Kinetic and Equilibrium Studies of Reactions of N-Heterocycles with Dimeric and Monomeric Oxorhenium(V) Complexes

James H. Espenson[a] and S. Masoud Nabavizadeh[a]**

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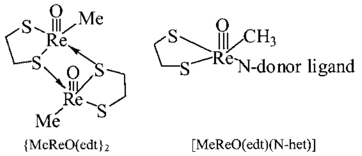
Equilibrium constants have been evaluated for the reaction $\{MeReO(edt)\}_2 + 2\ L \rightarrow 2\ MeReO(edt)L$, where edt is 1,2-ethanedithiolate and L is any of 13 N-donor heterocyclic ligands. The values of K range from $1.37(27)\times10^{-2}$ for pyrimidine to $1.95(6)\times10^{6}$ for imidazole at 25 °C in chloroform. A successful correlation of log$K$ with log (K_a) of HL^+ was realized except in the case of the 2-substituted ligands 2-picoline and quinoline, where steric effects make K smaller than expected from the proton basicity of L. The kinetics of the same reactions were studied; the rate law for the reaction in the forward direction is given by $-d[\{MeReO(edt)\}_2]/dt = \{k_a + k_b[L]\}[L] \times [\{MeReO(edt)\}_2]$. Except for 2-picoline and quinoline, the major pathway is provided by the term that shows the quadratic dependence on [L]. Values of log (k_b) also correlate with log K, and therefore necessarily with log (K_a).

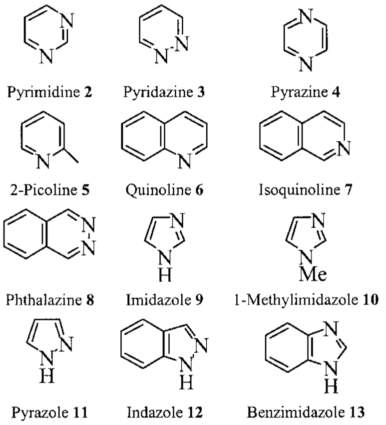
Introduction

We have studied the interaction of N-heterocycles with certain high-valent oxorhenium complexes. Our studies encompass the evaluation of equilibrium constants and rate constants for complexes of the core composition [MeRe(O)-(dithiolate)]. Actually, that core, with coordination number four, is never a detectable species, not even as a reaction intermediate. The stable species all show five-coordination as depicted in Scheme 1. The complexes of interest comprise dimers, {MeRe(O)(dithiolate)}$_2$,[1,2] and monomers, {MeRe(O)(dithiolate)L},[3,4] where L is pyridine (**1**) or any of the other N-heterocycles shown in Scheme 2.



Scheme 1. Structural formulas of methyl(oxo)rhenium(V) complexes

These complexes have soft metal centers; the chelating dithiolate is never displaced and (phosphane)rhenium complexes, although not a subject of this study, are more stable than those with hard bases such as pyridines.[4] We have explored correlations between the equilibrium and rate constants for experimental studies carried out in chloroform.



Scheme 2. Structural formulas of N-heterocycles

In addition, the equilibrium constants for the coordination of N-heterocycles (L) were correlated with the aqueous pK_a values of HL^+.

One finds in the literature values of stability constants for 1:1 complexes of several imidazoles with many divalent metal ions.[5–7] A correlation was identified between the equilibrium constants and pK_a values, except for benzimidazole (**13**), which could be attributed to the steric hindrance this particular ligand poses for coordination to a metal site. Complexes of the general formula $[M(CN)_5L]^{n-}$ offer the advantage that there is but a single open coordination site. Their coordination chemistry — including structure, spectroscopy and kinetics — have been reported for M = Fe, Ru, and Os.[8] Because of the particular steric effects of 2-substituted imidazole ligands, their interactions have been the subject of a separate investigation.[9] In addition, rate constants for the formation and dissociation of

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[a] Department of Chemistry, Iowa State University
Ames, IA 50011, USA
Fax: (internat.) + 1-515/294-5233
E-mail: espenson@iastate.edu

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$[Ru^{II}(CN)_5L]^{3-}$ ions (L = Py, ImH etc.) have been reported.[10]

Results

Equilibrium Studies

Values of the equilibrium and rate constants have been evaluated for the reactions represented by Equation (1).

$$\{MeReO(edt)\}_2 + 2L = 2\ MeReO(edt)L \qquad K = \frac{[MeReO(edt)L]^2}{[\{MeReO(edt)\}_2] \times [L]^2} \tag{1}$$

The absorbance of a solution at equilibrium is the sum of the larger component from the monomer and the smaller one from the dimer [Equation (2)].

$$Abs_{eq} = \varepsilon_D[\{MeReO(edt)\}_2]_{eq} + \varepsilon_{ML}[MeReO(edt)L]_{eq} = \varepsilon_D[D]_{eq} + \varepsilon_{ML}[ML]_{eq} \tag{2}$$

Mass balance for rhenium must also be maintained [Equation (3)].

$$[Re]_T = 2 \times [\{MeReO(edt)\}_2]_{eq} + [MeReO(edt)L]_{eq} = 2 \times [D]_{eq} + [ML]_{eq} \tag{3}$$

The simultaneous solution of these equations, which is presented in the Supporting Information (see footnote on page 1 of this article), affords an exact expression for the equilibrium absorbance in which the indicated equilibrium is sustained [Equation (4)], where [L] represents the equilibrium ligand concentration.[4]

$$Abs_{eq} = \varepsilon_D[D]_0 + \left(\varepsilon_{ML} - \frac{\varepsilon_D}{2}\right) \times \left[\frac{-K + \sqrt{K^2 + \frac{16K[D]_0}{[L]^2}}}{4/[L]^2}\right] \tag{4}$$

The values of K were determined for most of the ligands by fitting the equilibrium absorbances to Equation (4) by the method of nonlinear least squares. Such solutions contained L at a known concentration because $[L]_T \approx [L]_{eq} >> [Re]_T$. Figure 1 presents repetitive scan spectra showing the equilibrium progression from D to ML for L = pyridine (**1**), with increasing ligand concentration. Tight isosbestic points were found, showing that only the two rhenium species were present throughout the set of experiments. The inset of Figure 1 shows the fit to Equation (4) of the absorbance values at one wavelength, 364 nm. For L = pyridine, the value of K so determined is $1.04(16) \times 10^4$ L·mol^{-1} in chloroform at 25.0 °C.

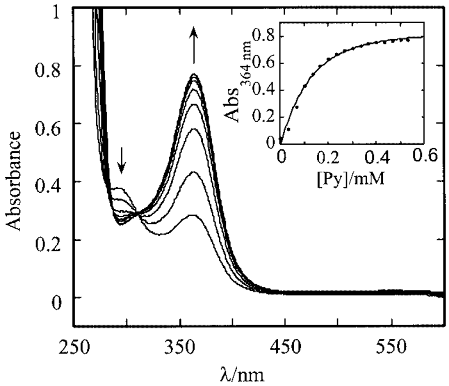


Figure 1. Absorbance changes as a solution of $[MeReO(edt)]_2$ was titrated with pyridine; isosbestic points were noted at 283 and 311 nm; the inset shows the analysis of the spectrophotometric data to evaluate the equilibrium constant according to Equation (4)

A more complex situation arises when K is quite large, as was the case for imidazole, 1-methylimidazole, and benzimidazole. Then, $[L]_T$ must not be >> $[Re]_T$ in order to realize the balance between D and ML needed for the evaluation of K. That is, $[L]_T \neq [L]_{eq}$. This situation requires an iterative solution. To do so, we made use of the program PSEQUAD.[11] The data for **11** were checked by both methods of calculation, and the agreement in the values of K was within the experimental error: 96±7 and 95±3 by nonlinear least-squares and by using the program PSEQUAD, respectively. The values of the equilibrium constants by the method most appropriate for the given complex are summarized in Table 1. The Supporting Information lists the initial concentration of $[MeReO(edt)]_2$ and the range of each ligand L used in the determination of the values of K.

Kinetic Studies

In many of the kinetics experiments, the reaction proceeded to completion. The gauge of this is whether the given [L] used for a particular experiment and the value of K inherent to it satisfied the condition $K[L]_{eq} >> 1$. In such cases, the data were analyzed by first-order kinetics. In terms of absorbance this is given by Equation (5) , where Abs_0 and Abs_∞ are the respective initial and final absorbance and k_{for} is the pseudo-first-order rate constant for the forward reaction.

$$Abs_t = Abs_\infty + (Abs_0 - Abs_\infty)\exp(-k_{for}t) \tag{5}$$

It was not always feasible to drive the reaction to completion at an attainable ligand concentration, particularly when K is small. Additionally, for ligands with intermediate values of K, some reactions proceeded to completion, for which Equation (5) applies, but other experiments at lower [L] did not. The data in these cases require treatment by a kinetic model that takes into account the opposing rates of the forward and reverse reactions, which appear as a rate *difference*. In general, the apparent rate *constants* for equilibration are the *sum* of those for the forward and reverse reactions. The data could thus be treated by Equation (6), in which the designations k^Ψ indicate rate constants that depend on [L].[4,15]

$$Abs_t = Abs_\infty + \frac{(1+q)\cdot[Abs_0 - Abs_\infty]\cdot e^{-k_e t}}{1 + q\cdot e^{-k_e t}}$$

$$\text{where } k_e = k^\Psi{}_{for} + 4k^\Psi{}_{rev}[M-L]_\infty,\ q = \frac{4k^\Psi{}_{rev}[ML]_\infty}{2k^\Psi{}_{for} + 4k^\Psi{}_{rev}[ML]_\infty} \text{ and } k^\Psi{}_{for} = k_e \times \frac{1-q}{1+q}. \tag{6}$$

Table 1. Kinetic and equilibrium data for monomerization with N-heterocycles at 25 °C in $CHCl_3$

Ligand	K_{eq}/L mol^{-1} [a]	k_a/L mol^{-1}s^{-1}	k_b/L^2 mol^{-2} s^{-2}	pK_a [b]	λ/nm[c]
1	$1.04(16)\times10^4$	–	$1.35(1)\times10^5$	5.23 (25 °C)	364
2	$1.37(27)\times10^{-2}$	$4.1(1)\times10^{-2}$	$9.9(8)\times10^{-1}$	1.23 (20 °C)	390
3	$1.12(10)\times10^1$	$5.2(10)\times10^{-1}$	$3.21(16)\times10^2$	2.24 (20 °C)	422
4	$7.71(77)\times10^{-2}$	$7.3(80)\times10^{-4}$	1.06(2)	0.65 (20 °C)	410
5	$5.7(6)\times10^{-2}$	$5.7(16)\times10^{-3}$	$4.9(9)\times10^{-2}$	5.97 (20 °C)	360
6	9×10^{-2}	$1.99(10)\times10^1$	–	4.90 (20 °C)	390
7	$3.00(34)\times10^2$	1.07(59)	$6.73(49)\times10^3$	5.40 (20 °C)	390
8	$1.04(10)\times10^2$	$5.3(9)\times10^{-1}$	$9.9(5)\times10^2$	3.47 (20 °C)	420
9	$1.95(6)\times10^6$	$3.49(18)\times10^4$	$6.98(2)\times10^6$	6.99 (25 °C)	365
10	$1.32(5)\times10^6$	$1.92(99)\times10^2$	$4.3(2)\times10^6$	6.95 (25 °C)	365
11	$9.58(72)\times10^1$	$8.44(82)\times10^1$	$4.34(1)\times10^4$	2.49 (25 °C)	362
12	3.35(13)	$1.96(42)\times10^1$	4.47(78)	1.25 (25 °C)	350
13	$5.0(3)\times10^4$	$5.6(64)\times10^{-1}$	$1.18(7)\times10^4$	5.53 (25 °C)	360

[a] K was evaluated by use of the nonlinear least-squares method except for ligands **9**, **10**, and **13** for which the program PSEQUAD was used. [b] K_a applies to the reaction $HL^+ = H^+ + L$ in aqueous solution at the specified temperature. Data are from refs.[12–14] [c] λ specifies the wavelength used for fitting data from equilibrium and kinetics studies.

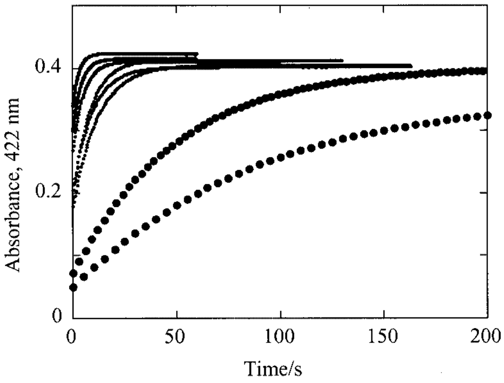


Figure 2. Absorbance-time curves for the reaction of $\{MeReO(edt)\}_2$ with pyridazine (**3**) in chloroform at 25.0 °C; data are shown for experiments with $[L]_0$ in the range 4.6–32.1 mM

The increase in absorbance for one typical family of kinetic experiments with L = pyridazine, **3**, is presented in Figure 2. The values of the pseudo-first-order rate constants for the reactions in the forward direction were determined as a function of [L]. The rate law in the general case contains two terms [Equation (7)], although in any specific case a contribution from one of the terms may be absent within the experimental error.

$$-\frac{d[\{MeReO(edt)\}_2]}{dt} = \{k_a[L] + k_b[L]^2\} \times [\{MeReO(edt)\}_2] \qquad (7)$$

Because this is the rate equation for the forward reaction, that for the reverse reaction follows from it [Equation (8)].

$$v_{rev} = \{k_{-a}[L]^{-1} + k_{-b}\}[MeReO(edt)L]^2 \qquad (8)$$

That is, one term of the reverse rate law shows inhibition by L. This feature is already incorporated in Equation (6). As a consequence of the equilibrium situation, we also have, by microscopic reversibility, the relation according to Equation (9).

$$K = \frac{k_a}{k_{-a}} = \frac{k_b}{k_{-b}} \qquad (9)$$

The weighted nonlinear least-squares fitting of the values of $k^\psi{}_{for}$ to Equation (7) is presented in Figure 3 for the same L. Values of k_a and k_b so obtained are also given in Table 1.

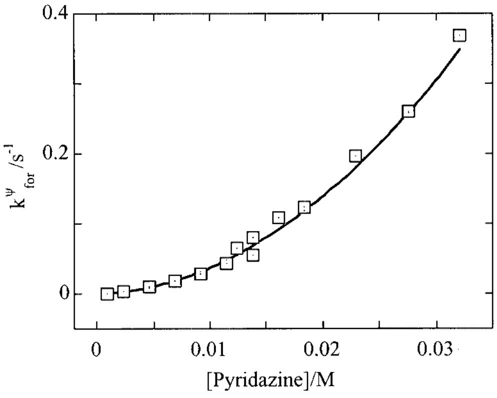


Figure 3. A representative set of kinetic data for L = pyridazine (**3**) depicting the weighted nonlinear least-squares fit to Equation (7), with linear and quadratic dependencies on [L]

Interpretation and Discussion

Correlation of Lewis and Brønsted Basicities

Figure 4 displays a plot of log$K$ for the reaction according to Equation (1) versus logK_a, for the acid ionization of HL^+.[12–14] Except for ligands **5** and **6**, a good correlation was found; the slope of the line in Figure 4 is −1.08±0.09. Exceptions for those two ligands are logical as well, in that they present a steric barrier for coordination to the rhenium center which is absent in the proton basicity. No deviation was found for benzimidazole (**13**), where a steric effect for the rhenium center might have been expected to exist. That steric effect would be smaller than the ones for **5** and **6**, because the bond angle between N, the ring C, and the C in the 2-position is 132° in **13** and 120° in **5** and **6**.

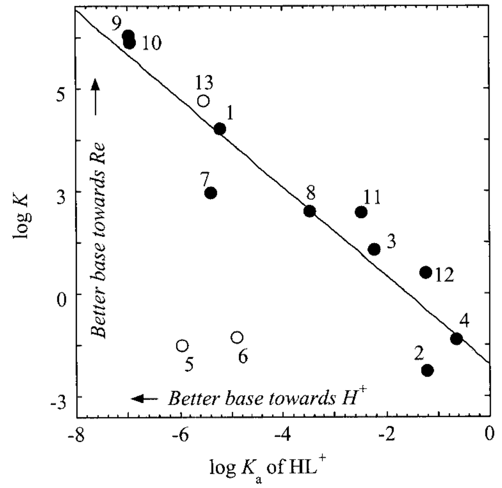


Figure 4. Plot showing a correlation between the equilibrium constants for monomerization of $[MeReO(edt)]_2$ by different ligands L in chloroform and the aqueous acid ionization constants of the same ligands, both on logarithmic scales; ligands **5**, **6**, and **13** were omitted from the linear fit

A study from the literature reported that **13** does indeed coordinate less strongly to Cu^{2+} and Zn^{2+} in aqueous solution than do the other members of a series of ligands all of which were imidazoles that lacked a substituent in the 2-position.[6] Aside from **13**, a good correlation between K and K_a exists except for N-heterocycles substituted in the 2-position.

One might raise an objection to the correlation presented in Figure 4, in that the y axis refers to data for a dirhenium species that incorporates two ligands in the equilibrium whereas the x axis refers to a single L. To address this point, we have used K values for two ligands to derive values of K' that refer to this reaction [Equation (10)].

$$MeReO(edt)L + L' = MeReO(edt)L' + L \qquad (10)$$

It is immaterial which L one chooses as the constant reference point because other ligands then constitute L′. We have arbitrarily selected MeIm as L. The value of K' for Equation (10) is given by Equation (11).

$$K' = \sqrt{\frac{K(L')}{K(MeIm)}} \qquad (11)$$

We then constructed a plot of logK' against log$K$ for proton transfer, as in the reaction $MeImH^+ + L' \rightleftarrows MeIm + HL'^+$. The result is shown in Figure 5. The correlation is fully acceptable, excluding the ligands with steric effects for coordination. The slope of the line in Figure 5, drawn without reference to such ligands is 0.54±0.07. That is, the equilibrium of ligand exchange at the rhenium center is less sensitive to the ligand than is ligand protonation.

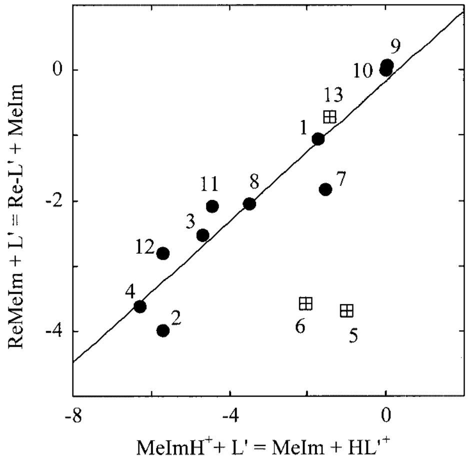


Figure 5. Correlation of the equilibrium constants for exchange of ligands at a rhenium center versus the equilibrium constants for proton exchange, both on logarithmic scales

Linear-Free Energy Correlations of Rate Constants

Two approaches will be explored. First, we ask whether there is a correlation between the equilibrium constants and the rate constants. Figure 6 depicts a plot of K versus k_b, which establishes that a reasonable correlation exists except for ligands **5** and **13**, where steric issues intrude most strongly. We take this to mean that the equilibrium and kinetic processes, both of which establish two new Re−N bonds, are governed by related factors. The same approach for log$K$ versus logk_a is less satisfactory, probably because a single Re−N bond is made in this kinetic step and because the k_a values are less precise, this being the minor kinetic pathway.

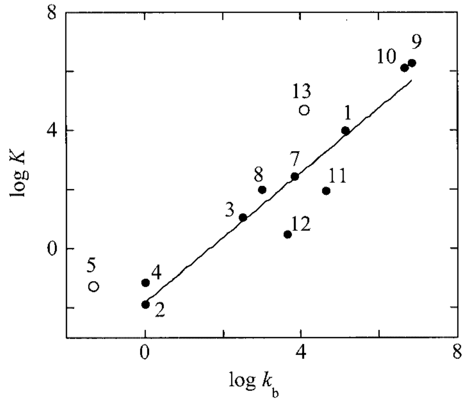
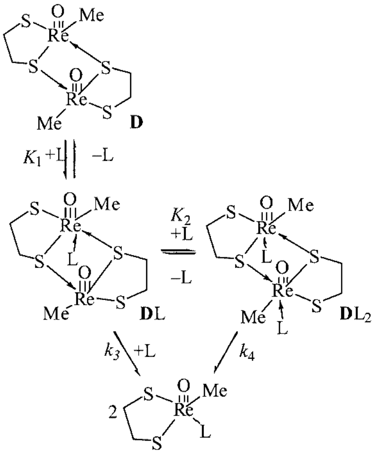


Figure 6. The linear-free energy correlation of equilibrium and kinetic data for the reaction according to Equation (1)

Mechanism

The kinetic data lead us to formulate the reaction steps that are consistent with the kinetic data by the model presented in Scheme 1. The ligands are shown as attacking the Re^V atom at the vacant coordination position trans to the Re≡O multiple bond. This is not generally a site for stable coordination, in that the binding constant for a sixth ligand is small. Indeed, in our studies such metastable transient species never accumulated to a concentration level at which they could be detected. Nonetheless, once one or two nucleophiles attack the Re^V atom, then further events rapidly ensue. In particular, either or both of the weaker S→Re coordinate bonds is released as the entering ligand L enters an equatorial position on the monomeric reaction product. This equation follows from Scheme 1 [Equation (12)].

$$-\frac{d[D]}{dt} = \frac{1}{2}\frac{d[ML]}{dt} = \left(\frac{k_3K_1[L] + k_4K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2}\right)[D] \qquad (12)$$



Scheme 1. Kinetic scheme for monomer formation

Equation (7) is a limiting form of Equation (12), when $K_1[L] + K_1K_2[L]^2 << 1$, according to which $k_a = k_3K_1$ and $k_b = k_4K_1K_2$. Further resolution is not possible; the values of the equilibrium constants K_1 and K_2 are too small to allow **D**L and **D**L_2 to attain concentrations that are significant compared to that of **D**. This, of course, is the basis for the inequality given.

In our original study of the monomerization of $[MeReO(dithiolate)]_2$ with a series of phosphane and pyridine ligands,[4] a rate law with linear and quadratic dependencies on [L] was found, just as in Equation (7) [see also Equation (12)]. We formulate the quadratic pathway in terms of an attack of two ligands, one on each rhenium atom. Following that, monomerization occurs as the coordinate S→Re bonds within the dimer are broken. The transition state for this pathway can be drawn as in the right-hand pathway of Scheme 1. On the other hand, our original assignment for the k_a pathway no longer seems credible. We no longer claim that the k_a pathway represents a scheme that generates equal amounts of the product MeReO(edt)L and an intermediate four-coordinate intermediate MeReO(edt). In none of our studies on catalysis or coordination chemistry has such a species been detected. Rather, we postulate that one of the S→Re coordinate bonds in the dimer has been broken, generating a half-opened dirhenium intermediate that reacts subsequently but rapidly with a second L. This idea is formulated in the pathway that is shown on the left-hand side of Scheme 1. The further advantage of the revised proposal is that it maintains a coordination number of five about both oxorhenium(V) atoms, which is the preferred geometry.

Conclusion

Equilibrium constants for reactions in which a series of N-heterocyclic ligands react with a dimeric oxorhenium(V) complex, leading to its monomerization, have been evaluated. Rate constants for the same reactions have been determined. The values of *K* and *k* correlate with one another and with the proton basicity of the ligands.

Experimental Section

The compound methyltrioxorhenium ($MeReO_3$ or MTO) was synthesized according to a literature procedure.[16] It was then used to prepare the rhenium complex that is the focus of this study, the dimer $[MeReO(edt)]_2$, which was known from previous research.[17] A new and more efficient synthetic procedure has since been devised.[18] MTO (1.0 mmol) was added to a stirred solution of PPh_3 (1.0 mmol) in toluene (10 mL), containing a catalytic amount of diphenylacetylene. After 5 min, 1,2-ethanedithiol (1.0 mmol) was added. The resulting mixture was stirred at room temperature for 6 h and layered with hexane (20 mL). After 2 d, a brown-black solid deposited, which was collected by washing with hexane. Further material could be obtained by concentrating the mother liquor and recrystallizing the residue from CH_2Cl_2/hexanes.The isolated compound was characterized by comparing its NMR and UV/Vis spectra with those of the previously prepared material, which had also been characterized by X-ray diffraction.[17] Other reagents, including the N-heterocyclic ligands, were purchased from commercial sources (Aldrich, except for pyridine, Fisher Scientific). They were used without further purification. Certain ligands that might have been included in the study were not reactive or were insufficiently soluble (2,5-dimethylpyrrole and 1,2,4-triazolo[1,5-*a*]pyrimidine). Chloroform was used as the solvent in these studies and the data were obtained at 25 °C. Spectrophotometric methods were used throughout. For equilibrium studies of the reaction according to Equation (1) and for the slower kinetics experiments, a Shimadzu Model 3101 instrument was used. Faster reactions were studied by stopped-flow spectrophotometry with an OLIS apparatus equipped with a rapid scanning monochromator. Absorbance-time data were extracted at single wavelengths for further analysis. Reagent-grade chloroform was used as the solvent for these studies. The ethanol stabilizer that accompanies the commercial solvent has no effect. Supporting Information (see footnote on the first page of this article) for this article comprises the derivation of Equation (4) and the list of concentrations used in the evaluation of *K*.

Acknowledgments

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[1] J. Jacob, I. A. Guzei, J. H. Espenson, *Inorg. Chem.* **1999**, *38*, 1040−1041.

[2] G. Lente, X. Shan, I. A. Guzei, J. H. Espenson, *Inorg. Chem.* **2000**, *39*, 3572−3576.

[3] J. Jacob, G. Lente, I. A. Guzei, J. H. Espenson, *Inorg. Chem.* **1999**, *38*, 3762−3763.

[4] G. Lente, I. A. Guzei, J. H. Espenson, *Inorg. Chem.* **2000**, *39*, 1311−1319.

[5] L. E. Kapinos, B. Song, H. Sigel, *Chem. Eur. J.* **1999**, *5*, 1794−1802.

[6] L. E. Kapinos, B. Song, H. Sigel, *Inorg. Chim. Acta* **1998**, *280*, 50−56.

[7] H. Sigel, A. Saha, N. Saha, P. Carloni, L. E. Kapinos, R. Griesser, *J. Inorg. Biochem.* **2000**, *78*, 129−137.

[8] L. M. Baraldo, P. Forlano, A. R. Parise, L. D. Slep, J. A. Olabe, *Coord. Chem. Rev.* **2001**, *219−221*, 881−921.

[9] E. M. Sabo, R. E. Shepherd, M. S. Rau, M. G. Elliott, *Inorg. Chem.* **1987**, *26*, 2897−907.

[10] J. M. A. Hoddenbagh, D. H. Macartney, *Inorg. Chem.* **1986**, *25*, 380−383.

[11] L. Zékány, I. Nagypál, in: *Computational methods for the determination of formation constants* (Ed.: D. Leggett), Plenum Press, New York, **1985**.

[12] R. M. Smith, A. E. Martell, *Critical Stability Constants*, Plenum Press, New York, **1974**.

[13] D. R. Lide, Editor-in-Chief, *CRC Handbook of Chemistry and Physics*, 81st ed., CRC Press, Boca Raton, **2000**.

[14] J. Catalan, R. M. Claramunt, J. Elguero, J. Laynez, M. Menendez, F. Anvia, J. H. Quian, M. Taagepera, R. W. Taft, *J. Am. Chem. Soc.* **1988**, *110*, 4105−11.

[15] E. L. King, *Int. J. Chem. Kinet.* **1982**, *14*, 1285.

[16] W. A. Herrmann, R. M. Kratzer, R. W. Fischer, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2652−2654.

[17] J. H. Espenson, X. Shan, Y. Wang, R. Huang, D. W. Lahti, J. Dixon, G. Lente, A. Ellern, I. A. Guzei, *Inorg. Chem.* **2002**, *41*, 2583−2591.

[18] X. Shan, J. H. Espenson, unpublished results.

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