1) 8.2 ppm, $J = 120$ Hz, symmetrical multiplet (intensity 3), −29.0 ppm, $J = 31$ Hz. Acid hydrolysis of the solid product followed by precipitation with aqueous KPF_6 gave $[(TMPD)BH_2]PF_6$, which was identified by its infrared spectrum.[5]

Infrared spectrum (KBr) of $[(TMPD)BH_2]B_3H_8$ in cm^{-1} (relative intensity): 3050 (vw), 3030 (vw), 3010 (w), 2990 (vw), (2940) (vw), 2480 (m), 2450 (s), 2390 (s), 2295 (w), 2275 (w,sh), 2120 (w), 2075 (w,sh), 1480 (m), 1465 (m,sh), 1455 (m), 1410 (w), 1255 (m), 1195 (m,sh), 1190 (s), 1180 (s), 1165 (s), 1148 (s), 1130 (s), 1110 (m), 1028 (w), (w), 1010 (s), 960 (m), 945 (w), 925 (s), 870 (w), 825 (s), 815 (m), 805 (m), 765 (s), 755 (m), 710 (w), 545 (w), 530 (m).

Reaction of $Me_3N{\cdot}B_3H_7$ with TMPD. A solution of 0.114 g (1.15 mmol) of $Me_3N{\cdot}B_3H_7$ and 0.224 g (1.36 mmol) of TMPD in ca. 1 mL of $CHCl_3$ at room temperature was periodically monitored by boron-11 NMR spectroscopy over 14 days. Neither the appearance of the solution nor the NMR spectrum (starting material) showed any change during this period.

Reaction of $THF{\cdot}B_3H_7$ with TMPD. A 0.178-g (1.59 mmol) sample of $THF{\cdot}B_3H_7$ reacted with 0.331 g (2.02 mmol) of TMPD in 5 mL of THF in a 100-mL vessel to produce a slightly turbid solution that did not change in appearance over a 1-h period. An experiment in an NMR reaction vessel using proportionally smaller quantities showed a boron-11 NMR spectrum characteristic of $[(TMPD)BH_2]B_3H_8$ (see above) and a weak broad structureless signal centered at −15.2 ppm. The 100-mL vessel was opened (a trace of noncondensable gas was present), and all volatile materials were removed by continuous pumping over a 2-day period, leaving 0.281 g of a colorless solid residue (weight calculated from eq 6, 0.275 g). The infrared spectrum of the residue contained all the bands of $[(TMPD)BH_2]B_3H_8$ plus those of an impurity, presumably $(THF{\cdot}BH)_x$. Recrystallization from water gave pure $[(TMPD)BH_2]B_3H_8$. Vacuum-line separation of volatile materials gave a small quantity of TMPD (IR spectrum) and THF free of borane contamination (acid hydrolysis).

Registry No. III, 79550-23-5; B_4H_{10}, 18283-93-7; TMPD, 704-01-8; $THF{\cdot}B_3H_7$, 12544-89-7; $Me_3N{\cdot}B_3H_7$, 12076-72-1.

Contribution from the Laboratory of Analytical Chemistry,
Faculty of Science, Nagoya University,
Chikusa, Nagoya 464, Japan

Activation Volumes for Substitution of Diaqua[*meso*-tetrakis(*N*-methyl-4-pyridyl)porphinato]cobalt(III) with Thiocyanate. Evidence for a Dissociative Mechanism

Shigenobu Funahashi, Masahiko Inamo, Koji Ishihara,
and Motoharu Tanaka*

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Reactions of metalloporphyrins with monodentate ligands have been extensively investigated in order to determine the mechanisms of axial ligand substitution in metalloporphyrins.[1] The overall reaction that takes place can be represented by eq 1, where MP, S, and X refer to metalloporphyrin, solvent

$$MPS_2 + 2X \rightleftharpoons MPX_2 + 2S \tag{1}$$

molecule, and monodentate ligand, respectively. The reactions are first order in the metalloporphyrin for all the cases studied. The plots of the first-order rate constants against ligand concentration are linear in most cases, while in some systems they show curvature and eventual saturation.

There are several reasonable mechanisms[2] for the axial ligand substitution in metalloporphyrins (see Mechanisms I–III).

Mechanism I

$$MPS_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MPS + S \tag{2}$$

$$MPS + X \xrightarrow{k_2} MPSX \tag{3}$$

$$MPSX + X \xrightarrow{\text{fast}} MPX_2 + S \tag{4}$$

Mechanism II

$$MPS_2 + X \overset{K}{\rightleftharpoons} MPS_2{\cdots}X \xrightarrow{k} MPSX + S \tag{5}$$

$$MPSX + X \xrightarrow{\text{fast}} MPX_2 + S \tag{6}$$

Mechanism III

$$MPS_2 + X \rightarrow [MPS_2X]^{\ddagger} \xrightarrow{\text{fast}} MPSX + S \tag{7}$$

$$MPSX + X \xrightarrow{\text{fast}} MPX_2 + S \tag{8}$$

The dissociative mechanism involves the dissociation of the solvent molecule coordinated to the central metal ion in metalloporphyrin to produce a pentacoordinated intermediate (step 2). This intermediate species then reacts with the entering ligand (step 3).

In Mechanism II the reaction proceeds via an interchange between a ligand and a solvent molecule in a rapidly formed outer-sphere complex ($MPS_2{\cdots}X$).

The third mechanism is an associative type. The first ligand incorporated in the metalloporphyrin labilizes the axial solvent molecules.[3-8] The intermediate MPSX reacts much faster with X than does the disolvato porphyrin complex, and thus the concentration of the intermediate is very low.

In Mechanism III the rate should be first order in X for all concentrations of X. In the reaction systems where first-order rate constants, k_0, increase with increasing concentration of X up to a limiting value, Mechanism III cannot be operating. Mechanisms I and II both predict a falling-off of the k_0 with increasing concentration of the incoming ligand. Mechanism I gives the following dependence of k_0 with respect to [X]:

$$k_0 = \frac{k_1[X]}{k_{-1}/k_2 + [X]} \tag{9}$$

For Mechanism II, we have

$$k_0 = \frac{k[X]}{K^{-1} + [X]} \tag{10}$$

Thus eq 10 is identical in form with eq 9 with

$$k_0 = \frac{p[X]}{q + [X]} \tag{11}$$

Under conditions ($q >> [X]$) where the increase of k_0 with [X] does not fall off, we obtain only $k_2k_1k_{-1}^{-1}$ or kK.

The reaction of [*meso*-tetrakis(*N*-methyl-4-pyridyl)porphine]cobalt(III) (represented by CoTMpyP) with thiocyanate ion has been studied by several groups[5,6] with similar results. Although the mechanisms have been discussed, no clear con-

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clusion has yet been reached.[7,8] We followed the above reaction at various pressures by a high-pressure stopped-flow technique[9] in order to elucidate the mechanism on the basis of activation volumes. This paper seems to be the first high-pressure study of substitution with metalloporphyrins.

Experimental Section

Reagents. Diaqua[*meso*-tetrakis(*N*-methyl-4-pyridyl)porphinato]cobalt(III) perchlorate, $[Co^{III}TMpyP(H_2O)_2](ClO_4)_5$, was synthesized from *meso*-tetrakis(*N*-methyl-4-pyridyl)porphine tetraiodide (Strem) and cobalt(II) perchlorate in a manner described by Ashley et al.[6] Reagent grade sodium thiocyanate was twice recrystallized from distilled water. The thiocyanate solution was standardized by the method of Volhard. Perchloric acid of special purity (Wakojunyaku) was used without further purification. The solution of sodium perchlorate was prepared as described previously.[10]

High-Pressure Stopped-Flow Apparatus. A high-pressure stopped-flow apparatus has been exploited, which enables us to follow reactions under pressure up to 1600 kg cm^{-2}.[9] The apparatus had a dead time of ca. 0.1 s due to fluctuation of pressure of ca. 80 kg cm^{-2} during flow because intensifiers I1 and I2 in Figure 1 of ref 9 were connected through nitrogen gas. Since in the present study I1 and I2 were connected with a rigid coupler, the perturbation of pressure during flow was effectively eliminated.[11] Thus the apparatus used here has a dead time of several milliseconds, which enabled us to follow reactions with half-lives longer than 10 ms. The half-life time of the reaction under the present experimental conditions is larger than 10 ms.

Kinetic Measurement. The reactions were followed by a stopped-flow technique using a usual stopped-flow apparatus (Type RA1100, Union Giken, Hirakata, Japan) at atmospheric pressure, while reactions under various pressures up to 1250 kg cm^{-2} were followed with a high-pressure stopped-flow apparatus described above. A thiocyanate solution at $[H^+] = (9.97 \pm 0.02) \times 10^{-2}$ mol kg^{-1} and $I = 2.20 \pm 0.01$ mol kg^{-1} (Na^+, H^+/ClO_4^-, SCN^-) was mixed with a CoTMpyP solution of the same hydrogen ion concentration and ionic strength. The reactions were followed by monitoring the change in absorbance in the Soret region. In all cases the thiocyanate concentration was at least 1000 times greater than that of the CoTMpyP. Under the present experimental conditions, the diaqua complex (represented by $CoP(H_2O)_2^{5+}$) reacts with SCN^- to give the dithiocyanato complex, $CoP(SCN)_2^{3+}$.[12] Thiocyanate and porphyrin solutions were prepared fresh each day, and porphyrin solutions were protected from sunlight and fluorescent light. Conditional first-order rate constants were determined from pseudo-first-order plots. Solutions were prepared at 25 °C on the basis of the molar concentration scale (mol dm^{-3} ≡ M). The molar concentrations of solutes were converted to the pressure-independent molal scale (mol kg^{-1}).

Results

The anation was first order in $CoP(H_2O)_2^{5+}$:

$$\frac{d[CoP(SCN)_2^{3+}]}{dt} = -\frac{d[CoP(H_2O)_2^{5+}]}{dt} = k_0[CoP(H_2O)_2^{5+}] \quad (12)$$

Here k_0 refers to a conditional first-order rate constant involving constants and concentrations like eq 9 and 10. The plot of k_0[15] vs. $[SCN^-]$ is shown in Figure 1. Since the increase of k_0 with $[SCN^-]$ falls off, Mechanism III can be ruled out. The k_0's for a series of ligand concentration at 15, 25, and 35 °C were fitted to eq 11 by a nonlinear least-squares

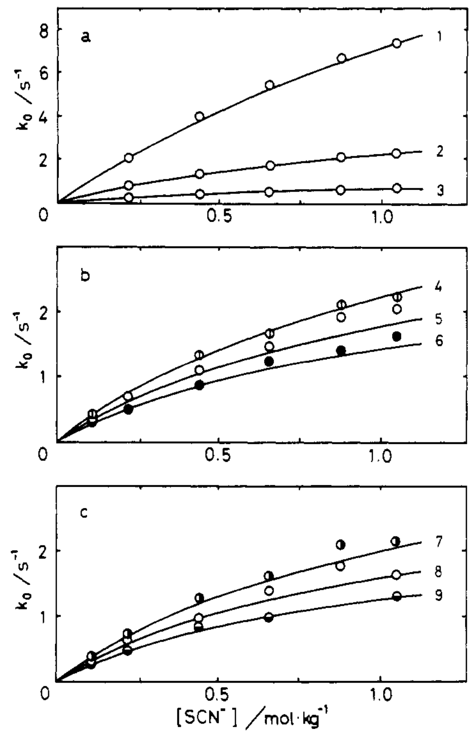

Figure 1. The dependence of the conditional first-order rate constant upon $[SCN^-]$ at various temperatures and pressures. $[H^+] = 9.97 \times 10^{-2}$ mol kg^{-1}, $I = 2.20$ mol kg^{-1}. a (at atmospheric pressure): curve 1, 35 °C; curve 2, 25 °C; curve 3, 15 °C. b (at 25 °C): curve 4, 1 kg cm^{-2}; curve 5, 500 kg cm^{-2}; curve 6, 1000 kg cm^{-2}. c (at 25 °C): curve 7, 250 kg cm^{-2}; curve 8, 750 kg cm^{-2}; curve 9, 1250 kg cm^{-2}. The individual points plotted are the average of several runs. The solid curves were calculated from eq 11 by using the values of *p* and *q* in Table I.

Table I. Kinetic Results for the Reaction of $CoP(H_2O)_2^{5+}$ with SCN^-[a]

temp/°C, press./kg cm^{-2}	p^b/s^{-1}	q^b/mol kg^{-1}
15, 1[c] (27)[d]	1.27 ± 0.03	1.06 ± 0.03
25, 1[c] (29)	5.88 ± 0.33	1.62 ± 0.09
35, 1[c] (30)	24.7 ± 2.8	2.40 ± 0.28
25, 1[e] (22)	5.05 ± 0.83	1.26 ± 0.21
25, 250[e] (25)	4.41 ± 0.46	1.21 ± 0.13
25, 500[e] (23)	3.84 ± 0.31	1.16 ± 0.09
25, 750[e] (22)	3.35 ± 0.48	1.11 ± 0.16
25, 1000[e] (21)	2.92 ± 0.42	1.06 ± 0.16
25, 1250[e] (19)	2.55 ± 0.47	1.01 ± 0.19

$$\left.\begin{aligned} \Delta H_p^\ddagger &= 107 \pm 3 \text{ kJ mol}^{-1} \\ \Delta S_p^\ddagger &= 129 \pm 8 \text{ J mol}^{-1}\text{ K}^{-1} \\ \Delta V_p^\ddagger &= 14 \pm 4 \text{ cm}^3\text{ mol}^{-1} \end{aligned}\right\} f$$

$$\left.\begin{aligned} \Delta H_q^\ddagger &= \Delta H_{-1}^\ddagger - \Delta H_2^\ddagger = 30 \pm 4 \text{ kJ mol}^{-1} \\ \Delta S_q^\ddagger &= \Delta S_{-1}^\ddagger - \Delta S_2^\ddagger = 105 \pm 14 \text{ J mol}^{-1}\text{ K}^{-1} \\ \Delta V_q^\ddagger &= \Delta V_{-1}^\ddagger - \Delta V_2^\ddagger = 5 \pm 4 \text{ cm}^3\text{ mol}^{-1} \end{aligned}\right\} g$$

$$\left.\begin{aligned} -\Delta H_q &= \Delta H = -30 \pm 4 \text{ kJ mol}^{-1} \\ -\Delta S_q &= \Delta S = -105 \pm 14 \text{ J mol}^{-1}\text{ K}^{-1} \\ -\Delta V_q &= \Delta V = -5 \pm 4 \text{ cm}^3\text{ mol}^{-1} \end{aligned}\right\} h$$

[a] Conditions: [CoTMpyP] = 10^{-5} mol kg^{-1}, $[SCN^-]$ = 0.110–1.05 mol kg^{-1}, $[H^+] = 9.97 \times 10^{-2}$ mol kg^{-1}, $I = 2.20$ mol kg^{-1}. [b] Given by eq 11. ± values are standard deviations. [c] Obtained by a standard stopped-flow assembly. [d] Figures in parentheses indicate the number of data points. [e] Obtained by a high-pressure stopped-flow assembly. [f] Activation parameters for *p* in the case of Mechanisms I and II. [g] Activation parameters for k_{-1}/k_2 in Mechanism I. [h] Thermodynamic parameters for *K* in Mechanism II.

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program.[16] With the assumption that the activation volume $\Delta V^\ddagger$ is independent of pressure,[17a] the conditional first-order rate constant is expressed as eq 13, where p^0 and q^0 are constants at zero pressure.

$$k_0 = \frac{p^0 \exp(-P\Delta V_p^\ddagger/RT)[\mathrm{SCN^-}]}{q^0 \exp(-P\Delta V_q^\ddagger/RT) + [\mathrm{SCN^-}]} \qquad (13)$$

Values of p^0, q^0, $\Delta V_p^\ddagger$, and $\Delta V_q^\ddagger$ [18] were obtained by a nonlinear least-squares fit to all six sets of data (132 data points) simultaneously. Values of p^0 and q^0 were revealed to be the same as corresponding values obtained at atmospheric pressure. All the parameters obtained are tabulated in Table I.

Discussion

The p and q values correspond to k_1 and k_{-1}/k_2 in Mechanism I and k and K^{-1} in Mechanism II, respectively. In Mechanism I, for

$$\mathrm{MP(H_2O)_2^{5+}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{MP(H_2O)^{5+}} + \mathrm{H_2O} \qquad (14)$$

$$\mathrm{MP(H_2O)^{5+}} + \mathrm{SCN^-} \xrightarrow{k_2} \mathrm{MP(H_2O)(SCN)^{4+}} \xrightarrow[\text{fast}]{\mathrm{SCN^-}} \mathrm{MP(SCN)_2^{3+}} + \mathrm{H_2O} \qquad (15)$$

the value of $\Delta V_p^\ddagger$ for k_1 should be positive and almost equal to or a little lower than the partial molal volume of water (+18 $\mathrm{cm^3\ mol^{-1}}$), since the partial molal volume of the five-coordinated metalloporphyrin does not differ much from that of the six-coordinated metalloporphyrin. The $\Delta V_q^\ddagger$ value for k_{-1}/k_2 seems to be small: the effect of the partial charge neutralization in the transition state of the k_2 path should be small, since the positive charge on the metalloporphyrin is largely delocalized over the whole porphyrin nucleus. In Mechanism II for

$$\mathrm{MP(H_2O)_2^{5+}} + \mathrm{SCN^-} \overset{K}{\rightleftharpoons} \mathrm{MP(H_2O)_2^{5+}\cdots SCN^-} \qquad (16)$$

$$\xrightarrow{k} \mathrm{MP(H_2O)(SCN)^{4+}} + \mathrm{H_2O} \xrightarrow[\text{fast}]{\mathrm{SCN^-}} \mathrm{MP(SCN)_2^{3+}} + 2\mathrm{H_2O} \qquad (17)$$

the ΔV value for K should be positive because of partial relieving of electrostriction by ion-pair formation[19-21] and the $\Delta V_p^\ddagger$ value for k should be small. From these considerations together with the results given in Table I, we conclude that the substitution of $\mathrm{CoP(H_2O)_2^{5+}}$ with $\mathrm{SCN^-}$ occurs by a dissociative mechanism. Negative pressure effect on the reaction makes Mechanism III unlikely.

Pasternack et al.[5] studied the reaction of $\mathrm{CoP(H_2O)_2^{5+}}$ with $\mathrm{SCN^-}$ to produce the monothiocyanato complex $\mathrm{CoP(H_2O)(SCN)^{4+}}$ and obtained the activation parameters $\Delta H^\ddagger = 82.8$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^\ddagger = 44.8$ J $\mathrm{mol^{-1}\ K^{-1}}$. In the present case, these values correspond to $\Delta H_p^\ddagger - \Delta H_q^\ddagger = 77$ kJ $\mathrm{mol^{-1}}$ and $\Delta S_p^\ddagger - \Delta S_q^\ddagger = 24$ J $\mathrm{mol^{-1}\ K^{-1}}$, respectively. The agreement of their results with ours is good, when we take into account the experimental errors involved. Available evidence suggests that the similar reactions proceed via an $\mathrm{S_N1}$ type mechanism in which the rate-determining step involves the breaking of a cobalt(III)–water bond.[6,22]

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Registry No. $\mathrm{CoP(H_2O)_2^{5+}}$, 51405-04-0; $\mathrm{SCN^-}$, 302-04-5.

Supplementary Material Available: Table SI, a listing of the conditional first-order rate constants obtained under the various conditions (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
Washington State University, Pullman, Washington 99164, and
University of Edinburgh, Edinburgh, United Kingdom

^{31}P NMR Spin–Lattice Relaxation Time Measurements on Platinum(II)- and Ruthenium(II)-Substituted Phosphine, Diphenylphosphinito, and Dimethyl Phosphito Complexes

Donald M. Appel,[1a] Alan S. F. Boyd,[1b] Iain W. Robertson,[1b]
D. Max Roundhill,*[1a] and T. Anthony Stephenson*[1b]

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In a continuing synthetic effort on the coordination chemistry of diphenylphosphinous acid and dimethyl phosphite, we have observed considerable intensity differences between nonequivalent phosphorus nuclei in the ^{31}P NMR spectra of the metal complexes with these ligands. These intensity variations could have their origin in spin–lattice time (T_1) differences between the separate phosphorus nuclei. In view of the very small amount of published work on the ^{31}P spin–lattice relaxation time in transition-metal phosphine complexes,[2] we have carried out a series of T_1 measurements to try and learn more about the factors influencing line intensities in complexes of platinum(II) and ruthenium(II) with diphenylphosphinito and dimethyl phosphito ligands.

Results and Discussion

The measured T_1 data for a series of platinum(II) and ruthenium(II) complexes are shown in Table I. For comparison T_1 values for $\mathrm{[NH_4][S_2PPh_2]}$, $\mathrm{Ph_2PH(O)}$, and $\mathrm{(MeO)_2PH(O)}$ are also given. The compound $\mathrm{[NH_4][S_2PPh_2]}$ has a long relaxation time of 30.0 s, a value comparable with that reported for triphenylphosphine.[3] For the methyl compound $\mathrm{Na[S_2PMe_2]}$, the corresponding T_1 value is 20.0 s. The compound $\mathrm{Ph_2PH(O)}$ has a short relaxation time of 2.5 s. Such a short time arises because of the dipole–dipole relaxation contribution from the vicinal hydrogen directly bonded to the phosphorus. The efficiency of the dipole mechanism is proportional to the sixth power of the phosphorus–hydrogen separation,[4,5] and hence, a directly bonded proton will make a dominant dipole–dipole contribution to the relaxation. The value found

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