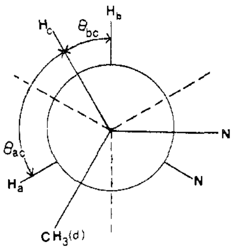
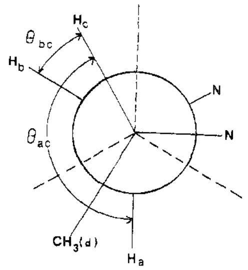
and low-field signals in the five-line multiplet due to $H_c$ is 26.9 Hz. This value should be equal to $3J_{CH_3(d)-H_c} + J_{bc}$, if the spin–spin coupling scheme described above is correct. The observed value for this difference and the value of $J_{bc}$ give a value for $J_{CH_3(d)-H_c}$ of 7.0 Hz, which is the same as the observed coupling constant for the $CH_3$(d) doublet at 1.31 ppm.

**Conformation of the Five-Membered Chelate Rings.** There are two possible conformers for the 3,10-meso complex: those with $CH_3$(d) equatorial and axial, respectively, to the five-membered chelate ring. Since one of the nitrogen atoms is an imine nitrogen, the five-membered chelate rings of this complex are expected to have distorted gauche forms. The vicinal spin–spin coupling for this three-spin system differs for the two conformers. The $CH_3$(d) axial conformer would provide two distinct *distorted gauche* couplings, whereas the $CH_3$(d) equatorial conformer would provide one *distorted gauche* and one *distorted trans* coupling. Coupling constants have been reported for other metal complexes that have structures similar to structural components of the present complexes.[12-14] The reported values for gauche and trans coupling (dihedral angles $\theta$'s are close to 60 and 180°, respectively) are approximately 3.8–4.4 and 10.0–12.4 Hz, respectively.

The observed values for $J_{bc}$ and $J_{ac}$ indicate that the five-membered rings are substantially distorted. The value of $J_{bc}$ is close to, but a little larger than, those commonly observed for gauche couplings. This complex can have either of two conformational forms: one (structure III) involves an axial methyl group and the other (structure IV) an equatorial methyl group. It must be emphasized that the very small value of $J_{ac}$ suggests that $\theta_{ac}$ is a good bit larger than 60° but substantially less than 120° (around 90° if the original Karplus equation[15] is assumed with $J_{ac} = 0$). These facts lead uniquely to structure III. It is also concluded that the $H_a$ (2.24 ppm) and $H_b$ (2.86 ppm) protons are the equatorial and axial methylene protons, respectively. The difference in the chemical shifts between these two protons may be explained in terms of the magnetic anisotropy of square-planar $d^8$ transition metal ions.[5] It is also worth mentioning that detailed stereochemical analysis of this structure reveals that the absolute configuration of adjacent asymmetric nitrogen and carbon atoms must be *R* and *S* or *vice versa.*



III



IV

A similar analysis based on spin-decoupling experiments has been applied to the three-spin system of the deuterated 3*R*,10*R* complex (Table II), leading to the conclusion that the five-membered chelate ring has a distorted δ gauche form (IUPAC, 1966) with the $CH_3$(d) group axial. This accords well with the result of the preliminary X-ray work on this isomer by Curtis, *et al.*[2b] The observed coupling constants for the three-spin system of the 3*R*,10*R* isomer are $J_{ab} = 11.5$, $J_{bc} = 5.5$, and $J_{ac} \simeq 0$ Hz. The similarity of these values to those of the 3,10-meso isomer suggests that the conformations of the two sets of five-membered chelate rings are quite similar. The absolute configuration of the secondary amine nitrogen atoms is *S*.

## Experimental Section

**Materials.** (3*R*,10*R*)-3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) perchlorate was prepared by the template reaction,[2a] whereas the 3,10-meso complex perchlorate was synthesized by the direct reaction of the free-ligand salt with the nickel(II) salt.[2b] The chlorides were prepared from the perchlorates by ion exchange (Dowex 1X8).

**Deuteration Experiments.** Deuteration was accomplished by dissolving the chloride salts in $D_2O$ at pH 10–11 (anhydrous $Na_2CO_3$ or NaOD). The secondary amine protons, the imine methyl protons, and the methylene protons of six-membered rings exchanged within 24 hr at room temperature, as shown by the intensities of their pmr signals.

**Measurements.** All pmr spectra were obtained in $D_2O$ solutions using a JEOL pmr spectrometer, Model JNM-MH-100. Chemical shifts were measured relative to sodium 2,2-dimethyl-2-silapentane-5-sulfonate internal standard.

**Acknowledgment.** We wish to thank the National Science Foundation for financial support of this work.

**Registry No.** 3,10-*meso* complex ion, 51349-38-3; 3*R*,10*R*-complex ion, 51349-39-4.

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[12] S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 3184 (1969).

[13] T. Ito and N. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 155 (1970).

[14] T. Ito, H. Saito, and H. Ito, *Inorg. Nucl. Chem. Lett.*, **6**, 607 (1970).

[15] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

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## Dissociation Kinetics of Pentacyanoiron(II) Complexes of Ammonia and Methylamine

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For the purpose of studying metal-to-ligand back-bonding interactions we recently investigated the aqueous kinetics of amine exchange in complexes of the general formula $Fe(CN)_5L^{n-}$, where iron is in the oxidation state II and L is an aromatic N heterocycle.[1] In that work the specific rates of breakage of the bonds between iron(II) and several unsaturated amines were shown to correlate with the energies of observed metal-to-ligand electron-transfer transitions in the complexes. The relationship was ascribed to an increase in $d\pi$-$p\pi$ back-bonding capacity along the series of ligands 4-methylpyridine, pyridine, isonicotinamide, and pyrazine. However, it was not possible to assess the effect of the base strengths of the leaving ligands on their rates of dissociation.

We now present a study of the dissociation kinetics of the pentacyanoiron(II) complexes of two saturated nitrogen bases, methylamine and ammonia. In these complexes back-bonding to the leaving group is impossible. The results permit the estimate of an upper limit to back-bonding stabi-

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[1] H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039, 2084 (1973).

**Table I.** Temperature Dependence of the Saturation-Limited Rate[a]

| Reactant | Temp, °C | $10^3 k_{\mathrm{obsd}}$, sec$^{-1}$ | Temp, °C | $10^3 k_{\mathrm{obsd}}$, sec$^{-1}$ |
|---|---|---|---|---|
| $Fe(CN)_5NH_3^{3-}(aq)$ | 10.0 | 2.2 | 20.0 | 8.5 |
| | 12.5 | 3.5 | 22.5 | 12.9 |
| | 15.0 | 4.3 | 25.0 | 17.5 |
| | 17.5 | 6.5 | 29.8 | 30 |
| $Fe(CN)_5CH_3NH_2^{3-}(aq)$ | 10.0 | 0.35 | 25.0 | 2.9 |
| | 15.0 | 0.76 | 30.0 | 5.7 |
| | 19.8 | 1.46 | | |

[a] $\mu = 1.0\ M$, lithium perchlorate.

**Table II.** Kinetic Parameters for Dissociation of Pentacyanoiron(II) Complexes of Aromatic N Heterocycles[a]

| Ligand | $10^3 k_{-1}$, sec$^{-1}$ | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu | $pK_{\mathrm{HL}}$ | $E_{\mathrm{ET}}$, kK |
|---|---|---|---|---|---|
| 4-Methylpyridine | 1.15 | 24 | 9 | 6.1 | 28.1 |
| Pyridine | 1.10 | 24.8 | 11 | 5.3 | 27.6 |
| Isonicotinamide | 0.73 | 26 | 14 | 3.7 | 23.0 |
| Pyrazine | 0.42 | 26.4 | 14 | 0.6 | 22.2 |

[a] See ref 1. Conditions: 25°, $\mu = 1\ M$.

lization in the pentacyanoiron(II) complexes of unsaturated ligands.

## Experimental Section

**Preparation of the Complexes.** Sodium pentacyanoammineiron(II) used in the kinetics experiments was prepared from sodium nitroprusside[2] (Carlo Erba Chemical Co.) and recrystallized several times from saturated aqueous ammonia at ice temperature. *Anal.*[3] Calcd for $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$: C, 18.4; H, 2.7; N, 25.7. Found: C, 18.3; H, 2.6; N, 25.6.

Sodium pentacyanomethylaminoiron(II) was prepared as the solid by the procedure of Kenney, *et al.*,[4] and also in solution using methods which have been described previously for other complexes.[1] Both modes of preparation gave identical experimental results.

**Kinetics Experiments.** For the kinetics experiments with pentacyanoiron(II) complexes a sufficient amount of the sodium salt to give a $10^{-5}\ M$ solution was dissolved in a 0.10 $M$ aqueous solution of ammonium or methylammonium chloride containing a $5 \times 10^{-3}$ $M$ concentration of the free amine. Solutions of *N*-methylpyrazinium iodide or isonicotinamide were prepared similarly. Aqueous lithium perchlorate was included to maintain 1.0 $M$ ionic strength. Reactions were carried out immediately on dissolution of the iron(II) salt by mixing the two reactant solutions in a thermostated 1-cm cuvette located in the cell compartment of a Cary 14 spectrophotometer. In an alternate procedure solutions of the attacking ligand were added directly to the solid iron(II) salt in the spectrophotometer cell, which was shaken and placed in the cell compartment. Employing either method reproducible absorbance readings, at $\lambda_{\max}$ 655 and 435 nm for formation of the *N*-methylpyrazinium or isonicotinamide complex, respectively, could be registered within 10 sec after mixing. Temperature control was ±0.3°. Errors in individual rate constants, which were rigorously first order over at least 2 half-lives, were estimated at less than 2%. Probable errors quoted for activation parameters were obtained by an analysis of variance about regression[5] employing Student's $t$ values for 90% confidence limits.

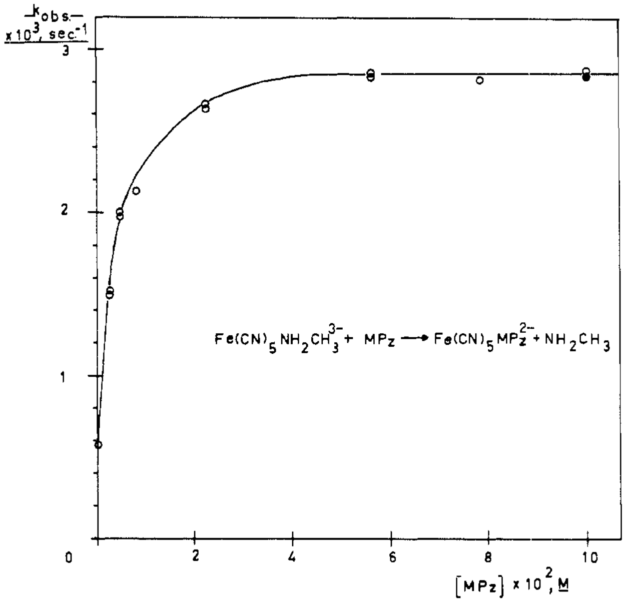

Figure 1. Plot of $k_{\mathrm{obsd}}$ *vs.* attacking ligand concentration, showing rate saturation. Black point is for isonicotinamide (25°, $\mu = 1.0$, pH 8.6).

## Results and Discussion

The rate of substitution of the *N*-methylpyrazinium ion ($Mpz^+$) for the ligand L ($NH_3$ or $CH_3NH_2$), described by eq 1

$$Fe(CN)_5L(aq)^{3-} + Mpz^+(aq) = Fe(CN)_5Mpz^{2-}(aq) + L(aq) \qquad (1)$$

for complexes of the type $Fe(CN)_5L^{3-}(aq)$, was measured. On introducing a substantial excess of $Mpz^+(aq)$ into a solution containing $Fe(CN)_5L^{3-}(aq)$ and a slight excess of L(aq), the first-order specific rate of approach of the system to equilibrium, $k_{\mathrm{obsd}}$, was determined spectrophotometrically by following the formation of the $Mpz^+$ complex (log $\epsilon_{\max}$ = 4.08 at 655 nm). For both of the ligands L the dependence of $k_{\mathrm{obsd}}$ on the concentration of $Mpz^+(aq)$, given in Figure 1 for the methylamine complex, showed a rate increase at low, increasing values of [$Mpz^+(aq)$] and rate saturation at high [$Mpz^+(aq)$]. The following mechanism is consistent with this observation[1]

$$Fe(CN)_5L^{3-}(aq) \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} Fe(CN)_5^{3-}(aq) + L(aq)$$

$$Fe(CN)_5^{3-}(aq) + H_2O \overset{K}{\rightleftharpoons} Fe(CN)_5H_2O^{3-}(aq)$$

$$Fe(CN)_5^{3-}(aq) + Mpz^+(aq) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(CN)_5Mpz^{2-}(aq)$$

The rate law, derived using the steady-state approximation for the concentrations of the intermediate species,[6] is

$$\frac{d[Fe(CN)_5Mpz^{2-}]}{dt} = k_{\mathrm{obsd}}\{[Fe(CN)_5L^{3-}] - [Fe(CN)_5L^{3-}]_{t=\infty}\}$$

where

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[2] G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd ed, Academic Press, New York, N. Y., 1965, p 1511.

[3] Microanalysis performed by the Stanford Microanalytical Laboratory, Stanford University.

[4] D. J. Kenney, T. P. Flynn, and J. B. Gallini, *J. Inorg. Nucl. Chem.*, 20, 75 (1961).

[5] H. A. Laitinen, "Chemical Analysis," McGraw-Hill, New York, N. Y., 1960, pp 563-570.

[6] The data do not permit a choice between the five- and six-coordinate intermediates as the reactive iron(II) species in the $k_2$ step. Assumption of either produces the same rate law.

$$k_{\text{obsd}} = \frac{k_{-1}k_2[\text{Mpz}^+] + k_1k_{-2}[\text{L}]}{k_1[\text{L}] + k_2[\text{Mpz}^+]} \qquad (2)$$

At high $\text{Mpz}^+$(aq) concentration $k_{\text{obsd}}$ reduces to $k_{-1}$, the specific rate of loss of the coordinated ligand L. In this region of rate saturation the observed rate constant should be independent of the nature of the incoming ligand. This was verified by experiments in which isonicotinamide was substituted for $\text{Mpz}^+$(aq) (black point in Figure 1).

The variation of $k_{-1}$ with temperature for the two leaving ligands was studied in the 10–30° temperature range, and the results are presented in Table I. Variation of $k_{-1}$ with $[\text{H}^+]$ in the narrow pH range employable in this study was neither expected nor encountered.

The dependence of $k_{-1}$ on temperature for the two complexes was investigated in the 10–30° interval, and the results are presented in Table I. Calculated activation parameters for amine loss from the ion $\text{Fe(CN)}_5\text{NH}_3{}^{3-}$(aq) are $\Delta H^{\ddagger} = 22.2 \pm 1.3$ kcal/mol and $\Delta S^{\ddagger} = 8 \pm 4$ cal deg$^{-1}$ mol$^{-1}$ with $k_{-1} = (1.75 \pm 0.05) \times 10^{-2}$ sec$^{-1}$ at 25°, pH 7.2, and $\mu = 1$ *M*. For the complex $\text{Fe(CN)}_5\text{NH}_2\text{CH}_3{}^{3-}$(aq), $\Delta H^{\ddagger} = 23.0 \pm 1.3$ kcal/mol and $\Delta S^{\ddagger} = 7 \pm 4$ cal deg$^{-1}$ mol$^{-1}$ with $k_{-1} = (2.8 \pm 0.1) \times 10^{-3}$ sec$^{-1}$ at 25°, pH 8.6, and $\mu = 1$ *M*.

The results of a study of the kinetics of dissociation of pentacyanoiron(II) complexes of aromatic N heterocycles[1] are summarized in Table II. These are similar to the results of the experiments described in this work in that analogous rate laws were observed in the two studies. Also, in both cases moderately positive entropies of activation were calculated for the $k_{-1}$ step, implying a common dissociative-type mechanism.

However, other aspects of the two sets of results are dissimilar. The specific rates of dissociation of the saturated amine complexes are 2–40-fold greater than those of the unsaturated class. Also, the $k_{-1}$ values found for the saturated ligands correlate inversely with the ligand basicities, whereas for the unsaturated leaving groups, $k_{-1}$ increases slightly with increasing ligand basicity.

If the steric factors affecting $k_{-1}$ are considered constant for the pentacyanoiron(II) complexes treated herein, the following estimate can be made of back-bonding stabilization energies in the complexes of aromatic N heterocycles. Given that the rate of ligand loss for the two saturated amine complexes correlates inversely with ligand basicity, we propose that the rate of dissociation of a particular nitrogen base should be related to its $\text{p}K_{\text{HL}}$ value by an equation of the form $\log k_{-1} = A + B(\text{p}K_{\text{HL}})$.[7] Using appropriate values of $k_{-1}$ and the $\text{p}K_{\text{HL}}$ values of the ammonium and methylammonium ions, one can calculate values of $k_{-1}$ based on the $\text{p}K_{\text{HL}}$ values of the ligands in Table II. For 4-methylpyridine, pyridine, isonicotinamide, and pyrazine, the calculated $k_{-1}$ values exceed the measured ones by factors of $10^3$, $3 \times 10^3$, $4 \times 10^4$, and $4 \times 10^6$, respectively. The rate factors may be converted, employing transition-state theory,[8] into enthalpy factors, 4.1, 4.7, 6.3, and 8.9 kcal/mol, respectively.

These values are the enthalpies of activation required for dissociation of the $\text{Fe(CN)}_5{}^{3-}$ complexes of certain unsaturated N heterocycles after accounting for the effect of the relative ligand basicities. The values can be considered as approximate upper limits to the back-bonding energies. Because they probably include effects other than $\pi$ bonding,[9] the enthalpies may be significantly greater than the true back-bonding stabilization energies.

**Acknowledgment.** The authors gratefully acknowledge financial support from the Conselho National de Pesquisas, the Atlantic Petroleum Co. of Brazil, the Agency for International Development, the National Science Foundation, the National Academy of Sciences, and the Atlantic Richfield Corp. of the U. S. Professor Ernesto Giesbrecht is thanked for his kind cooperation and support.

**Registry No.** $\text{Fe(CN)}_5\text{NH}_3{}^{3-}$, 13717-31-2; $\text{Fe(CN)}_5\text{CH}_3\text{NH}_2{}^{3-}$, 20774-55-4.

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[7] A relationship of this form has been described for a series of aqueous nickel(II) complexes of related ligands by P. Moore and R. G. Wilkins, *J. Chem. Soc.*, 3454 (1964).

[8] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 5.

[9] R. L. Courtwright, R. S. Drago, J. A. Nusz, and M. S. Nozari, *Inorg. Chem.*, 12, 2809 (1973).

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## Phosphorus-31 Nuclear Magnetic Resonance Spectra of Catalytically Active Nitrosyl Complexes

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Numerous workers have shown recently that transition metal–nitrosyl complexes may function as hydrogenation catalysts.[1-5] Catalysis by coordinatively saturated species is unusual. One interpretation[1] suggests that phosphine dissociation occurs (eq 1). Osmometric molecular weights of

$$\text{M(NO)L}_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{M(NO)L}_{n-1} + \text{L} \qquad (1)$$

300 and 800 were determined for $\text{RhNO(PPh}_3)_3$ and $\text{IrNO(PPh}_3)_3$ (formula weights 920 and 1009, respectively).[6] The second suggestion[2] for the efficacy of metal nitrosyls as catalysts involves an intramolecular redox process $\text{M}^q(\text{NO}^+) \rightarrow \text{M}^{q+2}(\text{NO}^-)$, with simultaneous decrease in the MNO bond angle from 180 to 120–140°.

We present here the results of a $^{31}$P nmr study of $\text{MNO(PPh}_3)_3$ (M = Co, Rh) and $\text{Rh(NO)Cl}_2(\text{PPh}_3)_2$. Phosphine exchange in $\text{RhNO(PPh}_3)_3$ is shown to occur *via* a dissociative pathway.

### Experimental Section

**Materials.** $\text{CoNO(PPh}_3)_3$[7] and $\text{RhNOCl}_2(\text{PPh}_3)_2$[8] were prepared by literature methods. $\text{RhNO(PPh}_3)_3$ was prepared by two routes.[2,8] Tetrahydrofuran (THF) was distilled from Na-K alloy. Nmr samples were prepared by degassing separately the solids and solvents (three

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[1] W. Strohmeier and R. Endres, *Z. Naturforsch. B*, 27, 1415 (1972).

[2] J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 91, 5659 (1969).

[3] G. Dolcetti, N. W. Hoffman, and J. P. Collman, *Inorg. Chim. Acta*, 6, 531 (1972).

[4] G. Dolcetti, *Inorg. Nucl. Chem. Lett.*, 9, 705 (1973).

[5] S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, 93, 3068 (1971).

[6] Equation 1 alone cannot yield apparent molecular weights less than 50% of the formula weight.

[7] G. La Monica, G. Navazio, P. Sandrini, and S. Cenini, *J. Organometal. Chem.*, 31, 89 (1971).

[8] J. J. Levinson and S. D. Robinson, *J. Chem. Soc. A*, 2947 (1970).