

# Electron Self-Exchange of $\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4^{0/+}$ (X = Cl, Br) by $^1\text{H}$ NMR Line Broadening in Methylene Chloride

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The kinetics of the electron self-exchange reaction of the redox couple  $\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4/[\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  (X = Cl, Br) has been measured as a function of temperature and reactant concentration in methylene chloride by the  $^1\text{H}$  NMR line-broadening method. The self-exchange rate constants were obtained from broadening of the methyl singlet on the phosphine ligand in the fast-exchange limit. Extrapolated to 298 K from lower temperatures, they are  $2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for X = Cl and  $4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for X = Br. The corresponding activation parameters are  $\Delta H^\ddagger = 9.3 \pm 0.6 \text{ kcal/mol}$  and  $\Delta S^\ddagger = 10.9 \pm 2.2 \text{ cal/(mol K)}$  for X = Cl and  $\Delta H^\ddagger = 8.1 \pm 0.7 \text{ kcal/mol}$  and  $\Delta S^\ddagger = 8.1 \pm 2.9 \text{ cal/(mol K)}$  for X = Br. As expected, on the basis of previous cross-reaction studies, the reactivity of the dirhenium complexes is high. The previously calculated apparent self-exchange rate constant from cross-reaction studies for  $\text{Re}_2\text{Br}_4(\text{PMe}_2\text{Ph})_4^{0/+}$  was  $2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (298 K). The inner- and outer-sphere reorganization energies for  $\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$  are estimated to be 1.3 and 4.4 kcal/mol, respectively, indicating a large contribution to the rate constant from solvation. These results are consistent with studies of the heterogeneous electron transfer of these complexes and are compared to studies of other metal complexes in methylene chloride.

## Introduction

This paper presents the first directly measured electron self-exchange rate constant of a metal–metal multiple bonding containing redox couple,  $\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4/[\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  (X = Cl, Br) ( $\text{Re}_2^0/\text{Re}_2^+$ ), and is an extension of our previous studies involving cross reactions of mononuclear and dinuclear rhenium complexes with cobalt clathrochelates<sup>1,2</sup> as well as other electron-transfer reactions in nonaqueous solution.<sup>3</sup> Although complexes of this type have been an active area of research for many years,<sup>4</sup> very little attention has been given to their homogeneous electron-transfer reactivity. The series of complexes  $\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4^{0/+}$  is an attractive choice to study since they possess multiple stable oxidation states that are formed by reversible electron transfer and have been studied extensively with regard to electrochemical, structural, and spectroscopic properties. Additionally, because of the unusual electron configuration of the triply bonded neutral complex ( $\sigma^2\tau^4\delta^2\delta^*2$ ), the three oxidation states differ only in the occupation of the  $\delta^*$  orbital and, therefore, the Re–Re bond order.<sup>5</sup> The directly measured self-exchange rate constants for  $\text{Re}_2\text{Br}_4(\text{PMe}_2\text{Ph})_4^{0/+}$  determined in this study can be compared to estimates of the apparent self-exchange rate constants calculated from extensive characterization of a cross reaction between  $[\text{Co}(\text{nox})_3(\text{BButyl})_2]\text{BF}_4$  (nox = 1,2-cyclohexanedione dioximate) and the neutral Re complex.<sup>2</sup> Also, the experimentally determined free energy of activation for the self-exchange reaction of  $\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4^{0/+}$  can be compared to the value calculated from Marcus theory.<sup>6</sup>

## Experimental Section

**Material Preparation.** Starting materials for the preparation of the Re complexes were purchased from Strem Chemical Co. or Aldrich

Chemical Co. and used as received.  $\text{CD}_2\text{Cl}_2$  was purchased from Aldrich as 99.8% purity and used as received.  $\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4^7$  and  $[\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4]\text{PF}_6^5$  were prepared according to the literature and recrystallized several times from  $\text{CH}_2\text{Cl}_2/\text{diethyl ether}$  or  $\text{acetone}/\text{diethyl ether}$  until NMR shifts and widths were constant. Purity was also confirmed by cyclic voltammetry and UV–visible spectroscopy.

Standard 5 mm NMR tubes containing mixtures of the diamagnetic and paramagnetic complexes were prepared as follows: A solution of paramagnetic  $[\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  in  $\text{CD}_2\text{Cl}_2$  was prepared in a 2 mL volumetric flask. Varying amounts of this solution were then added by volume and mass into tubes containing weighed amounts of the neutral diamagnetic Re complex. Finally,  $\text{CD}_2\text{Cl}_2$  was added to the tube by volume and weight to obtain a final volume near 0.5 mL. The mole fraction of the paramagnetic complex calculated from the weighed solutions and that determined by the chemical shifts agreed to within about 10%. Solutions of the pure complexes and mixtures were stable over the period of the experiments (*ca.* 12 h), as indicated by the invariance in the NMR spectra.

**NMR Measurements.** Spectra were collected using a Bruker AMX300 spectrometer operating at 300.12 MHz taking 32–256 scans with a sweep width of 3000–7500 Hz. All spectra were recorded with a 1 s acquisition time, 200  $\mu\text{s}$  preacquisition delay, and 100  $\mu\text{s}$  pulse width. All peaks were referenced to residual  $\text{CDHCl}_2$  ( $\delta = 5.32 \text{ ppm}$ ). The temperature was controlled by using an  $\text{N}_2$  gas-flow unit consisting of a heating coil immersed in a Dewar of liquid  $\text{N}_2$  connected to the NMR probe. The temperature was calibrated by the method of Van Geet as reported by Raiford,<sup>8</sup> adjusted to 300 MHz using a sealed tube of acidified methanol as an external standard over the range of the measurements. Rate constants were obtained for as large a range of temperature and reactant concentration as experimentally possible.<sup>9</sup>

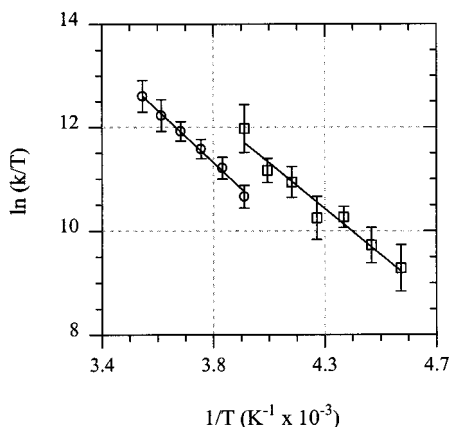
**Data Analysis.** Line widths and shifts for all samples were calculated by fitting the methyl peak of the phosphine ligand to a Lorentzian function using the WIN-NMR software package. In many cases, for both reactions the residual  $\text{H}_2\text{O}$  resonance overlapped with the methyl peak and the peaks were fit to a sum of two Lorentzian functions. Excellent fits were achieved for the X = Cl reaction, but for some of the X = Br spectra, the methyl peak was slightly asymmetric and deviated somewhat from the Lorentzian function. Line widths and shifts for the pure complexes *vs* temperature were fit to

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**Figure 1.** Eyring plot for the self-exchange reaction with X = Cl (○) and X = Br (□). The fit lines are the result of a linear least-squares analysis to all the points. The upper and lower bound for the error bars are the standard deviation of the 4–7 points at each temperature.

linear functions, and these fit lines were used in the calculation of the rate constants.

## Results and Discussion

The resonance due to the phosphine methyl group was fit and used for the calculation of all rate constants. No splitting was observed due to coupling with phosphorous. The widths of the methyl peak for the paramagnetic species increased with decreasing temperature from 450 to 800 Hz for X = Cl and 750 to 1000 Hz for X = Br. For the diamagnetic species, the width for X = Cl increased with decreasing temperature from 7 to 17 Hz while for X = Br the width decreased with decreasing temperature from 11 to 9 Hz. The shift for the diamagnetic species was invariant with temperature but varied for the paramagnetic complexes from  $-4.22$  to  $-5.12$  ppm with decreasing temperature for X = Cl and  $-5.28$  to  $-6.69$  ppm for X = Br.

Second-order rate constants were calculated using the following line-width equation, eq 1, assuming the fast-exchange limit,<sup>10</sup> where  $f_p$  = mole fraction of paramagnetic  $\text{Re}_2^+$ ,  $W_p$  = full width at half-height of pure  $\text{Re}_2^+$ ,  $W_{DP}$  = width of a mixture,  $W_D$  = width of diamagnetic  $\text{Re}_2^0$ ,  $C_{\text{tot}}$  = total  $[\text{Re}_2]$ , and  $\delta\nu$  = contact shift. The results of an Eyring analysis are shown in

$$k = \frac{f_p(1 - f_p)4\pi\delta\nu^2}{[W_{DP} - \{f_p W_p + (1 - f_p)W_D\}]C_{\text{tot}}} \quad (1)$$

Figure 1, where the fit lines are from the linear least-squares analysis of all the points for each reaction. The resulting activation parameters for X = Cl are  $\Delta H^\ddagger = 9.3 \pm 0.6$  kcal/mol and  $\Delta S^\ddagger = 10.9 \pm 2.2$  cal/(mol K) and for X = Br are  $\Delta H^\ddagger = 8.1 \pm 0.7$  kcal/mol and  $\Delta S^\ddagger = 8.1 \pm 2.9$  cal/(mol K). The rate constants, extrapolated to 298 K, are  $2.3 \times 10^8$  and  $4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for X = Cl and Br, respectively.

Within a certain range of temperatures for diamagnetic  $\text{Re}_2\text{X}_4(\text{PMe}_2\text{Ph})_4$  ( $<247$  K for X = Cl and 260–280 K for X

= Br), the peaks in the NMR spectrum for the diamagnetic complexes became several times more broad and asymmetric, precluding any determination of rate constants. Outside these temperature ranges, the width and shift were relatively constant and the methyl peak was well described by the Lorentzian function and varied with temperature as discussed above. It is reasonable, based on the observation of the crystal structures, that a fluxional process involving motion of the methyl groups or phenyl rings on the phosphine ligand could occur. This idea is further supported by the fact that the phenomenon appeared at a higher temperature for the more sterically congested X = Br structure. Outside of limiting the temperature range for the collection of spectra, this did not seem to affect the experimental results and was not investigated further.

Despite achieving good quality fits to the NMR spectra, the relatively large errors in the activation parameters are a result of the scatter in the individual rate constants and the limited range of temperatures that was available due to decreased solubility at lower temperatures, lack of exchange broadening at higher temperatures, and nonideal line shapes in certain temperature ranges, as discussed above. The scatter in the rate constants reflects some uncertainty in the line widths since many of the peaks that were fit were very broad due to the large range of  $f_p$  that was employed.

Although some cross-reaction studies involving metal complexes of this charge type in methylene chloride have demonstrated a dramatic decrease in rate with increased concentration of ionic species,<sup>2</sup> no effect was observed in this study within our experimental error. Addition of an electrolyte such as tetrabutylammonium tetrafluoroborate is precluded due to interference from the electrolyte protons. Additionally, second-order rate constants at each temperature were independent of total reactant concentration and  $f_p$ .

The directly measured self-exchange rate constant of  $\text{Re}_2\text{Br}_4(\text{PMe}_2\text{Ph})_4^{0/+}$  of  $4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  obtained here can be compared to the apparent self-exchange rate constant,  $2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , calculated from the cross reaction of the Re complex with the cobalt clathrochelate  $[\text{Co}(\text{nox})_3(\text{BButyl})_2]\text{BF}_4$  ( $\text{nox} = 1,2\text{-cylcohexanedione dioximate}$ ) reported previously<sup>2</sup> and the Marcus cross reaction relationship.<sup>11</sup> These two values are identical within experimental error.

Single-crystal structure and spectral data are available for both oxidation states of  $\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4^{0/+}$ , it is possible to estimate the free-energy barrier to electron transfer using Marcus theory<sup>6</sup> and, hence, the rate constant. The rate constant is expressed as the total barrier to reorganization,  $\Delta G^*$  multiplied by a pre-exponential factor, eq 2,<sup>12</sup> where  $\kappa$  = transmission coefficient (assumed to be 1) and  $Z$  = collision frequency ( $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ ).

$$k = \kappa Z e^{-(\Delta G_o^* + \Delta G_i^*)/RT} \quad (2)$$

$\Delta G_o^*$  is the outer-sphere (solvent) contributions to the total reorganization energy, and  $\Delta G_i^*$  is the inner-sphere (bond length changes) contribution. The outer-sphere contribution to the total reorganization,  $\Delta G_o^*$ , can be calculated using eq 3,<sup>12</sup> where  $e$  = electronic charge,  $R^*$  = distance from center to center of the reactants in the transition state,  $D_{op}$  = optical dielectric constant,

(9) Four to seven separate conditions of the reactant concentration and fraction of paramagnetic species were studied for six temperatures from 253 to 281 K for X = Cl and seven temperatures from 220 to 253 K for X = Br. The range of concentrations were 3.22–5.89 mM for  $\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ , 0.12–3.11 mM for  $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ , 5.3–6.3 mM for  $\text{Re}_2\text{Br}_4(\text{PMe}_2\text{Ph})_4$ , and 0.009–1.05 mM for  $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ . The mole fraction range of the paramagnetic species was from 0.03 to 0.50 for X = Cl and 0.01 to 0.16 for X = Br. For the spectra of the pure complexes, the concentration of each species was about 5.5 mM.

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(11) The apparent self-exchange parameters for  $[\text{Co}(\text{nox})_3(\text{BButyl})_2]\text{BF}_4$  were calculated from the cross reaction between the cobalt complex and decamethylferrocene<sup>1</sup> using the Marcus cross relation and self-exchange parameters for  $\text{FeCp}_2$ .<sup>10</sup> This resulted in a self-exchange rate constant of  $k_{11}(298 \text{ K}) = 1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  for the Co complex. This value was then used in the cross reaction of the cobalt complex with  $\text{Re}_2\text{Br}_4(\text{PMe}_2\text{Ph})_4$  ( $k_{12} = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ,  $K_{\text{eq}} = 1.4 \times 10^4$ ) to arrive at a  $k_{11}(298 \text{ K})$  of  $2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

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and  $D_s$  = static dielectric constant. The value for the inner-

$$\Delta G_o^* = \frac{e^2}{4R^*} \left( \frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) \quad (3)$$

sphere barrier was obtained from the literature as 1.3 kcal/mol.<sup>13</sup> To calculate the outer-sphere barrier,  $R^*$  was estimated as  $9 \pm 2$  Å, taken as a range around the radius that gives the same total volume as the complex with radii of about 9, 5, and 15 Å. The  $\Delta G_o^*$  value calculated in this way is 4.4–2.9 kcal/mol, which gives an overall free energy barrier of 5.7–4.2 kcal/mol. This compares reasonably to the measured value of 6.1 kcal/mol, especially the larger value that reflects the closer and more likely side-on approach of the reactants. The major contribution to the overall reorganization energy is from the outer-sphere term, which has been suggested for other complexes in methylene chloride<sup>14</sup> and for these complexes with regard to heterogeneous electron transfer.<sup>13</sup>

For the reaction studied here, the observed  $\Delta H^\ddagger$  is much greater than the inner-sphere reorganization energy alone, but this is not always the case.<sup>3</sup> Considering the nonspherical shape of the reactants and without resolving the influence of ion pairing, further discussion is not warranted.

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The rate constants for the self-exchange are large, which reflects the small change in structure accompanied by electron transfer to or from the  $\delta^*$  orbital.<sup>4,5</sup> The rate constants for the  $\text{Re}_2$  complexes are about 5–100-fold larger than those for metallocene self-exchange reactions under similar conditions,<sup>12,15</sup> with the possible exception of  $\text{NiCp}_2^{0/+}$ .<sup>16</sup> Presumably, for all these reactions  $\Delta G_o^* \gg \Delta G_i^*$  and solvent reorganization is the major contribution to the reaction barrier. For reactions in the same solvent, the rate constant should roughly correlate with the size of the reactants, and the data here are consistent with this idea. Additionally, the larger reactants in the  $\text{X} = \text{Br}$  reaction show slightly larger rate constants than that for  $\text{X} = \text{Cl}$ . Further discussion is limited by the small amount of data for similar reactions in methylene chloride.

**Supporting Information Available:** Spectra of pure  $\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$  and  $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  at 298 K, figures of the methyl region of the spectrum for various mixtures of the two complexes at 278 K along with plots of the width and shift of the methyl peak for the pure complexes *vs* temperature, and tables of the conditions of the concentration, temperature, width, and shift for all spectra (12 pages). Ordering information is given on any current masthead page.

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