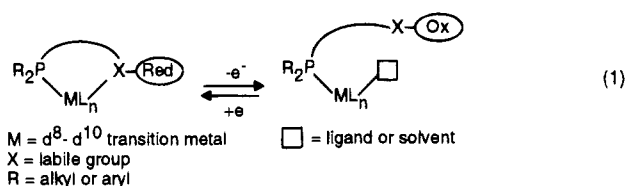*J. Am. Chem. Soc.* **1995**, *117*, 11379—11380

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Degenerate Exchange Reactions: A Novel and General Way To Determine the Thermodynamic Perturbations on Transition Metal Complexes That Result from Ligand Oxidation

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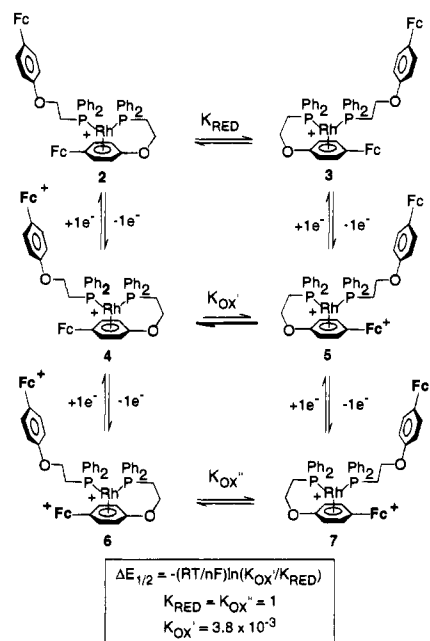2145 Sheridan Road, Evanston, Illinois 60208*

Redox-active ligands have been used to tune the electronic properties of transition metal centers through both inductive and electrostatic effects.[1a–d] Previously, we reported a new class of ligands termed redox-switchable hemilabile ligands (RHLs)[2] which give electrochemical control over both the electronic and steric environment of a Rh(I) transition metal center. These ligands have a substitutionally inert group and a substitutionally labile one. The binding affinity of the labile group for a transition metal can be controlled by adjusting the oxidation state of a redox group in close proximity to it, eq 1.

$$M = d^8\text{-}d^{10} \text{ transition metal} \qquad \square = \text{ligand or solvent}$$
$$X = \text{labile group}$$
$$R = \text{alkyl or aryl}$$

$$(1)$$

Others have used both metal-based and ligand-based strategies to control the binding affinity of a ligand for a metal ion. For example, Kochi has shown that for certain Mn complexes the binding properties of a redox-inactive ligand, such as diphos or CH$_3$CN, can be affected by either the oxidation or reduction of the metal center.[1e,f] In addition, Geiger has demostrated redox-induced hapticity changes of an arene ligand bound to Rh from η^6 to η^4 upon reduction of the Rh(III) center to Rh-(I).[1g] Finally, studies by Gokel and Beer have explored ferrocenyl-containing redox-switched receptors whose binding constants for metal cations are changed significantly upon oxidation of the ferrocenyl group, often resulting in the expulsion of the metal center.[1h,i] The RHL design, however, allows one to change the binding properties of a ligand without changing the oxidation state of the metal center nor removing the ligand completely from the metal coordination sphere.

A central issue regarding this new class of ligands is the extent to which a RHL can stabilize or destabilize a transition metal complex as a function of RHL oxidation state. Moreover, how does one experimentally quantify this effect? We now report the synthesis and characterization of a new type of RHL based on phosphine and arene moieties, (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$C$_6$H$_4$-OCH$_2$CH$_2$PPh$_2$) (**1**), and its complexation to Rh(I) to form an 18-electron, bis(phosphine), η^6-arene piano stool complex **2**, Scheme 1. Unlike previously reported RHL complexes, **2**

(1) (a) Lorkovic, I. M.; Duff, R. R., Jr.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 3617. (b) Lorkovic, I. M.; Wrighton, M. S.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6220. (c) Kotz, J. C.; Nivert, C. L. *J. Organomet. Chem.* **1973**, *52*, 387. (d) Kotz, J. C.; Nivert, C. L.; Lieber, J. M.; Reed, R. C. *J. Organomet. Chem.* **1975**, *91*, 87. (e) Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1988**, *27*, 2574. (f) Hershberger, J. W.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1982**, 212. (g) Bowyer, W. J.; Merkert, J. W.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191. (h) Medina, J. C.; Goodnow, T. T.; Rojas, M. T.; Atwood, J. L.; Lynn, B. C.; Kaifer, A. E.; Gokel, G. W. *J. Am. Chem. Soc.* **1992**, *114*, 10583. (i) Beer, P. D. *Chem. Soc. Rev.* **1989**, *18*, 409.

(2) (a) Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1624; *Angew. Chem.* **1995**, *107*, 1725. (b) Allgeier, A. M.; Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Organometallics* **1994**, *13*, 2928.

Scheme 1

$$\Delta E_{1/2} = \text{-}(RT/nF)\ln(K_{OX''}/K_{RED})$$
$$K_{RED} \approx K_{OX''} \approx 1$$
$$K_{OX'} = 3.8 \times 10^{-3}$$

undergoes an intramolecular, degenerate η^6-arene, free arene exchange reaction. Since the equilibrium constant for a degenerate process is by definition 1, the equilibrium constant for the nondegenerate exchange reaction involving the mixed-valent compounds **4** and **5** (the one-electron, ferrocenyl-based oxidation products of **2** and **3**) can be determined via cyclic voltammetry or differential pulse voltammetry experiments. This equilibrium constant can then be used to calculate, in terms of free energy, the magnitude of the thermodynamic perturbation of the metal complex that results from RHL oxidation. Significantly, *this novel approach can be extended to any RHL metal complex where a degenerate exchange process involving the redox-active labile portion of a ligand is possible.* Ultimately, by quantifying the free energy perturbations that occur in a number of systems, we will be able to (1) understand the factors that play a role in the utility of RHLs to selectively labilize coordination sites at a metal center (i.e., electrostatic and inductive effects) and (2) rationally design electroactive materials with electrochemically controllable reactivity (either stoichiometric or catalytic).

The synthesis of **2** begins by refluxing ferrocenylphenol[3] (1.8 mmol), KOH (1.8 mmol), ClCH$_2$CH$_2$Cl (90.0 mmol), and a catalytic amount of *n*-Bu$_4$NI in 25 mL of distilled H$_2$O for 15 h to form (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$C$_6$H$_4$OCH$_2$CH$_2$Cl) in 46% yield. The reaction of (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$C$_6$H$_4$OCH$_2$CH$_2$Cl) (1.1 mmol) with 1.05 equiv of KPPh$_2$ in 70 mL of THF at 0 °C yields ligand **1** in 80% yield. The Rh(I) piano stool complex **2** was synthesized by the reaction of [RhCl(COT)$_2$]$_2$[4] (COT = cyclooctene) with 2 equiv of AgBF$_4$ in CH$_2$Cl$_2$ and subsequent dilution and reaction of the resulting solution with 4 equiv of **1** at −78 °C. A pure sample of **2** was isolated as a red-orange powder after numerous recrystallizations using CH$_2$Cl$_2$/ether.[5]
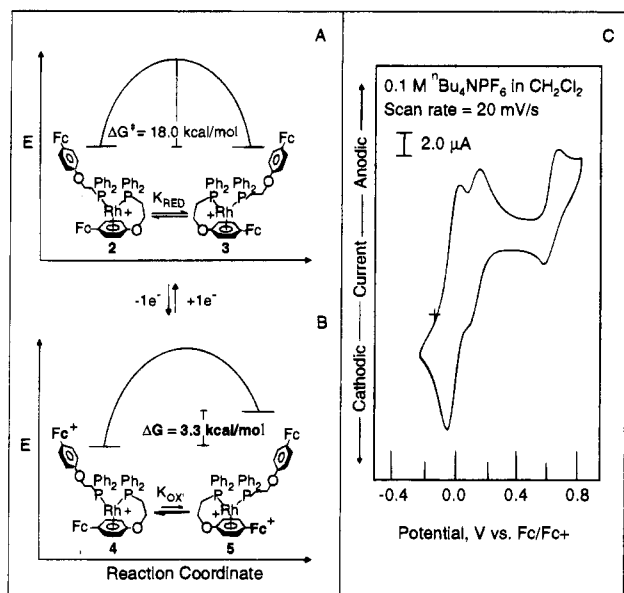
The spectroscopic data for **2** in CD$_2$Cl$_2$ is consistent with an analogous Rh(I) phosphinoalkyl arene piano stool complex which does not have a redox-active ferrocenyl group.[6] Compound **2** undergoes an intramolecular exchange reaction between the η^6-bound arene and the free arene at moderate temperatures (15—35 °C) in CD$_2$Cl$_2$, Figure 1a. Although too slow for detection by ^{1}H and ^{31}P NMR experiments, the dynamic chemical exchange of **2** can be detected by two-dimensional

(3) Weinmayr, V. *J. Am. Chem. Soc.* **1955**, *77*, 3012.
(4) Porri, L.; Lionetti, A.; Immirizi, A. *Chem. Commun.* **1965**, 356.

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Figure 1. Energy diagram depicting the exchange reaction between (A) degenerate compounds **2** and **3** and (B) nondegenerate mixed-valence isomers **4** and **5**. (C) Cyclic voltammetry of **2** at a glassy carbon electrode.

^{1}H NMR exchange (EXSY) spectroscopy ($k = 0.36$ s^{-1}, T = 20 °C).[7] The activation parameters of $\Delta G^{\ddagger} = 18.0$ kcal/mol, $\Delta H^{\ddagger} = 22.5$ kcal/mol, and $\Delta S^{\ddagger} = 15.3$ cal/(mol K) at 20 °C have been determined by collecting rate of exchange data as a function of temperature and modeling it according to the Eyring equation.[8]

The cyclic voltammetry of **2** exhibits three reversible waves, Figure 1c. The first wave is assigned to the Fe^{II}/Fe^{III} couple of the ferrocene next to the free arene since the $E_{1/2}$ value of -30 mV vs Fc/Fc$^+$ is identical, within experimental error, to that of the free ligand under similar conditions.[5] The second wave at $E_{1/2} = 113$ mV vs Fc/Fc$^+$ corresponds to the oxidation of the ferrocenyl group attached to the η^6-bound arene. This is confirmed by the simultaneous disappearance of the second wave and increase of the first upon addition of CH$_3$CN which displaces the η^6-arene moiety to form a mixture of *cis*- and *trans*-[Rh(η^1-(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$C$_6$H$_4$OCH$_2$CH$_2$PPh$_2$))$_2$(CH$_3$-CN)$_2$]BF$_4$. On the basis of previous work, the wave at $E_{1/2} = 630$ mV vs Fc/Fc$^+$ is consistent with a Rh^I/Rh^{II} oxidation for a rhodium center in a piano stool geometry.[2a,6]

(5) (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$C$_6$H$_4$OCH$_2$CH$_2$Cl): ^{1}H NMR (CDCl$_3$) δ 3.81 (t, 2H, CH$_2$Cl), 4.01 (s, 5H, η^5-C$_5$H$_5$), 4.22 (t, 2H, OCH$_2$), 4.25 (t, 2H, η^5-C$_5$H$_4$), 4.55 (t, 2H, η^5-C$_5$H$_4$), 6.84 (m, 2H, C$_6$H$_4$), 7.39 (m, 2H, C$_6$H$_4$); MS (EI) M$^+$ = 340 *m/z*. Anal. Calcd (found) for C$_{18}$H$_{17}$ClFeO: C, 63.47 (63.47); H, 5.03 (4.83). Compound **1**: ^{1}H NMR (CDCl$_3$) δ 2.62 (t, 2H, CH$_2$PPh$_2$), 4.00 (s, 5H, η^5-C$_5$H$_5$), 4.09 (q, 2H, CH$_2$O), 4.23 (t, 2H, η^5-C$_5$H$_4$), 4.53 (t, 2H, η^5-C$_5$H$_4$), 6.71 (m, 2H, C$_6$H$_4$) 7.34 (m, 4H, C$_6$H$_4$ and PPh$_2$), 7.48 (m, 8H, PPh$_2$); ^{31}P NMR (CDCl$_3$) δ -22.2 (s); MS (EI) M$^+$ = 409 *m/z*; $E_{1/2}$ = -27 mV vs Fc/Fc$^+$ (CD$_2$Cl$_2$/0.1 M ^{n}Bu$_4$NPF$_6$). Compound **2**: ^{1}H NMR (CD$_2$Cl$_2$) δ 1.71 (q, 2H, CH$_2$PPh$_2$ chelated), 2.06 (m, 2H, CH$_2$PPh$_2$ free), 3.80–4.02 (m, 7H, CH$_2$O chelated and η^5-C$_5$H$_5$ free), 4.06 (s, 5H, η^5-C$_5$H$_5$ chelated), 4.14 (m, 2H, CH$_2$O free), 4.20 (m, 2H, η^5-C$_5$H$_4$), 4.23 (m, 2H, η^5-C$_5$H$_4$), 4.34 (m, 2H, η^5-C$_5$H$_4$), 4.65 (m, 2H, η^5-C$_5$H$_4$), 6.66 (m, 2H, C$_6$H$_4$ free), 6.86 (m, 4H, η^6-C$_6$H$_4$), 7.12 (m, 8H, PPh$_2$), 7.25–7.48, (m, 14H, C$_6$H$_4$ free and PPh$_2$); ^{31}P NMR (CD$_2$Cl$_2$) δ 34.9 (dd, J_{Rh-P} = 204.4 Hz, J_{P-P} = 34.9 Hz), 31.3 (dd, J_{Rh-P} = 209.7 Hz, J_{P-P} = 39.5 Hz); FAB-HRMS [M$^+$] calcd 1083.1353, found 1083.1313 *m/z*.

(6) Singewald, E. T; Mirkin, C. A.; Levy, A. D.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2473; *Angew. Chem.* **1994**, *106*, 2524.

(7) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935.

(8) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

For systems that involve more than two oxidation states, ladder diagrams relating reactants and products through chemical and electron transfer steps are used in conjunction with $E_{1/2}$ values to obtain important thermodynamic information. In the case of **2**, a ladder scheme was constructed, and the mathematical relationship between equilibrium constants and $E_{1/2}$ values is shown in Scheme 1. Significantly, since both K_{red} and $K_{ox''}$ are for degenerate exchange reactions and therefore equal to 1, it is possible to calculate $K_{ox'}$ if the $E_{1/2}$ values for the electrochemical reactions going from **2** to **4** and **3** to **5** are measurable. Even though the $E_{1/2}$ for the latter process is not obtainable experimentally, the $E_{1/2}$ for the process going from **4** to **6** can be assumed to be the same as that for the process going from **3** to **5**. This is a reasonable assumption since the electronic communication between the ferrocenyl group attached to the free arene and the formally charged Rh(I) center is negligible. Indeed, the $E_{1/2}$ of the ferrocenyl group attached to the free arene in complex **2** is virtually identical to that of the uncomplexed ligand **1**. Furthermore, because of the distance between the two ferrocenyl groups in **2**, electronic communication between them is also assumed to be negligible (e.g., the electronic communication between the two ferrocenyl groups in 1,2-diferrocenyltetramethylethane cannot be measured by electrochemical methods; the ethoxy−Rh−arene spacer in **2** is much longer than a tetramethylethyl spacer).[9]

The two ferrocene waves in the cyclic voltammogram in Figure 1c were better resolved using differential pulse voltammetry, and the measured $\Delta E_{1/2}$ of 143 mV was confirmed and used to calculate a $K_{ox'}$ of 3.8×10^{-3} and a ΔG of 3.3 kcal/mol at 20 °C, Figure 1b. The free energy, ΔG, is the thermodynamic perturbation of the complex that results from oxidation of the RHL ligand. Therefore, we have successfully measured the change in free energy the metal complex experiences by replacing the ferrocenylarene ligand with an arene moiety containing a ferrocenium group from a single cyclic voltammogram by utilizing intramolecular degenerate exchange reactions. It is important to note that, for a nondegenerate process, one cannot obtain the absolute thermodynamic perturbation that results from ligand oxidation. Instead, the cyclic voltammetry for such a process merely yields a ratio of equilibrium constants for the reactions involving the oxidized and reduced species. By simply changing the oxidation state of the **1**, we have been able to destabilize the metal complex by a measurable quantity, 3.3 kcal/mol. The majority of this effect must be associated with a decrease in arene−Rh bond strength. Further investigation of the factors that play a role in this effect (e.g., inductive and electrostatic effects) and studies of how the reactivity of the metal center (i.e., the kinetics for the exchange process) are changed by altering the binding ability of the labile arene ligand through oxidation of the pendant ferrocene are underway.

(9) Morrison, W. H., Jr.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998.