found: C, 79.53; H, 8.73; N, 7.10. Characteristic infrared bands are ν_{C≡N} = 1959 cm⁻¹ (broad) and a ring vibration at 1585 cm⁻¹. Hexakis(2,6-diisopropyl-

phenyl isocyanide)chromium(I) tetrafluoroborate (Cr(CNdipp)₆BF₄) was prepared according to the method of Treichel and Essenschacher⁹ except that AgBF₄ was used as the oxidant and the anion source. The complex was recrystallized from an acetone-hexane mixture to give bright yellow crystals. Anal. Calcd: C, 74.21; H, 8.14; N, 6.65; F, 6.02. Found: C, 73.12; H, 8.16; N, 6.49; F, 5.83. Characteristic infrared bands are ν_{C≡N} = 2060 (strong), 1432, and 1055 cm⁻¹. Tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) was prepared as previously described.¹⁰ Microanalysis was done by Galbraith Laboratories. Infrared spectra were collected by use of KBr pellets with a Perkin-Elmer 283-B instrument.

Methylene-d₂ chloride (MSD Isotopes, Merck) was degassed by three freeze-pump-thaw cycles and stored in an evacuated bulb, in the dark, until used. Samples were prepared by weighing the appropriate quantities of solid reagents into a 5-mm NMR tube (Wilmad Glass Co.) with a Teflon valve. The samples were placed on a vacuum line where methylene-d₂ chloride was vacuum transferred into the tube. The tubes were kept at -95 °C and in the dark until used. Concentrations were calculated from the weight of the solids and the weight of the solvent added to the NMR tube. The error in each weight is taken as 0.0001 g, giving a total concentration error of typically 3%.

Data were collected on a Nicolet NT200WB instrument operating at 200 MHz. Acquisition parameters were a 4.5-μs pulse width, a 500-μs postacquisition delay, a 4000-Hz sweep width, a 32K block size, and 256 pulses. To obtain accurate line widths, the field homogeneity was carefully adjusted for each spectrum on the basis of the amplitude of the ²H lock signal and the free-induction decay signal. All samples were spun. The accumulation time at each temperature was 18 min.

Temperature was controlled with the built-in gas-flow temperature controller. Dry nitrogen flows through a coil immersed in liquid nitrogen. The accuracy of the control was checked by use of the method of Van Geet¹¹ as modified by Raiford et al.,¹² corrected to 200 MHz, by adding a sealed capillary of methanol to the experimental sample. The accuracy is ±1 °C and the precision is ±0.5 °C. The temperature range used, -89 to +22 °C, was dictated by the freezing point of the solvent and the lack of line broadening observed at higher temperatures.

The stability of the solutions at room temperature was determined by measuring the line width and shift and checking for any new peaks at various time intervals. Solutions of the Cr(I) complex were stable for days. Solutions of the Cr(0) complex, ca. 3 mM, showed some initial oxidation (≤1%) but were then stable for 8 h, after which they slowly decomposed. However, 40 mM solutions showed no evidence of oxidation and were stable for 10 h.

The exact chemical shift and widths for the Cr(0) and Cr(I) complexes were determined from pure solutions of each complex at each

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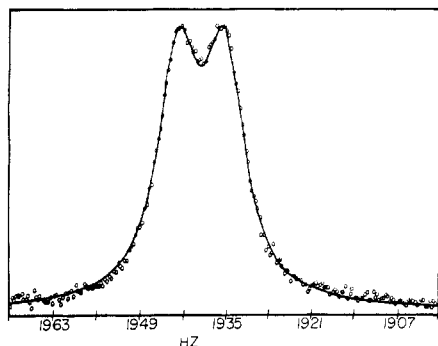


Figure 1. ^1H NMR spectrum of the meta proton of a $\text{Cr}(\text{CNDipp})_6^{0/+}$ mixture in CD_2Cl_2 at 1.8°C . The solid line is the theoretical fit, and the circles are the actual data points. $[\text{Cr}(\text{CNDipp})_6^{0/+}] = 2.2\text{ mM}$, $[\text{Cr}(\text{CNDipp})_6] = 9.1\text{ mM}$, and spectrometer frequency = 200 MHz .

temperature used. Line widths for the pure Cr(I) samples were obtained from a Lorentzian line fit by using the program LF on the Nicolet instrument. Typically 50–100 points were used in the fitting. These widths were found to be independent of concentration in the range used for the kinetics. Line widths for the meta and para protons of the pure Cr(0) complex at 40 mM , which display an eight-line second-order pattern, were obtained by use of the program NICSIMULATION on the Nicolet instrument. Errors in the ^1H line widths for Cr(I) and Cr(0) complexes are less than 5%.

Samples for kinetics measurements were prepared with 2–9 mM of the Cr(0) complex and 1–5 mM of the Cr(I) complex. The mole fraction of the Cr(0) complex varied from 0.30 to 0.90. It could be most accurately determined from the chemical shift of the meta proton resonance by using eq 1. Here χ_p and χ_d are the mole fraction of the paramagnetic

$$\nu_{dp} = \chi_p \nu_p + \chi_d \nu_d \quad (1)$$

(Cr(I)) and diamagnetic (Cr(0)) species, and ν is the resonance frequency (Hz) in the mixture (dp) or pure paramagnetic (p) or pure diamagnetic (d) solutions for the proton of interest. These results were found to be within 3% of values calculated from solute weights.

NMR Data Analysis. The rate analysis program used in this study calculates a theoretical spectrum by application of eq 2, superimposes it

$$v = \{[\text{Im}(G[(\chi_a - \chi_b)\delta + \omega][Q] + [k_a + k_b + \chi_a/T_{2b} + \chi_b/T_{2a}])[R]\gamma H M_0] / \{R^2 + Q^2\}\} \quad (2a)$$

$$Q = (k_a - k_b + 1/T_{2a} - 1/T_{2b})\delta + (k_a + k_b + 1/T_{2a} + 1/T_{2b})\omega \quad (2b)$$

$$R = \delta^2 - \omega^2 + k_a/T_{2b} + k_b/T_{2a} + 1/T_{2a}T_{2b} \quad (2c)$$

on the experimental spectrum, and calculates χ^2 , the sum of the squares of the differences between the calculated and observed intensities at each frequency. Equations 2 were derived from the Bloch equations¹³ for exchange between two sites with nonequal populations and widths including multiple pairs, assuming no saturation and steady-state conditions. Here v is proportional to the absorption intensity, T_{2a} and T_{2b} are the transverse relaxation times of sites a and b in the absence of exchange (half-width at half-maximum in Hz), δ is peak-to-peak splitting in Hz, k_a and k_b are pseudo-first-order rate constants for jumps from the a site to the b site and the b site to the a site, χ_a and χ_b are mole fractions of spins in the a site and the b site, ω is the deviation in Hz from the center frequency; γH is the applied rf field, M_0 is the equilibrium magnetization in the z direction. Depending on the width of the lines, 200–800 points were used in the fitting. This program was used to generate the best fits by using as input the chemical shifts and line widths of the pure Cr(0) and Cr(I) species, and then optimizing the pseudo-first-order rate constant k_a (the Cr(0) to Cr(I) jump rate) and the mole fraction χ_a . Assuming a simple bimolecular rate law, the self-exchange rate constant k is then given by $k_a/[\text{Cr(I)}]$. The line broadening observed for the meta ^1H doublet was used for the rate measurements because the difference in the chemical shift between the Cr(0) and Cr(I) species was large, the peaks were well separated from other proton resonances in the sample throughout the temperature range used, and the relative intensity was high. As a check, the rate constants were determined through analysis of the para ^1H resonance. In all cases, only one averaged signal was observed for each type of resonance in Cr(0)/Cr(I) mixtures. At room

Table I. Temperature Dependence of ^1H NMR Data for $\text{Cr}(\text{CNDipp})_6$,^a $\text{Cr}(\text{CNDipp})_6\text{BF}_4$, and CNDipp in CD_2Cl_2

temp, ^b °C	meta		para		methyl		methine	
	ν , ^c Hz	$\nu_{1/2}$, ^d Hz	ν , ^c Hz	$\nu_{1/2}$, ^d Hz	ν , ^c Hz	$\nu_{1/2}$, ^d Hz	ν , ^c Hz	$\nu_{1/2}$, ^d Hz
Cr(CNDipp)₆								
-89.3	1415 ^e	1.3 ^f	1400 ^e	1.3 ^f	214 d	1.7	705 h	3.2
-60.9	1415 ^e	1.3 ^f	1400 ^e	1.3 ^f	214 d	1.6	705 h	3.0
-29.4	1415 ^e	1.3 ^f	1400 ^e	1.3 ^f	214 d	1.6	705 h	3.0
2.2	1415 ^e	1.3 ^f	1400 ^e	1.3 ^f	214 d	1.6	705 h	3.0
22.2	1415 ^e	1.3 ^f	1400 ^e	1.3 ^f	214 d	1.5	705 h	3.0
Cr(CNDipp)₆BF₄								
-89.3	3232 d	6.0	-1282 b	17	146 b	12.7	1913 b	37
-60.4	2976 d	5.0	-868 t	6.0	155 b	10.5	1653 b	27
-30.3	2776 d	3.1	-555 t	4.1	163 b	10.0	1474 b	25
1.5	2615 d	2.7	-289 t	4.0	170 b	9.8	1333 b	23
20	2526 d	2.1	-157 t	3.5	177 b	9.7	1263 b	21 ^g
CNDipp								
20	1460 m		1460 m		253 d		680 h	

^a Abbreviations: CNDipp = 2,6-diisopropylphenyl isocyanide; d = doublet; t = triplet; m = multiplet; h = heptet; b = broad.

^b Temperature from a methanol standard; see text. ^c Referenced relative to internal TMS. ^d Full width at half-maximum height. ^e At 40 mM , $\text{Cr}(\text{CNDipp})_6$ spectra displayed second-order effects resulting in an eight-line pattern centered at 1407 Hz , see text. ^f Full width at half-maximum height, obtained by using 40 mM $\text{Cr}(\text{CNDipp})_6$ and fit as described in the text. ^g Coupling constants (Hz): $\text{Cr}(\text{CNDipp})_6$, $J_{\text{meta-para}} = 7.6$, $J_{\text{methyl-methine}} = 6.8$; $\text{Cr}(\text{CNDipp})_6(\text{BF}_4)$, $J_{\text{meta-para}} = 7.6$, $J_{\text{methyl-methine}} = 6.9$; CNDipp, $J_{\text{methyl-methine}} = 7.0$.

temperature the resonances were relatively sharp, but they broadened as the temperature was lowered. An example of an observed spectrum and the fit to it is given in Figure 1.

Results

All proton resonances were observed for the pure Cr(I) and Cr(0) species, and the shifts and widths of each resonance as a function of temperature are shown in Table I along with the naming scheme used for the protons. The resonance lines in the Cr(0) complex were split into multiplets due to ^1H - ^1H spin-spin coupling. A sharp doublet and heptet are observed for the methyl and methine protons. A complex second-order eight-line pattern was observed for the para and meta protons. None of the resonances of the Cr(0) complex showed any temperature dependence. Line widths for proton resonances in the Cr(0) complex were narrow, typically 1.3–3.3 Hz, and showed virtually no temperature dependence. A sharp doublet and a heptet are observed for the methyl and methine protons in the Cr(I) complex. A sharp doublet is observed for the meta proton and a triplet for the para proton.

The paramagnetic shifts, $\nu_{\text{Cr(I)}} - \nu_{\text{Cr(0)}}$, alternate in sign for the aromatic protons as previously seen⁶ for $\text{Mn}(\text{CNR})_6^{2+}$, but in the Cr system they also alternate sign in the alkyl groups on the ligand. The para proton resonance shifted the most, upfield about 1557 Hz . The meta and methine proton resonances shifted downfield by 1110 and 558 Hz , respectively. The magnitude of paramagnetic shift is about half as great for the alkyl resonances as for the aromatic resonances, for the same number of bonds from the metal center. The paramagnetic shift drops off dramatically in the alkyl groups; the methyl proton resonance only shifts about 37 Hz . The $\text{Cr}(\text{CNDipp})_6^{0/+}$ ^1H resonances shifted with temperature. In each case, decreasing temperature caused the paramagnetic shift to increase in magnitude.

The rate constants as a function of temperature and reactant concentration are displayed in Table II. Data as a function of added Bu_4NBF_4 are presented in Table III. Only a limited range of Bu_4NBF_4 concentrations was available due to dynamic range and solubility limitations at high salt concentration and signal-to-noise limitations at low reactant concentration.

The activation parameters for the $\text{Cr}(\text{CNDipp})_6^{0/+}$ were determined by a weighted least-squares fit of the variable temperature data to the Eyring equation, as shown in supplementary material. The enthalpy and entropy of activation were $1.5 \pm 0.2\text{ kcal/mol}$ and $-15.6 \pm 0.6\text{ cal/(K mol)}$, respectively.

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Table II. Temperature Dependence of the Electron Self-Exchange of Cr(CNdipp)₆^{0/+a} with No Added Salt in CD₂Cl₂

10 ³ [Cr(I)], ^b M	10 ³ [Cr(0)], M	T, ^c °C	10 ⁻⁷ k, ^d M ⁻¹ s ⁻¹
4.00	2.69	-89.3	1.9
2.16	2.96	-89.3	2.5
3.11	1.88	-89.3	2.5
0.67	5.55	-74.3	2.4
1.73	2.21	-74.0	5.3
0.69	5.53	-64.0	3.2
4.03	2.67	-60.7	4.1
4.69	3.00	-60.7	4.4
2.17	2.96	-60.7	5.5
4.77	2.92	-29.9	7.3
4.08	2.61	-29.9	7.6
1.54	4.58	-29.9	8.2
2.08	8.62	-29.9	8.0
2.22	2.91	-29.9	9.0
3.14	1.85	-29.9	10
2.21	8.49	-16.0	8.3
1.77	2.18	-15.0	14
1.79	2.15	0.0	19
2.15	8.55	1.8	9.9
4.14	2.55	1.8	13
2.24	2.88	1.8	14
1.60	4.52	1.8	14
3.16	1.82	1.8	18
2.25	8.44	22.0	13
4.27	2.42	22.0	14
1.60	4.52	22.0	16
2.31	2.82	22.0	16
1.86	2.08	22.0	23

^a Abbreviation: CNdipp: 2,6-diisopropylphenyl isocyanide.

^b Concentration determined from the weight of added solid and the weight of the added solvent. Error on each weight is taken as 0.0001 g giving a total concentration error of 3%. ^c Temperature from a methanol standard, see text. ^d Rate constants were calculated from the metal proton signal as discussed in text, error ±10%.

Table III. Ionic Strength Dependence for Electron Self-Exchange Rate Constants of Cr(CNdipp)₆(BF₄)_{0,1}^a at -60 °C^b in CD₂Cl₂

10 ³ [Cr(I)], ^c M	10 ³ [Cr(0)], M	[Bu ₄ NBF ₄], ^a M	10 ⁻⁷ k, ^d M ⁻¹ s ⁻¹
0.45	5.84	0.0	5.2
0.72	7.40	2.21	4.9
0.84	5.32	3.57	4.5
0.78	7.26	4.52	5.2
0.88	6.63	7.06	4.4
3.11	1.26	10.17	3.2
2.89	1.72	25.29	3.5

^a Abbreviations: CNdipp, 2,6-diisopropylphenyl isocyanide; Bu₄NBF₄, tetrabutylammonium tetrafluoroborate. ^b Temperature measured with a methanol standard with an accuracy of ±1 °C and a precision of ±0.5 °C; see text. ^c Concentration were determined from the weight of added solid and the weight of the added solvent. Error in each weight is taken as 0.0001 g, giving a total concentration error of typically 3%. ^d Rate constants were calculated from the meta proton as discussed in text with an error of ±10%.

Discussion

The electron self-exchange rate constant for Cr(CNdipp)₆^{0/+}, 1.8 × 10⁸ M⁻¹ s⁻¹ at 25 °C, is one of the highest such rate constants known, and the enthalpy of activation is especially low.^{1,14} However, on the basis of the Smoluchowski equation and Stokes' law (eq 3, where η is the viscosity of the solvent¹⁵), the measured

$$k_{\text{diff}} = 8RT/3\eta \quad (3)$$

rate constants are a factor of 50 below the diffusion limit at +25 °C and a factor of 90 below it at -90 °C. Because of this difference, no correction was made for diffusion. This equation can

also be used to predict ΔH* for diffusion based on the temperature dependence of η.¹⁶ Such an analysis yields a ΔH*_{diff} of 1.0 kcal/mol. For comparison, the same analysis for a reaction in water gives a value for ΔH*_{diff} of 4.0 kcal/mol. On the basis of this analysis, the reaction is not dominated by the formation of the precursor complex.

A Marcus theory analysis of the electron-transfer rate constant leads to the expectation that the rate constant will be high because both the inner-sphere and solvent reorganization energies are small. On the basis of the crystal structures of Cr(CNC₆H₅)₆ and Cr(CNC₆H₅)₆CF₃SO₃, the difference in Cr-C bond length between Cr(I) and Cr(0) complexes is only 0.037 Å.¹⁷ Assuming a force constant of 1.7 mdyne/Å,¹⁸ the inner-sphere reorganization energy is calculated to be only about 0.5 kcal/mol.¹⁵ By application of an elliptical transition state model¹⁹ and use of the dimensions previously estimated for hexakis(cyclohexyl isocyanide)manganese(I,II) or hexakis(benzyl isocyanide)manganese(I,II)⁵ and the solvent parameters of methylene chloride, the solvent reorganization energy can be estimated to be about 0.6 kcal/mol. This gives a total activation energy, primarily enthalpy, of 1.1 kcal/mol, which is still slightly less than the measured value but does not include any contributions from precursor complex formation. Since one of the reactants is neutral, there is no Coulombic work required to bring the reactants together. There may, however, be some precursor complex stabilization due to stacking interaction between phenyl rings. This would further lower the activation energy requirements compared with typical reactions between like charged species. These estimates of the activation energy terms are not particularly precise, but they do show that the low enthalpy of activation, 1.5 kcal/mol, is not inconsistent with expectations based on current theory.

These results can be compared to those of Nielson and Wherland³⁻⁶ on complexes of the type Mn(CNR)₆⁺²⁺, where R represents both aryl and alkyl groups. Their results are generally for conditions of higher ionic strength, for different solvents, and for a different charge type, but their rate constants for the aryl isocyanides are significantly lower. In CH₃CN and 0.1 M Bu₄NBF₄ at 26 °C where R is C₆H₁₁ and C₆H₄CH₃, the k_{ex} values, the electron self-exchange rate constants corrected for the electrostatic work required to form the precursor complex, are (1.3 ± 0.8) × 10⁶ M⁻¹ s⁻¹ and (6.1 ± 0.2e × 10⁷ M⁻¹ s⁻¹), respectively. The larger rate constant for the aryl complex compared to an alkyl isocyanide complex of comparable size has been attributed⁶ to the enhanced donor-acceptor orbital overlap provided by the π orbitals of the phenyl groups. The rate constant for the manganese(I,II) hexakis(cyclohexyl isocyanide) in CHCl₃ is significantly lower, 7 × 10⁴ M⁻¹ s⁻¹, than in CH₃CN. The origin of this difference may lie partially in the extensive ion pairing of the manganese complexes in CHCl₃, as well as in the lack of conjugation in the cyclohexyl group.

Three other systems have been studied that are not so similar chemically to Cr(CNdipp)₆^{0/+}, but which are isoelectronic and of the same charge type. Chan and Wahl²⁰ have studied the self-exchange reaction between a neutral and a singly charged complex, Ru(Me₂bpy)(hfac)₂^{0/+} where Me₂bpy is 4,4'-dimethyl-2,2'-bipyridyl and hfac is the hexafluoroacetylacetonate ion. In CD₂Cl₂ at 25 °C and similar total salt concentration the Ru(II,III) self-exchange rate constant is significantly lower, (3.5 ± 0.5) × 10⁷ M⁻¹ s⁻¹, than that of the Cr(0)/Cr(I) reaction. The second system is bis(η⁶-arene)chromium(0,I),²¹ where the arenes are C₆H₆ or C₆H₅CH₃; the self-exchange rate constants are 6.0 × 10⁷ M⁻¹ s⁻¹ and 3.3 × 10⁷ M⁻¹ s⁻¹, respectively at 22 °C in Me₂SO. Again these rate constants in a more polar solvent than CD₂Cl₂ are lower than those for the Cr(CNdipp)₆^{0/+} system. The

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third system, also studied by Wahl and co-workers²² is the electron self-exchange of ferrocene/ferrocenium and the decamethyl derivative. Both have been studied in dichloromethane. The rate constant at 25 °C and enthalpy of activation are $(4.3 \pm 0.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $1.7 \pm 1.3 \text{ kcal/mol}$ for the ferrocene/ferrocenium reaction and $(4.4 \pm 1.0) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $2.9 \pm 2.0 \text{ kcal/mol}$ for the decamethyl derivative. These are much smaller species than the isocyanide complexes, and thus are expected to have larger solvent reorganization barriers.¹ In a recent study by Weaver and co-workers,³ these reactions and their faster cobalt analogues have been investigated extensively and these authors have argued that solvent dynamics are influencing the rate constants.

Some of the variation in rate constant at each temperature is due to a variation in the total salt concentration. There was no added Bu_4NBF_4 in these experiments thus, the total salt concentration varied along with the Cr(I) complex concentration. When Bu_4NBF_4 was added, the dependence of the rate constant on salt concentration was not large or well-defined, so no attempt was made to adjust the rate constants for this effect. There is a detectable, slight trend toward a lower rate constant with in-

creasing electrolyte concentration. A similar trend is seen with the $\text{Mn}(\text{CNR})_6^{+/2+}$ system in chloroform where R is C_6H_{11} .⁴ In a system with a neutral and a singly charged complex, $\text{Co}(\text{dmg})_3(\text{BF}_4)_2(\text{BF}_4)$ (dmg is the doubly deprotonated dimethylglyoxime ligand) and ferrocene in ethylene dichloride,²³ a decrease in k_{12} with added electrolyte is seen and is most pronounced at total electrolyte concentrations below those attainable in the current experiments. This effect has been attributed to ion pairing, with the ion-paired cobalt clathrochleate reacting more slowly than the free cobalt complex.

This work is being extended through study of the Cr-(CNdipp)^{+/2+} self-exchange reaction and investigation of complexes of other aryl isocyanides.

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Supplementary Material Available: A figure showing the Eyring plot (1 page). Ordering information is given on any current masthead page.

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Notes

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Pressure and Temperature Effects on the Ruthenocene/Bromoruthenocene Electron Self-Exchange in CD_3CN

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The majority of temperature and pressure studies on electron self-exchange reactions have been carried out on outer-sphere reactions. These experimental and theoretical studies have led to considerable progress in this area. However, little work has been done on inner-sphere electron-transfer processes. The reason for this is the difficulty in finding well-behaved systems in terms of stability, solubility, and suitable time scales for kinetics measurements. Recently, Taube et al.¹ reported on an unusual two-electron, apparently inner-sphere, self-exchange reaction between ruthenocene and various haloruthenocenes in CD_3CN and CD_3NO_2 , which is the first known report on this reaction type. Classical inner-sphere reactions involve at least one substitution-labile complex. The activation process involves the expulsion of a ligand during precursor formation, in contrast to an outer-sphere process. In the title reaction both complexes are substitution inert and no initial release of ligand is required. Thus, a quite different behavior is expected. A comparison to the ferrocene-ferrocenium system, for which ΔV^\ddagger parameters have been obtained recently,² may prove to be interesting.

In the present paper we report on kinetics investigations at various temperatures and pressures up to 200 MPa for the ruthenocene-bromoruthenocene electron self-exchange in the solvent CD_3CN .

Experimental Section

Materials. Ruthenocene was obtained from Strem Chemical, Inc., and purified by one vacuum sublimation. $[\text{Ru}(\text{cp})_2\text{Br}]\text{PF}_6$ was prepared as described in the literature.³ The compound was recrystallized twice from hot acetonitrile/dichloromethane and precipitated with *n*-heptane within a period of 1 h. All solvents used for the purification of $\text{Ru}(\text{cp})_2\text{Br}^+$ were purchased from J. T. Baker Chemicals and purified by literature methods.⁴ The deuterated acetonitrile (99.7% D) was purchased from MSD Isotopes and was used as obtained. Solutions were prepared within a dry-argon-atmosphere glovebox.

¹H NMR Experiments. The temperature-dependence data were recorded by the use of a Nicolet NT200WB instrument. The acquisition parameters were a 4.5- μs pulse with a 500-ms postacquisition delay, a 2000-Hz sweep width, an 8K block size, and 256 pulses. The high-pressure measurements were performed by using a Bruker WH-90 spectrometer. For the variable-pressure experiments, a nonspinning sample tube, similar to one described in the literature,⁵ was used. It consisted of a 3.5-cm section taken from the bottom of a 5-mm NMR tube and extended with ca. 3 cm of heat-shrinkable Teflon tubing to transmit pressure. This was plugged with a tapered glass rod. A total of 200 scans (1.5- μs pulse, 4-s repetition rate, 4K data points, 1000-Hz sweep width) were used. The digitized data from both spectrometers were transferred to a personal computer based on an 8286 processor running Quick Basic and treated by a complete line-shape analysis to obtain the second-order electron self-exchange rate constants. The theoretical spectra were calculated by using a modified Bloch's equation for two exchanging sites.⁶ The nonlinear least-squares program adjusted the pseudo-first-order electron jump rate constant to minimize reduced χ^2 . With this procedure it was possible to determine the rate constant within $\pm 5\%$. NMR line widths and chemical shifts, relative to tetramethylsilane, for the pure compounds were measured at various temperatures and pressures. Both the temperature and the pressure dependence of their shifts and widths were negligible over the range studied. Mixtures of the two complexes were stable for several days.

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