Table I. Logarithmic Equilibrium Constants[a] of Transition-Metal-NTMP Complexes at I = 0.1 M (KNO_3)

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}		Zn^{2+}	Cd^{2+}
log K_{ML}	10.9	13.5	14.0	11.7	17.2	16.9^b	14.6	12.0
log K_{MHL}	7.37	6.49	6.18	8.11	6.33	6.50^b	6.34	7.14
log K_{MH_2L}	5.93	5.41	5.09	5.56	4.53	4.69^b	5.12	5.76
log K_{MH_3L}	4.7	4.2	3.6	3.5	3.5	3.6^b	3.9	4.0

[a] $K_{ML} = [ML]/[M][L]$, $K_{MH_mL} = [MH_mL]/[H][MH_{m-1}L]$. Uncertainties of the constants are ±0.1 for log K_{ML} (±0.2 for log K_{CuL} with pH titration), ±0.02 for log K_{MHL}, ±0.04 for K_{MH_2L}, and ±0.1 for K_{MH_3L}. [b] With pCu electrode.

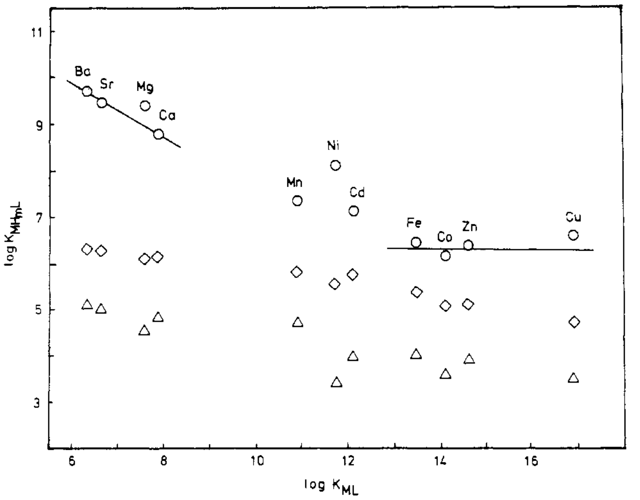

Figure 1. Plot of logarithmic protonation constants, log K_{MH_mL}, as a function of logarithmic formation constants of NTMP complexes, log K_{ML}: ○, K_{MHL}; ◇, K_{MH_2L}; △, K_{MH_3L}.

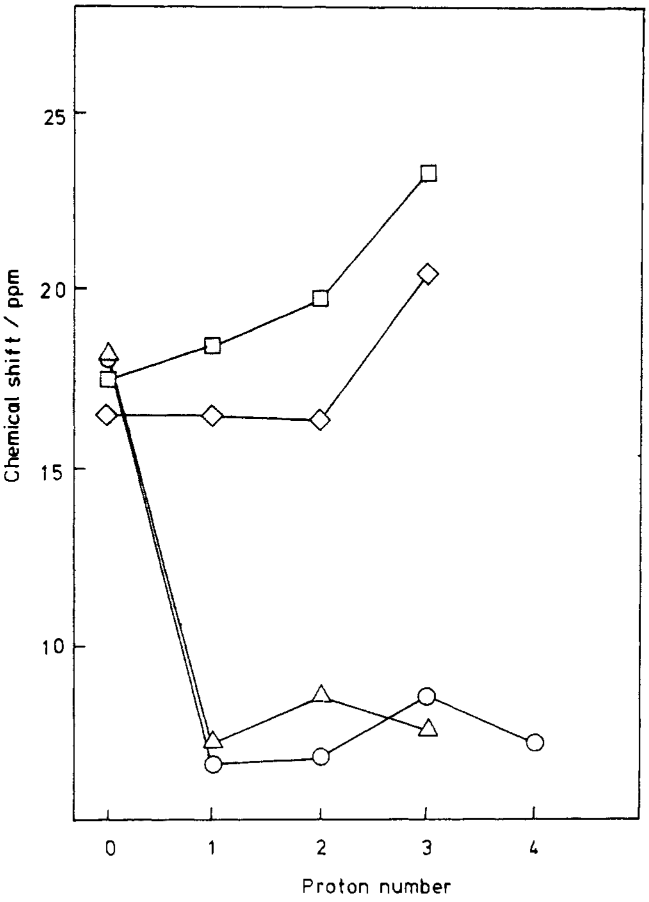

Figure 2. ^{31}P chemical shifts of NTMP (○) and Zn (□), Cd (◇), and Sr complexes (△) as a function of the number of protons bound to the ligand (H_nL), n, or metal complex (MH_mL), m.

of the signal is not observed at any step of protonation. These results support the conclusion that the protonation of the transition-metal complexes occurs on the phosphonate groups (structure III) throughout the protonation, from the first to the third step.

Experimental Section

The purity of nitrilotris(methylenephosphonic acid) (NTMP, H_6L) (Dojin) purified by a method described elsewhere[8] was more than 99.8%. The pH titration and ^{31}P NMR measurements were carried out as reported in the previous paper.[8] The copper ion selective electrode was calibrated with copper(II) standard solutions. The chemical shifts of ^{31}P NMR spectra are reported as the values relative to the aqueous 85% H_3PO_4 reference. The downfield shift is denoted by the positive sign of the chemical shift.

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Volume of Activation for the Axial Substitution Reaction of Monoligated Chloro(5,10,15,20-tetraphenylporphinato)chromium(III) via a Limiting Dissociative Mechanism

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Much attention has been drawn to the mechanisms of the axial ligand substitution reactions of metalloporphyrins of various metal ions.[3-17] In order to study the mechanism on the basis of the pressure effect, anation reactions of some water-soluble metalloporphyrins in aqueous solution have been followed at high pressure.[4c,18,19] The purpose of our present work is to investigate

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(1) Aichi University of Education.
(2) Nagoya University.
(3) O'Brien, P.; Sweigart, D. A. *Inorg. Chem.* **1982**, *21*, 2094-2095.
(4) (a) Ashley, K. R.; Leipoldt, J. G.; Joshi, V. K. *Inorg. Chem.* **1980**, *19*, 1608-1612. (b) Leipoldt, J. G.; Basson, S. S.; Rabie, D. R. *J. Inorg. Nucl. Chem.* **1981**, *43*, 3239-3244. (c) Leipoldt, J. G.; Meyer, H. *Polyhedron* **1987**, *6*, 1361-1364. (d) Ashley, K. R.; Kuo, J. *Inorg. Chem.* **1988**, *27*, 3556-3561.
(5) Krishnamurthy, M. *Inorg. Chim. Acta* **1978**, *26*, 137-144.
(6) Fleischer, E. B.; Krishnamurthy, M. *J. Coord. Chem.* **1972**, *2*, 89-100.
(7) Fleischer, E. B.; Krishnamurthy, M. *J. Am. Chem. Soc.* **1971**, *93*, 3784-3786.
(8) Byers, W.; Cossham, J. A.; Edwards, J. O.; Gordon, A. T.; Jones, J. G.; Kenny, E. T. P.; Mahmood, A.; McKnight, J.; Sweigart, D. A.; Tondreau, G. A.; Wright, T. *Inorg. Chem.* **1986**, *25*, 4767-4774.
(9) Jones, J. G.; Tondreau, G. A.; Edwards, J. O.; Sweigart, D. A. *Inorg. Chem.* **1985**, *24*, 296-300.
(10) Pasternack, R. F.; Gillies, B. S.; Stahlbush, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 2613-2619.
(11) Kolski, G. B.; Plane, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 3740-3744.
(12) Mahmood, A.; Liu, H.; Jones, J. G.; Edwards, J. O.; Sweigart, D. A. *Inorg. Chem.* **1988**, *27*, 2149-2154.
(13) Ashley, K. R.; Au-Young, S. *Inorg. Chem.* **1976**, *15*, 1937-1939.
(14) Ashley, K. R.; Berggren, M.; Cheng, M. *J. Am. Chem. Soc.* **1975**, *97*, 1422-1426.
(15) Pasternack, R. F.; Cobb, M. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 866-873.
(16) Ashley, K. R.; Shyu, S.; Leipoldt, J. G. *Inorg. Chem.* **1980**, *19*, 1613-1616.
(17) Storm, C. B.; Turner, A. H.; Swann, M. B. *Inorg. Chem.* **1984**, *23*, 2743-2746.
(18) Funahashi, S.; Inamo, M.; Ishihara, K.; Tanaka, M. *Inorg. Chem.* **1982**, *21*, 447-449.
(19) Leipoldt, J. G.; van Eldik, R.; Kelm, H. *Inorg. Chem.* **1983**, *22*, 4146-4149.

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the transition state of the axial ligand substitution of metalloporphyrins in terms of the activation volume.

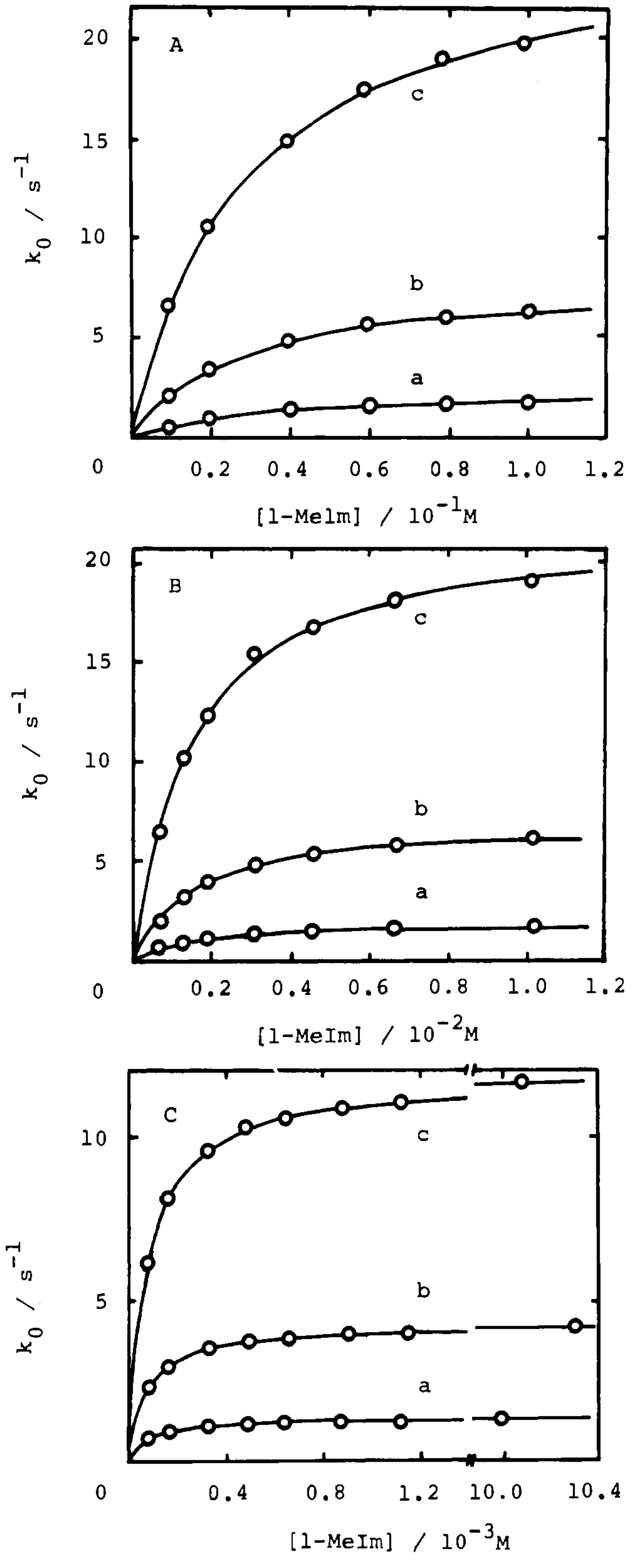

Figure 1. Dependence of the conditional first-order rate constant k_0 on the concentration of 1-methylimidazole at various temperature under ambient pressure: (A) [CrTPP] = 4.98 × 10^{-6} M ((a) 15.0 °C, [py] = 3.11 × 10^{-2} M; (b) 25.0 °C, [py] = 3.00 × 10^{-2} M; (c) 35.0 °C, [py] = 3.11 × 10^{-2} M); (B) [CrTPP] = 4.54 × 10^{-6} M, [Qui] = 0.101 M ((a) 14.8 °C; (b) 25.2 °C; (c) 35.0 °C); (C) [CrTPP] = (3.85–4.74) × 10^{-6} M, [PPh_3] = 9.06 × 10^{-2} M ((a) 15.0 °C; (b) 25.0 °C; (c) 35.0 °C). The solid curves were calculated by using the activation parameters obtained.

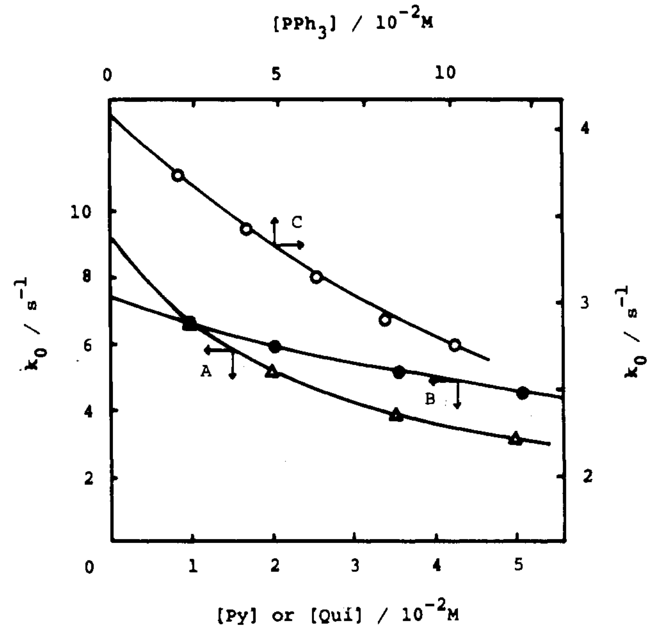

Figure 2. Dependence of the conditional first-order rate constant k_0 on the concentration of free L at 25.0 °C and 0.1 MPa: (A) L = py, [CrTPP] = 6.10 × 10^{-6} M, [1-MeIm] = 3.06 × 10^{-2} M; (B) L = Qui, [CrTPP] = 6.63 × 10^{-6} M, [1-MeIm] = 1.76 × 10^{-3} M; (C) L = PPh_3, [CrTPP] = 3.91 × 10^{-6} M, [1-MeIm] = 1.79 × 10^{-4} M.

Reaction 1 has been studied in toluene with various types of ligands (L and X) at ambient pressure at 25 °C:[3]

$$\mathrm{Cr(TPP)(Cl)(L) + X \rightleftharpoons Cr(TPP)(Cl)(X) + L} \qquad (1)$$

where TPP is 5,10,15,20-tetraphenylporphine and L and X are leaving and entering ligands, respectively. Regretably, the activation parameters for these reactions are not available. Reaction 1 is the substitution reaction at only one axial position, and the chloride ion is not displaced by nitrogen or phosphorus ligands. The axial substitution of Cr(TPP)(Cl)(L) (eq 1) has been interpreted to proceed via a limiting dissociative mechanism. In this paper we will describe, in particular, the pressure effect on reaction 1, where an entering ligand (X) is 1-methylimidazole (1-MeIm) and leaving ligands (L) are rather bulky ligands such as pyridine (py), quinoline (Qui), and triphenylphosphine (PPh_3).

Experimental Section

Reagents. TPP (Strem Chemicals, Inc.) was purified to remove any tetraphenylchlorin impurity by using the method of Barnett et al.[20] The preparation and purification of Cr(TPP)Cl were performed by the literature method.[21] Reagent grade toluene, 1-methylimidazole, pyridine, and quinoline were dried and purified. Triphenylphosphine was recrystallized twice from ethanol.

Measurements. The temperature of reaction solutions was controlled to within ±0.1 °C. Uncertainty of pressure was ca. 0.5 MPa. Kinetic measurements were performed with a Type RA 401 stopped-flow instrument (Union Giken, Hirakata, Japan) at ambient pressure and a high-pressure stopped-flow apparatus (Type FIT-3) at elevated pressures.[22] The concentrations of the leaving and entering ligands were kept in a large excess over that of chromium(III) porphyrin to guarantee the pseudo-first-order conditions. Total concentration of Cr(TPP)Cl was approximately (4–8) × 10^{-6} M (1 M = 1 mol dm^{-3}). Conditional first-order rate constants were obtained from a nonlinear least-squares analysis of reaction curves with at least 3 half-lives and represent the average of five to eight runs. Reproducibilities of the values of k_0 were better than ±3%. No effect of added water on both the visible absorption spectra and the reaction rates was confirmed up to [H_2O] = 4 × 10^{-2} M.

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[20] Barnett, G. H.; Hudson, M. F.; Smith, K. M. *Tetrahedron Lett.* **1973**, *No. 30*, 2887–2888.

[21] Summerville, D. A.; Jones, R. D.; Hoffman, B. M.; Basolo, F. *J. Am. Chem. Soc.* **1977**, *99*, 8195–8202.

[22] Ishihara, K.; Funahashi, S.; Tanaka, M. *Rev. Sci. Instrum.* **1982**, *53*, 1231–1234.

Table I. Activation Parameters[a] for the Axial Substitution Reaction of the Cr(TPP)(Cl)(L) Complex with 1-Methylimidazole in Toluene

	L		
	py	Qui	PPh_3
k_1/s^{-1} (25 °C)	8.0 ± 0.3	7.0 ± 0.2	4.2 ± 0.1
ΔH_1^*	86.1 ± 1.3	85.3 ± 1.1	78.2 ± 1.1
ΔS_1^*	61 ± 5	57 ± 4	29 ± 4
ΔV_1^*	25.7 ± 0.5	23.8 ± 0.6	19.6 ± 0.2
k_2/k_3 (25 °C)	$(9.2 \pm 0.3) \times 10^{-1}$	$(1.52 \pm 0.05) \times 10^{-2}$	$(7.3 \pm 0.2) \times 10^{-4}$
$\Delta H_2^* - \Delta H_3^*$	−1.9 ± 1.8	−3.1 ± 1.5	4.3 ± 2.0
$\Delta S_2^* - \Delta S_3^*$	−7 ± 6	−45 ± 5	−45 ± 7
$\Delta V_2^* - \Delta V_3^*$	1.3 ± 1.1	−1.9 ± 1.6	2.0 ± 0.6
k_4/s^{-1} (25 °C)	$(2.8 \pm 0.3) \times 10^{-2}$	$(3.6 \pm 0.4) \times 10^{-2}$	$(3.6 \pm 0.4) \times 10^{-2}$
		av $(3.3 \pm 0.6) \times 10^{-2}$	

[a] Units: ΔH^*/kJ mol^{-1}, ΔS^*/J K^{-1} mol^{-1}, $\Delta V^*/cm^3$ mol^{-1}. Errors are one standard deviation.

Results

Values of the equilibrium constant (K = [Cr(TPP)(Cl)(1-MeIm)][L][Cr(TPP)(Cl)(L)]$^{-1}$[1-MeIm]$^{-1}$) of reaction 1 were determined by a conventional spectrophotometric method. Values of log K at 25 °C were determined to be 2.50 ± 0.01 for py, 4.10 ± 0.02 for Qui, and 5.21 ± 0.03 for PPh_3. Errors quoted are standard deviations. Available values of log K are 2.5 ± 0.1 for py and 4.8 ± 0.3 for PPh_3.[3] The former agrees with ours.

Reaction 1 was first order with respect to Cr(TPP)(Cl)(L) (L = py, Qui, and PPh_3):

$$-d[\mathrm{Cr(TPP)(Cl)(L)}]/dt = k_0[\mathrm{Cr(TPP)(Cl)(L)}] \quad (2)$$

where k_0 is a conditional first-order rate constant involving rate constants and concentrations of ligands. Dependence of k_0 on the concentration of an entering ligand 1-MeIm at various temperatures is shown in Figure 1, for pyridine, quinoline, and triphenylphosphine as leaving ligands. In Figure 2 is shown the contribution of free L in the bulk solution to rates as a function of the concentration of L. The increase of the concentration of L causes the decrease of k_0 value under the constant concentration of X. These features can be interpreted to imply a dissociative mechanism (eq 3 and 4). By applying the steady-state approximation to the Cr(TPP)(Cl) intermediate and knowing negligible k_4 path from the values of K, we obtained eq 5 as the conditional first-order rate constant

$$\mathrm{Cr(TPP)(Cl)(L)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cr(TPP)(Cl)} + \mathrm{L} \quad (3)$$

$$\mathrm{Cr(TPP)(Cl)} + \text{1-MeIm} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{Cr(TPP)(Cl)(1\text{-}MeIm)} \quad (4)$$

$$k_0 = k_1[\text{1-MeIm}](k_2[\mathrm{L}]/k_3 + [\text{1-MeIm}])^{-1} \quad (5)$$

Enthalpies ΔH^* and entropies ΔS^* of activation were estimated by fitting the variable-temperature data at ambient pressure to eq 5 and the Eyring equation simultaneously with a nonlinear least-squares program and are listed in Table I.

Although we attempted to follow the reaction of five-coordinated Cr(TPP)(Cl) with triphenylphosphine of 2×10^{-3} M by monitoring the absorbance change after mixing the toluene solutions of Cr(TPP)(Cl) and triphenylphosphine by using the stopped-flow apparatus, the reaction was too fast to be monitored. This result indicates that the second-order rate constant k_2 exceeds 1×10^7 M^{-1} s^{-1}.

The pressure effect on the substitution reaction was measured under various pressures up to 100 MPa. Figure 3 shows the pressure dependence of k_0 for three reaction systems. Activation volumes ΔV^* were estimated by analyzing all variable-pressure data for each reaction system simultaneously with eq 5 and 6,

$$k_i = k_i^0 \exp(-\Delta V_i^* P/RT) \quad (6)$$

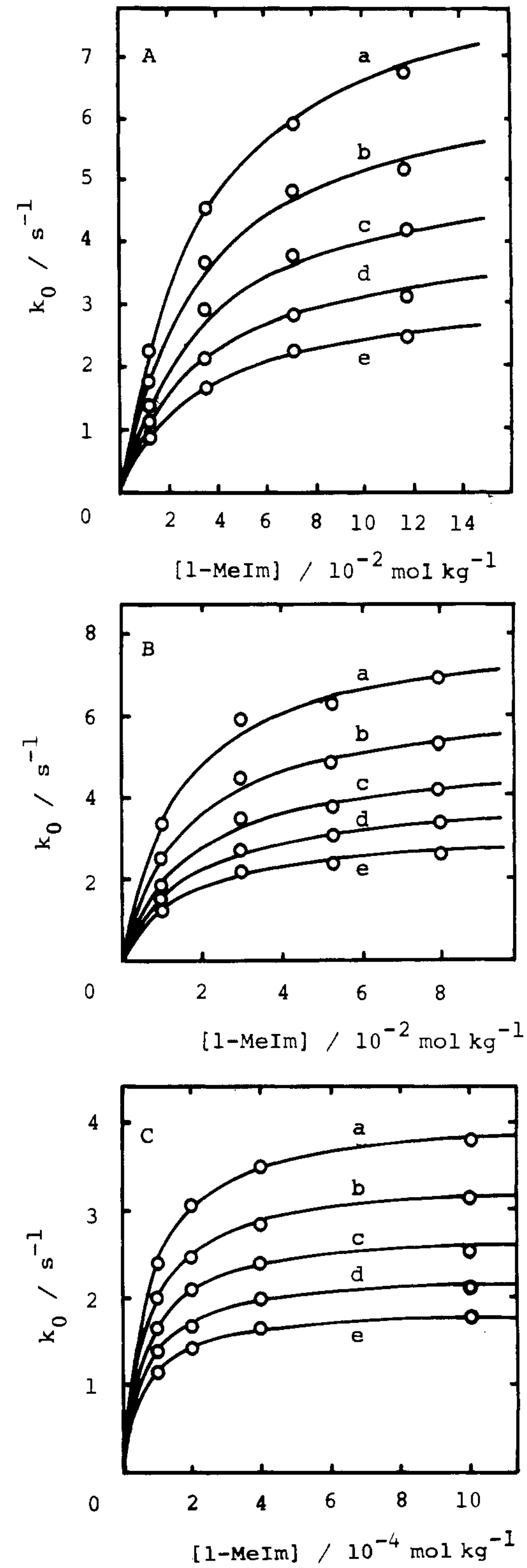

Figure 3. Dependence of the conditional first-order rate constant k_0 on the concentration of 1-methylimidazole under various pressures at 25.0 °C: (A) [CrTPP] = (5.45–7.47) × 10^{-6} mol kg^{-1}, [py] = 3.90 × 10^{-2} mol kg^{-1}; (B) [CrTPP] = (7.86–9.10) × 10^{-6} mol kg^{-1}, [Qui] = 0.119 mol kg^{-1}; (C) [CrTPP] = (3.46–5.85) × 10^{-6} mol kg^{-1}, [PPh_3] = 0.119 mol kg^{-1}. Pressures (MPa): (a) 0.1; (b) 24.5; (c) 49.0; (d) 73.6; (e) 98.1. The solid curves were depicted by using the activation parameters obtained.

where k_i^0 is the rate constant of k_i at zero pressure (i = 1, 2, 3). Values of k_1^0 and k_2^0/k_3^0 were in close agreement with those obtained at ambient pressure. Obtained ΔV^* values are listed in Table I.

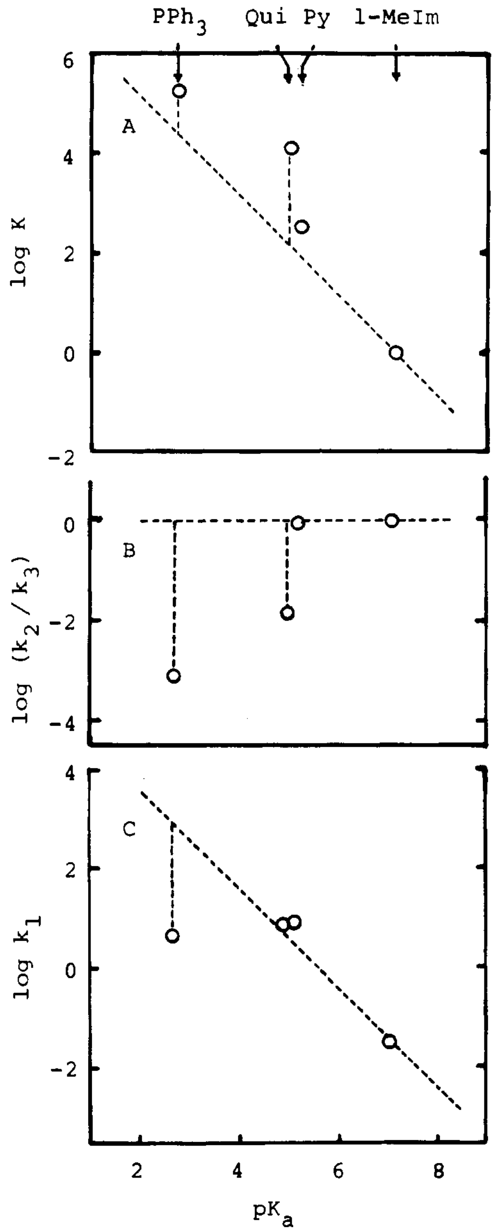

Figure 4. Correlation between pK_a and equilibrium constants and rate constants. The dotted straight lines with the slope of negative unity in A and C and with the slope of zero in B were drawn through the data points for 1-MeIm. k_4 for 1-MeIm corresponds to k_1 for the other systems.

The rate constant (k_4) of the dissociation of 1-MeIm from Cr(TPP)(Cl)(1-MeIm) has not been measured directly in the present work, but the value can be estimated with the following relationship: $K = k_1k_3k_2^{-1}k_4^{-1}$. The k_4 value at 25 °C is obtained as $(2.8 \pm 0.3) \times 10^{-2}\ s^{-1}$, $(3.6 \pm 0.4) \times 10^{-2}\ s^{-1}$, and $(3.6 \pm 0.4) \times 10^{-2}\ s^{-1}$ for the py, Qui, and PPh_3 systems, respectively, giving the average value of $(3.3 \pm 0.5) \times 10^{-2}\ s^{-1}$.

Discussion

In Figure 4 are plotted logarithmic values of k_1, k_2/k_3, and K against the pK_a value of the nucleophile conjugate acid (LH^+) (pK_a = 2.73 (PPh_3H^+),[23] 4.97 ($QuiH^+$), 5.31 (pyH^+), 7.06 ($1\text{-}MeImH^+$)). The equilibrium constants (K) for substitution reaction of leaving ligands by 1-MeIm decrease in the order PPh_3 > Qui > py > 1-MeIm. This is also the order of increase in the proton basicity of nucleophile L (see Figure 4A). Thus, the trend suggests that the Cr(III) center is quite hard and that σ-bonding involving the ligand L is probably predominant.

The ligand uptake by the five-coordinate intermediate Cr(TPP)(Cl), which is represented as the k_2 path for the py, Qui, and PPh_3 systems and as the k_3 path for the reaction with 1-MeIm, is thought to be very fast ($>10^7\ M^{-1}\ s^{-1}$). In the Qui and PPh_3 systems the rate constants of this process are smaller than those of the py and 1-MeIm systems (Figure 4B). The activation entropy of the k_2 path of the Qui system, normalized by the value for 1-MeIm, is smaller than that of the py system by about 38 $J\ K^{-1}\ mol^{-1}$, while the activation enthalpies are similar to each other for the two systems. Furthermore, the k_2 process for PPh_3 is significantly slower: large entering ligands may not favor the bimolecular reaction due to the low probability of relative geometrical arrangement of the colliding molecules, and in addition the $\Delta H^{\ddagger}$ value for PPh_3 higher than that for 1-MeIm by about 6 $kJ\ mol^{-1}$ implies that the five-coordinate intermediate Cr(TPP)(Cl) energetically prefers 1-MeIm to PPh_3.

The k_1 and k_4 paths are for the cleavage of the axial bond between Cr and nitrogen or phosphorus atoms of the leaving ligand in Cr(TPP)(Cl)(L). The rate constant for axial ligand dissociation is parallel with pK_a values of ligands (Qui, py, and 1-MeIm) that have nitrogen atom as a donor atom, while the PPh_3 system is an exception (see Figure 4C). Such a correlation is expected only among the similar ligands. The relative inertness of the Cr–P bond indicates not only σ-bond but also π-bond character.

Structural features of the transition state for the k_1 path will be discussed on the basis of the activation volume. To a first approximation, the activation volume of the limiting dissociative reaction can be given as the product of the cross section of the leaving ligand (S) and the elongation of the bond in the course to the transition state ($\Delta r^{\ddagger}$): $\Delta V^{\ddagger} = S\Delta r^{\ddagger}$.[24-27] Cross sections of ligands with respect to the axis of the bond to the central metal ion were estimated by using the molecular models using van der Waals radii. The cross sections have been evaluated as 21 $Å^2$ for pyridine, 30 $Å^2$ for quinoline, and 90 $Å^2$ for triphenylphosphine. If the axial ligands could rotate with respect to the bond axis between the central metal and the ligand, corresponding evaluated cross sections may increase to be 31 $Å^2$, 90 $Å^2$, and 130 $Å^2$, respectively. On the above assumptions, the extent of elongation of the bond of the leaving ligand in the transition state is calculated to be 2.0 Å (1.4 Å), 1.4 Å (0.5 Å), and 0.4 Å (0.3 Å), respectively, where figures in parentheses correspond to $\Delta r^{\ddagger\prime}$ values for the situation of rotation of the axial ligands. However, since in the case of the quinoline complex a steric repulsion exists between the electron cloud of the porphyrin molecule and the 8-hydrogen atom of quinoline, the bond between the nitrogen atom of quinoline and the central chromium ion is bent and the quinoline does not rotate around the bond axis, while the pyridine at the axial site should easily rotate. Therefore, the elongation of the Cr–N bond in the transition state for both the py and Qui systems may be $\Delta r^{\ddagger}$ = ca. 1.4 Å. On the other hand, in the case of PPh_3 the extent of elongation is much shorter (0.3–0.4 Å). In fact, the different in the elongation may reflect the fact that the chromium–phosphorus bond (ca. 2.4 Å)[28,29] is significantly longer than the chromium–nitrogen bond (ca. 2.1 Å).[30,31]

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(23) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985–987.

(24) le Noble, W. J. *J. Chem. Educ.* **1967**, *44*, 729–739.

(25) Stranks, D. R.; Vanderhoek, N. *Inorg. Chem.* **1976**, *15*, 2645–2648.

(26) Brower, K. R.; Chen, T. *Inorg. Chem.* **1973**, *12*, 2198–2199.

(27) Spitzer, U.; van Eldik, R. *Inorg. Chem.* **1982**, *21*, 4008–4014.

(28) Gray, L. R.; Hale, A. L.; Levason, W.; McCullough, F. P.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1984**, 47–53.

(29) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265–272.

(30) Abrams, M. J.; Faggiani, R.; Lock, C. J. L. *Inorg, Chim. Acta* **1985**, *106*, 69–74.

(31) Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 681–682.