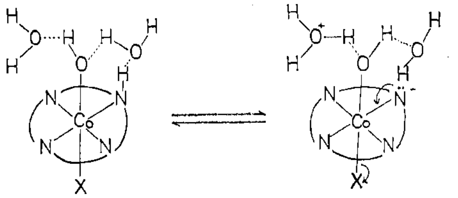
course of exchange, an "internal amido conjugative base" is momentarily generated. The amido group,



NH_2^-, which is cis to the leaving group can now facilitate a dissociative reaction and profitably stabilize a tetragonal-pyramidal intermediate. This mechanism may, therefore, put the aquation rate of trans hydroxo complexes qualitatively midway between the rates of the base hydrolysis and aquation of other Co(III)-amine complexes. It is interesting to note that the 7.5 times increase in the aquation rate at 25° of *trans*-Co(cyclam)OHCl$^+$ compared to that of *trans*-Co(en)$_2$OHCl$^+$ agrees very well with the 8.0 times increase in the rate of base hydrolysis.[6,16] This high degree of consistency suggests that both types of reactions may very well proceed by the same mechanism. In the above comparison, the acid dissociation constants (of the amino proton) of the complexes would have been canceled out, thus making their difference unimportant in the above discussion.

Acknowledgments.—We thank Professor D. S. Payne for his interest and the Committee on Higher Degrees and Research Grants of the University of Hong Kong for financial support.

Contribution from the Department of Chemistry,
State University of New York at Binghamton, Binghamton, New York 13901

Substitution Reactions of Metallic Complexes of β,β',β''-Triaminotriethylamine. V. Kinetics of Acid Hydrolysis of Difluoro(triaminotriethylamine)cobalt(III)Ion[1]

By KING-WEN KUO and STANLEY K. MADAN*

Received June 9, 1970

The kinetics of the primary acid hydrolysis reaction of $[Co(tren)F_2]^+$ ion [tren = β,β',β''-triaminotriethylamine, $N(CH_2CH_2NH_2)_3$] were studied in both neutral and acidic aqueous solutions. In acidic solutions, the reaction proceeded *via* an acid-independent pathway and also *via* an acid-catalyzed pathway involving an equilibrium between $Co(tren)F_2^+$ and $Co(tren)FFH^{2+}$ ions. The rate of the reaction is described by the rate law $-dC_t/dt = \{(k_0 + k_HK_{eq}[H^+])/(1 + K_{eq}[H^+])\}C_t$, where C_t is the total concentration of the complex in both protonated and nonprotonated forms, k_0 and k_H are the first-order rate constants for the acid hydrolysis reaction of the nonprotonated complex and protonated complex, respectively, and K_{eq} is the equilibrium constant for the protonation reaction. At 25.0°, the value of k_0 is 9.0×10^{-6} sec^{-1}, and the product k_HK_{eq} at ionic strength 0.5 *M* is 3.5×10^{-3} sec^{-1} M^{-1}. The activation parameters were calculated: $\Delta H^{\ddagger} = 22.3 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.5 \pm 2.0$ cal deg^{-1} mol^{-1} for the acid-independent path (k_0); $\Delta H^{\ddagger} = 21.0 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2.3 \pm 1$ cal deg^{-1} mol^{-1} for the acid-catalyzed path (k_HK_{eq}) at ionic strength 0.5 *M*.

Introduction

Extensive investigations have been carried out on the kinetics of substitution reactions of cobalt(III) complexes of the type $Co(A)_4X_2^+$ where A represents a nonreplaceable monodentate or polydentate amine ligand and X represents the replaceable group, such as F^-, Cl^-, Br^-, and NO_2^-.[2]

In this laboratory we have been interested in the synthesis and kinetics of substitution reactions of octahedral cobalt(III) complexes of β,β',β''-triaminotriethylamine (tren).[3] As part of our study of the kinetics of acid hydrolysis reactions of dihalotriaminotriethylaminecobalt(III) complexes, we have investigated in this work the primary acid hydrolysis reaction of the difluoro(triaminotriethylamine)cobalt(III) ion. The results are presented and compared with similar data for the dichloro- and dibromo(triaminotriethylamine)cobalt(III) complexes and with those of the other fluoro-amine complexes.

Experimental Section

Materials.—Deionized water and reagent grade chemicals were used in all procedures. Sodium perchlorate used to adjust the ionic strength was anhydrous reagent grade quality. The deuterium oxide was obtained from Columbia Chemicals Co., Inc., and had an assay of 99.77%.

Preparation of Compounds. (1) **β,β',β''-Triaminotriethylamine Trihydrochloride.**—This compound was prepared by the method of Paoletti, Ciampolini, and Sacconi.[4]

(2) **Carbonato(triaminotriethylamine)cobalt(III) Perchlorate Monohydrate.**—The method of Scheidegger[5] was used for the preparation of this compound. *Anal.* Calcd for $[Co(tren)CO_3]ClO_4 \cdot H_2O$: C, 21.95; H, 5.23; N, 14.62; ClO_4, 26.00. Found: C, 22.53; H, 5.45; N, 14.40; ClO_4, 26.10.

(3) **Difluoro(triaminotriethylamine)cobalt(III) Perchlorate**

---

* Author to whom inquiries should be addressed.

[1] Presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 15, 1970.

[2] For review see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967.

[3] (a) Part I: S. K. Madan, W. M. Reiff, and J. C. Bailar, Jr., *Inorg. Chem.*, **4**, 1366 (1965); (b) Part II: S. K. Madan and J. Peone, Jr., *ibid.*, **6**, 463 (1967); (c) Part III: S. K. Madan and J. Peone, Jr., *ibid.*, **7**, 824 (1968); (d) Part IV: W. V. Miller and S. K Madan, *ibid.*, **9**, 2362 (1970).

[4] P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

[5] H. A. Scheidegger, Doctoral Thesis, E.T.H., Zurich, 1966.

Monohydrate.—In a polyethylene container, finely powdered $[Co(tren)CO_3]ClO_4 \cdot H_2O$ (2 g) was suspended in anhydrous ether (300 ml), and dry HF gas was bubbled into the solution with vigorous magnetic stirring at 10–15°. After the color change of the solid from red to reddish purple was completed (about 30 min), the solution was covered and stirring was continued for at least 12 hr at room temperature. The resulting fine reddish purple precipitate was collected by filtration, washed with a large quantity of ether, and dried *in vacuo* at room temperature. *Anal.* Calcd for $[Co(tren)F_2]ClO_4 \cdot H_2O$: C, 20.00; H, 5.56; N, 15.15; ClO_4, 27.60; F, 10.56. Found: C, 20.16; H, 5.44; N, 15.50; ClO_4, 27.50; F, 10.34.

(4) ***cis*-Difluorobis(ethylenediamine)cobalt(III) Nitrate.**—This compound was prepared according to a procedure described by Matoush and Basolo.[6] The electronic absorption spectrum of this compound obtained in neutral aqueous solution at room temperature exhibited absorption maxima at 510 and 367 nm. The molar absorptivities were 84 and 50 M^{-1} cm^{-1}, respectively. Both the wavelengths and the molar absorptivities of the absorption maxima were in good agreement with those of the reported spectrum of *cis*-$Co(en)_2F_2^+$.[7]

Electronic Absorption Spectra.—The absorption spectra in the 300–700-nm region of various complexes were obtained with a Cary Model 14M recording spectrophotometer and matched cells of 1-cm path length were used.

Kinetic Measurements. (a) Spectrophotometric Method.—The acid hydrolysis reaction of $Co(tren)F_2^+$ was carried out in covered 1-cm quartz spectrophotometric cells. Procedures used for handling solutions and for taking spectrophotometric measurements were the same as described previously.[3a] The change in the visible absorption spectrum of $Co(tren)F_2^+$ during the acid hydrolysisre action in 0.118 *M* perchloric acid showed three well-defined isosbestic points at 520, 417, and 359 nm. The wavelength chosen for this kinetic study was 550 nm because of the large difference between the molar absorptivities of the reactant and the product at this wavelength. The reaction rate was also determined at 600 nm. At 25.0° and in 0.118 *M* perchloric acid solution, the rate constants determined at 550 and 600 nm are 3.2×10^{-4} and 3.2×10^{-4} sec^{-1}, respectively, and show good agreement. Consecutive runs always agreed to within 3%.

(b) Fluoride Ion Electrode Method.—The reaction in the neutral solution (pH 6.5) at 25.0° was also followed by determining the released fluoride ion concentration. For this method a fluoride ion activity electrode (Model 94-09, Orion Research, Inc.) was used with a standard calomel reference electrode and a Beckman Expandomatic SS-2 pH meter. Standard sodium fluoride solutions were used to calibrate the fluoride ion electrode. The reaction mixture was immersed in a thermostat during the course of the reaction. The concentration of the complex was 3.0×10^{-3} *M*. A plot of log $[(a - x)/a]$ *vs.* time, where a and x are formal concentration of complex and released fluoride ion, respectively, gave a straight line whose slope was used to obtain the rate constant. Results show a relative error of approximately 1% between the two methods: at pH 6.5 and 25.0° in H_2O, by fluoride ion electrode method a rate constant of 9.1×10^{-6} sec^{-1} was obtained *vs.* a rate constant of 9.0×10^{-6} sec^{-1} at 550 nm by the spectrophotometric procedure. Based on loss of one fluoride per molecule of the complex, the measured concentration of uncomplexed fluoride ion after 7 half-lives indicates that the primary acid hydrolysis reaction of $Co(tren)F_2^+$ is at least 98% complete.

Results and Discussion

As in the case of most metallic complexes containing coordinated fluoride ion,[8-11] the acid hydrolysis of $Co(tren)F_2^+$ reaction was found to be acid catalyzed, whereas the corresponding dichloro and dibromo complexes showed no hydrogen ion concentration dependence of the acid hydrolysis reaction rate at a pH value below 6.[3a,b]

The pseudo-first-order rate constants for the primary acid hydrolysis reaction of $Co(tren)F_2^+$ ion in acidic solution at 25.0° and ionic strengths 1.0, 3.0, and 4.0 *M* are presented in Table I.

TABLE I

VALUES OF THE PSEUDO-FIRST-ORDER RATE CONSTANTS MEASURED AT VARIOUS CONCENTRATIONS OF PERCHLORIC ACID AND IONIC STRENGTHS[a]

$\mu = 1.0\ M^b$		$\mu = 3.0\ M^b$		$\mu = 4.0\ M^b$	
$[HClO_4]$, *M*	10^4k_{obsd}, sec^{-1}	$[HClO_4]$, *M*	10^3k_{obsd}, sec^{-1}	$[HClO_4]$, *M*	10^3k_{obsd}, sec^{-1}
0.093	4.6	0.186	1.7	0.186	2.7
0.186	8.7	0.371	3.5	0.371	4.7
0.371	17	0.557	5.2	0.557	7.8
0.557	25	0.742	7.4	0.742	9.7
0.742	32	0.928	8.8	0.928	12
0.928	40	1.48	12	1.85	20
		1.85	15	2.78	25
		2.41	18	3.71	32
		2.78	19		

[a] $[Co(tren)F_2^+] = 3.0 \times 10^{-3}$ *M* at 25.0°. [b] Ionic strength maintained with sodium perchlorate.

The plots of the pseudo-first-order rate constant, k_{obsd}, *vs.* $[H^+]$ have been made (Figures 1 and 2). The positive intercept obtained by extrapolating to zero hydrogen ion concentration indicates the presence of a reaction pathway, the reaction rate of which is independent of the hydrogen ion concentration from the reaction medium and for which the stoichiometry can be represented by

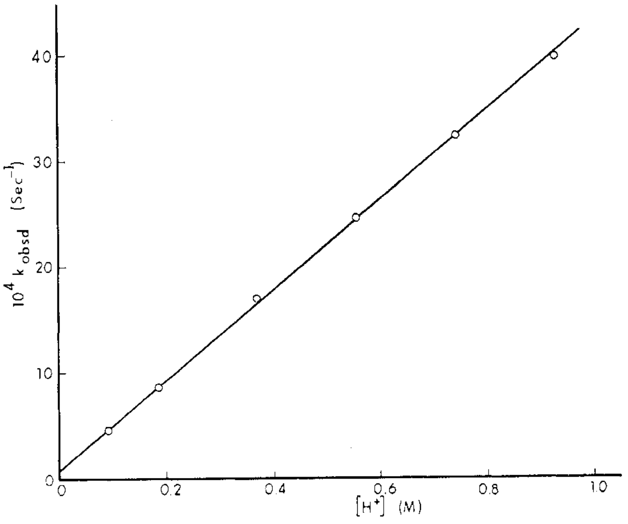


Figure 1.—Dependence on hydrogen ion concentration of the pseudo-first-order rate constant for the primary acid hydrolysis of $Co(tren)F_2^+$ ion at 25.0° and an ionic strength of 1.0 *M*.

$$Co(tren)F_2^+ + H_2O \xrightarrow{k_0} Co(tren)FH_2O^{2+} + F^- \qquad (1)$$

where k_0 is the first-order rate constant of reaction 1. The rate of the second pathway depends on the hydro-

---

[6] W. R. Matoush and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 3972 (1956).

[7] W. R. Matoush, Doctoral Dissertation, Northwestern University, 1955.

[8] F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Amer. Chem. Soc.*, **78**, 4883 (1956).

[9] S. C. Chan, *J. Chem. Soc.*, 2375 (1964).

[10] K. R. A. Fehrmann and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 1276 (1961).

[11] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

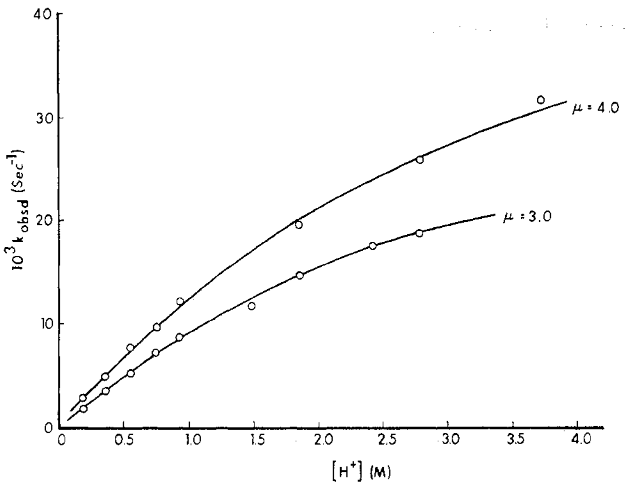


Figure 2.—Dependence on hydrogen ion concentration of the pseudo-first-order rate constant for the primary acid hydrolysis reaction of $Co(tren)F_2^+$ at 25.0° and ionic strengths of 3.0 and 4.0 *M*.

gen ion concentration and presumably involves a rapid and reversible acid–base preequilibrium followed by a slower acid hydrolysis of the protonated complex

$$Co(tren)F_2^+ + H^+ \underset{}{\overset{K_{eq},\ \text{fast}}{\rightleftarrows}} Co(tren)FFH^{2+} \qquad (2)$$

$$Co(tren)FFH^{2+} + H_2O \xrightarrow[\text{slow}]{k_H} Co(tren)FH_2O^{2+} + HF \qquad (3)$$

where K_{eq} is the equilibrium constant for the protonation reaction 2 and k_H is the first-order rate constant for reaction 3. Under the pseudo-first-order condition of given hydrogen ion concentration, combination of eq 1–3 leads to the rate law

$$\frac{-dC_t}{dt} = k_{obsd}C_t = \frac{k_0 + k_H K_{eq}[H^+]}{1 + K_{eq}[H^+]} C_t \qquad (4)$$

where C_t represents the total concentration of the complex in both protonated and nonprotonated forms. Equation 4 reduces to

$$\frac{-dC_t}{dt} = k_{obsd}C_t = (k_0 + k_H K_{eq}[H^+])C_t \qquad (5)$$

when $K_{eq}[H^+] \ll 1$. This latter expression, eq 5, is essentially correct, as is shown by the straight line obtained from a plot of k_{obsd} *vs.* $[H^+]$ at 25.0° and an ionic strength of 1.0 *M* (Figure 1). However, a nonlinearity at higher ionic strengths (Figure 2) is consistent with eq 4. A similar behavior has been observed in other related systems.[12-14] This is believed to be a result of both the high acid concentration and the greater value of K_{eq} at high ionic strength, since their product appears in the denominator of the rate equation (eq 4).

The ionic strength dependence of the primary acid hydrolysis reaction of $Co(tren)F_2^+$ ion was also studied in both 0.590 *M* $HClO_4$ at 25.0° and neutral solution (pH 6.5) at 39.5°. The data obtained are given in Table II. It was found that in the acidic solution the reaction rate increases with increasing ionic strength.

TABLE II

VALUES OF THE PSEUDO-FIRST-ORDER RATE CONSTANT MEASURED AT A VARIETY OF IONIC STRENGTHS[a]

In 0.59 *M* $HClO_4$ and at 25.0°		In neutral soln and at 39.5°	
μ^b	$10^3 k_{obsd}$, sec^{-1}	μ^b	$10^5 k_{obsd}$, sec^{-1}
0.59	2.4	*c*	6.4
0.69	2.7	0.5	6.4
1.09	2.9	1.0	6.4
1.59	3.5	2.0	6.4
2.09	4.1		
2.59	4.6		

[a] $[Co(tren)F_2^+] = 1.5 \times 10^{-3}$ *M*. [b] Ionic strength maintained with sodium perchlorate. [c] No sodium perchlorate added.

However, there is no significant ionic strength effect upon the acid hydrolysis reaction rate in the neutral solution. Although there are no data available for the acid hydrolysis reaction of *cis*-$Co(en)_2F_2^+$ at different values of μ, no ionic strength effect was observed in the acid hydrolysis reaction rate of *trans*-$Co(en)_2F_2^+$ ion in neutral solution at different concentrations of KNO_3.[8] We prepared *cis*-$[Co(en)_2F_2]NO_3$ and the primary acid hydrolysis reaction rates were determined in 0.460 *M* $HClO_4$ with different concentrations of $NaClO_4$. The result indicates that there is a significant increase of rate with increasing ionic strength. Recently, Wakefield and Schaap[13] also found that the rate of the acid hydrolysis reaction of $Cr(H_2O)_5CN^{2+}$ at a given acid concentration increases markedly with increasing ionic strength. This observation was attributed to the larger value of K_{eq} at higher ionic strength. Because of the very low hydrogen ion concentration in the neutral solution, eq 4 reduces to

$$\frac{-dC_t}{dt} = k_{obsd}C_t \approx k_0 C_t \qquad (6)$$

Therefore, k_{obsd} should not be greatly influenced by the ionic strength of the reaction medium.

In order to substantiate further the reaction mechanism, the rate of acid hydrolysis of $Co(tren)F_2^+$ was measured in D_2O with *p*-toluenesulfonic acid added to adjust the acidity. It was found that in 0.2 *M* D^+ the hydrolysis rate constant of 1.0×10^{-3} sec^{-1} was nearly twice as large as in H_2O (6.5×10^{-4} sec^{-1}) under identical conditions. This effect is due to the weaker acidity of the protonated complex in D_2O relative to H_2O and has also been observed by Basolo and coworkers in the similar hydrolysis reaction of *trans*-$Co(en)_2F_2^+$.[8]

The rate constants were also determined at various temperatures in both neutral solution and acidic solutions at constant ionic strength. The data obtained are presented in Table III. At constant temperature and low ionic strength (0.5 *M*), the plots of the observed rate constant, k_{obsd}, against hydrogen ion concentration were straight lines. The least-squares best slopes, corresponding to the value of $k_H K_{eq}$, calculated by using a computer program at 25.0, 35.0, and 40.0° are 3.5×10^{-3}, 1.2×10^{-2}, and 2.0×10^{-2} sec^{-1} M^{-1}, respectively.

The activation parameters corresponding to k_0 and $k_H K_{eq}$ were obtained from linear Arrhenius plots over the ranges 25.0–60.0 and 25.0–40.0°, respectively.

---

(12) F. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).
(13) D. K. Wakefield and W. B. Schaap, *ibid.*, **8**, 512 (1969).
(14) D. K. Wakefield and W. B. Schaap, *ibid.*, **8**, 811 (1969).

TABLE III

PSEUDO-FIRST-ORDER RATE CONSTANTS IN NEUTRAL AND ACIDIC SOLUTIONS AT VARIOUS TEMPERATURES[a]

In neutral soln[b]		In acidic soln[c]			
			25°	35°	40°
Temp, °C	$10^5 k_0$, sec^{-1}	$[HClO_4]$, M	$10^4 k_{obsd}$, sec^{-1}	$10^4 k_{obsd}$, sec^{-1}	$10^3 k_{obsd}$, sec^{-1}
25.0	0.90	0.0453	2.0	6.4	1.1
39.5	6.4	0.136	5.2	17	3.0
49.7	19	0.226	8.3	28	4.8
59.7	59	0.317	11	37	6.7
		0.453	16	54	9.4

[a] $[Co(tren)F_2]^+ = 3.0 \times 10^{-3}$ M. [b] No $HClO_4$ or $NaClO_4$ was added. [c] Ionic strength of reaction medium (0.5 M) maintained with $NaClO_4$.

For the acid-independent path (k_0), the activation parameters are $\Delta H^{\ddagger} = 22.3 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.5 \pm 2$ cal deg^{-1} mol^{-1}, while for the acid-catalyzed path ($k_H K_{eq}$), the parameters are $\Delta H^{\ddagger} = 21.0 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2.3 \pm 1.0$ cal deg^{-1} mol^{-1}.

In the neutral solution, it was found that the acid hydrolysis reaction rate of $Co(tren)F_2^+$ ion at 25.0° (9.0×10^{-6} sec^{-1}) was about three times greater than that of *cis*-$Co(en)_2F_2^+$ ion (3.06×10^{-6} sec^{-1}).[7] Previous studies[3a,b] have indicated that the greater rates of acid hydrolysis of dichloro- and dibromo(triaminotriethylamine)cobalt(III) ions, as compared with the rates of corresponding complexes of bis(ethylenediamine), are due to steric strain produced by the peculiar geometry of the tren complex. The same conclusion may be drawn with regard to the $Co(tren)F_2^+$ ion. The positive intercept at zero hydrogen ion concentration in the plot of k_{obsd} *vs.* $[H^+]$ is due to the contribution from the acid-independent pathway to the overall rate. However, only a one-term rate law

$$k_{obsd} = k_H K_{eq}[H^+] \qquad (7)$$

was found for the acid hydrolysis reaction in acidic solution of other fluoro-containing amminecobalt(III) complexes,[8,9] where the acid-independent pathway is not significant.

On comparison of the acid-independent acid hydrolysis reaction rate of $Co(tren)F_2^+$ ion at 25.0° to those of $Co(tren)Cl_2^+$[3a] and $Co(tren)Br_2^+$[3b] ions (2.96×10^{-3} and 2.81×10^{-2} sec^{-1}, respectively), it is observed that the rate increases in the order F < Cl < Br. This was also observed for other haloamminecobalt(III) complexes.[8,9] The faster rate observed for the acid-catalyzed reaction is due to a weakening of the Co–F bond as a result of hydrogen bonding to form Co–FH.

Acknowledgment.—The authors wish to thank Mr. Warren V. Miller for helpful discussions and Mr. T. Lyons for drawing the figures.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

Kinetics and Mechanism of the Reactions of Di-μ-carbonyl-bis(cyclopentadienyl)dinickel(0) with Monodentate Ligands

BY PAUL C. ELLGEN

Received June 17, 1970

The ligands carbon monoxide, triphenylarsine, triphenyl phosphite, triphenylphosphine, ethyldiphenylphosphine, and tri-*n*-butylphosphine react with di-μ-carbonyl-bis(cyclopentadienyl)dinickel(0) to give nickelocene and diliganddicarbonylnickel(0) (eq 1). The kinetics of these reactions have been studied by following the carbonyl region infrared spectra of reaction mixtures or by manometric observation of carbon monoxide absorption. Complicated behavior is observed with tri-*n*-butylphosphine. The dependence on carbon monoxide concentration was not studied, but reaction according to (1) is much slower than the rate reported for carbon monoxide exchange. For the other ligands studied, a second-order rate law, first order in each reactant, is observed: $-d[Ni_2(CO)_2(C_5H_5)_2]/dt = k[Ni_2(CO)_2(C_5H_5)_2][L]$. The reaction mechanism is discussed. A complex mechanism can be shown to be quantitatively consistent with the data for the reaction with tri-*n*-butylphosphine.

Introduction

While reactions of tetracarbonylnickel(0) with monodentate ligands have been extensively studied,[1-4] there are few reports of such reactions with di-μ-carbonyl-bis(cyclopentadienyl)dinickel(0). King has shown that tris(dimethylamino)phosphine (tdp) reacts with $Ni_2(CO)_2(C_5H_5)_2$ to give $Ni(CO)_2(tdp)_2$ and nickelocene[5] (eq 1, L = tdp), while a recent report[6] describes the reaction of $Ni_2(CO)_2(C_5H_5)_2$ with bis(diphenylphosphino)acetylene to give $Ni_2(CO)_2[(C_6H_5)_2PC_2P(C_6H_5)_2]_3$. Interestingly, both reactions involve the displacement of a cyclopentadienyl moiety from nickel. It has been found (*vide infra*) that monodentate ligands (phos-

$$Ni_2(CO)_2(C_5H_5)_2 + 2L \longrightarrow Ni(CO)_2L_2 + Ni(C_5H_5)_2 \qquad (1)$$

---

(1) L. S. Meriwether and M. L. Fiene, *J. Amer. Chem. Soc.*, **81**, 4200 (1959).

(2) J. P. Day, F. Basolo, R. G. Pearson, L. F. Kangas, and P. M. Henry, *ibid.*, **90**, 1925 (1968).

(3) J. P. Day, F. Basolo, and R. G. Pearson, *ibid.*, **90**, 6927 (1968).

(4) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(5) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(6) A. J. Carty, A. Efraty, and T. W. Ng, *Can. J. Chem.*, **47**, 1429 (1969).