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Kinetics of the Addition Reactions of Tetracyanoethylene to $MX(CO)L_2$ (M = Rh, Ir) Type Complexes

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Received October 31, 1975　AIC50790F

The kinetics of the addition reactions of tetracyanoethylene (TCNE) to the complexes *trans*-$RhX(CO)L_2$ (X = Cl, L = $P(p\text{-}CH_3OC_6H_4)_3$, $P(p\text{-}CH_3C_6H_4)_3$, PPh_3, $P(p\text{-}ClC_6H_4)_3$, PPh_2Me, $AsPh_3$, $P(O\text{-}o\text{-}CH_3C_6H_4)_3$, $P(OPh)_3$; X = Br, I, NCO, NCS, L = PPh_3), $RhCl(CS)(PPh_3)_2$, and *trans*-$IrCl(CO)(PPh_3)_2$ in acetone, tetrahydrofuran, or benzonitrile, were investigated employing stopped-flow techniques. The kinetics were found to obey the rate law for a reversible reaction, $-d[MX(CO)L_2]/dt = k_2[MX(CO)L_2][TCNE] - k_{-1}[(TCNE)MX(CO)L_2]$, where k_2 and k_{-1} are the forward second-order and the backward first-order rate constants, respectively. The rate constant k_2 increases in the following orders of the anionic ligand X for *trans*-$RhX(CO)(PPh_3)_2$ and of the neutral ligand L for *trans*-$RhCl(CO)L_2$ respectively: X = NCS $\simeq$ Br < Cl $\simeq$ NCO and L = $P(O\text{-}o\text{-}CH_3C_6H_4)_3 < P(p\text{-}ClC_6H_4)_3 < PPh_3 < P(OPh)_3 < P(p\text{-}CH_3C_6H_4)_3 < P(p\text{-}CH_3OC_6H_4)_3 < AsPh_3 \ll PPh_2Me$. $IrCl(CO)(PPh_3)_2$ reacts with TCNE about 9 times faster than $RhCl(CO)(PPh_3)_2$ in acetone at 25 °C. The k_2 value also increases with increasing solvent polarity. Plots of log k_2 and log k_{-1} against log K ($=k_2/k_{-1}$) give straight lines with slopes of 0.55 and −0.45, respectively. In addition, the formation of the TCNE anion radical was observed in some reactions in benzonitrile or acetone. From these results, it is concluded that the reaction involves a dipolar activated complex formed by the nucleophilic attack of the metal complex on TCNE.

Introduction

The metal–olefin binding process plays an important role in homogeneous catalytic reactions by transition metal complexes, such as olefin hydrogenation, hydroformylation, and olefin dimerization.[1] As a model compound for the intermediate in these reactions, cyanoolefin complexes of transition metals have received considerable attention in the preparative and structural studies.[2] Related quantitative studies on the metal–olefin interaction have so far been made for the reactions of *trans*-$IrCl(CO)(PPh_3)_2$ with *trans*-$CF_3(CN)C{=}C(CF_3)CN$[3] and *trans*-$CH_3OCOCH{=}CHCOOCH_3$[4] and of $[Rh(RNC)_2(PR'_3)_2]^+$ with tetracyanoethylene (TCNE).[5]

The present work was undertaken to elucidate the effect of ligands attached to the metal atom on the rate of reaction of TCNE toward a series of $MX(CO)L_2$ (M = Rh, Ir) type complexes. TCNE was chosen for the olefin which not only affords stable metal complexes but also in some cases acts as a one-electron oxidizing reagent.[6,7]

Experimental Section

Materials and Instrumentation. $RhCl_3{\cdot}3H_2O$ and $(NH_4)_2IrCl_6$ were of reagent grade and used as supplied. Commercial TCNE was sublimed twice. Para-substituted tertiary phosphines[8] and $P(O\text{-}o\text{-}CH_3C_6H_4)_3$[9] were prepared by literature methods. Solvents were distilled twice and deoxygenated by bubbling N_2 at least for 30 min before use. Acetone was treated with an acidic $KMnO_4$ solution and then a basic $AgNO_3$ solution,[10] followed by drying over Drierite. Tetrahydrofuran (THF) was dried over lithium aluminum hydride, and benzonitrile, over phosphorus pentoxide.

Infrared spectra were recorded in Nujol mulls or in acetone on a Hitachi Perkin-Elmer 225 grating spectrophotometer. Electronic spectra were obtained by using a 1-cm quartz cell on a Hitachi 124 spectrophotometer.

Preparations of Complexes. All experimental manipulations were performed under nitrogen. The complexes *trans*-$RhX(CO)L_2$ (X = Cl, L = $P(p\text{-}CH_3OC_6H_4)_3$, $P(p\text{-}CH_3C_6H_4)_3$, PPh_3, $P(p\text{-}ClC_6H_4)_3$, PPh_2Me, $AsPh_3$; X = Br, I, NCO, NCS, L = PPh_3), $RhCl(CS)(PPh_3)_2$, and *trans*-$IrCl(CO)(PPh_3)_2$ were prepared by literature methods[11] and characterized by melting points, elemental analyses, and ir spectra.

The corresponding tertiary phosphite complexes of rhodium were prepared by an improved method. *o*-Tolyl phosphite (0.84 g, 2.42 mmol) in CH_2Cl_2 (10 ml) was added slowly to $[Rh(C_8H_{12})Cl]_2$ (0.3 g, 0.61 mmol) in CH_2Cl_2 (10 ml) at room temperature. Carbon monoxide was bubbled through the solution for about 5 min, during which time the color changed from orange to yellow. Ethanol (10 ml) was added to the solution and the solvent was partially removed under reduced pressure. The resulting precipitate was separated from the solution and recrystallized from benzene–*n*-hexane to give *trans*-$RhCl(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)_2$ (0.74 g, 70 %), mp 130–132 °C. Anal. Calcd for $C_{43}H_{42}O_7ClP_2Rh$: C, 59.29; H, 4.86. Found: C, 59.43; H, 4.73. *trans*-$RhCl(CO)(P(OPh)_3)_2$ was similarly prepared (90 % yield); mp 157–160 °C. Anal. Calcd for $C_{37}H_{30}O_7ClP_2Rh$: C, 56.47; H, 3.84. Found: C, 56.43; H, 3.84.

Table I. ν(CO) Frequencies of the Rh(I) and Ir(I) Complexes and Their TCNE Adducts, cm^{-1} [a]

Complex	Freq of complex	Freq of TCNE adduct
$RhCl(CO)(PPh_3)_2$	1975	2065
$RhCl(CO)(PPh_2Me)_2$	1972	2064
$RhCl(CO)(AsPh_3)_2$	1973	2061
$RhCl(CO)(P(OPh)_3)_2$	2013	2041
$RhCl(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)_2$	2008	2035
$RhCl(CO)(P(p\text{-}ClC_6H_4)_3)_2$	1982	2080
$RhCl(CO)(P(p\text{-}CH_3C_6H_4)_3)_2$	1972	2061
$RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2$	1972	2057
$RhCl(CS)(PPh_3)_2$	1304[b]	1348[b]
$Rh(NCO)(CO)(PPh_3)_2$	1980	2085
$Rh(NCS)(CO)(PPh_3)_2$	1984	2080
$RhBr(CO)(PPh_3)_2$	1976	2065[c]
$RhI(CO)(PPh_3)_2$	1980	2084[c]
$IrCl(CO)(PPh_3)_2$	1965	2053

[a] In acetone. [b] ν(CS) in CH_2Cl_2. [c] These complexes showed complicated spectra, which have been assigned by comparing with those of other adducts.

Isolation and Identification of the Addition Products. TCNE (45 mg, 0.35 mmol) was added to $RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2$ (0.3 g, 0.34 mmol) in benzene (30 ml) at room temperature. After being stirred for 30 min, the solution was concentrated under reduced pressure. The resulting product was recrystallized from CH_2Cl_2–*n*-hexane to give orange crystals of $RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2(TCNE)$ (0.3 g, 88 %), mp 175–180 °C. Anal. Calcd for $C_{49}H_{24}N_4O_7ClP_2Rh$: C, 58.90; H, 4.23; N, 5.60. Found: C, 58.98; H, 4.01; N, 5.54. Although the addition product of $RhCl(CO)L_2$ (L = $P(OPh)_3$, $P(O\text{-}o\text{-}CH_3C_6H_4)_3$, $P(p\text{-}CH_3C_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$) with TCNE has not been isolated, its existence in solution was ascertained by the high-frequency shifts of the CO stretching band (Table I). Other 1:1 adducts were already isolated and characterized by Baddley[12] or Varshavskii et al.[13]

Kinetic Measurements. Reaction rates were determined using a Union RA-1100 stopped-flow spectrophotometer as described elsewhere.[5] The initial concentration of the metal complexes in solution was in the range 3×10^{-4} to 3×10^{-3} M. The Lambert–Beer law was shown to be valid over this concentration range of $RhCl(CO)(PPh_3)_2$ in acetone and was assumed in other systems. All reactions were carried out under pseudo-first-order conditions, using at least a tenfold excess of TCNE. Restrictions were imposed on the selection of solvents by the low solubility of the parent complex and by the fact that TCNE forms charge-transfer complexes with many

Table II. Values of k_2, k_{-1}, and K for the Reaction of $MX(CO)L_2$ with TCNE in Acetone

Compd	Temp, °C	$10^{-3}k_2$, $M^{-1}\ s^{-1}$	k_{-1}, s^{-1}	$K\ (=k_2/k_{-1})$, M^{-1}
$RhCl(CO)(PPh_3)_2$	15.5	1.97 ± 0.05	3.88 ± 0.44	508 ± 59
$RhCl(CO)(PPh_3)_2$	25.0	2.89 ± 0.10	7.86 ± 0.86	370 ± 43
				(330 ± 40)^c
$RhCl(CO)(PPh_3)_2$^{a}	25.0	1.36 ± 0.12	23.3 ± 0.8	58 ± 5
$RhCl(CO)(PPh_3)_2$^{b}	25.0	7.44 ± 0.30	3.57 ± 1.31	2 000 ± 700
$RhCl(CO)(PPh_3)_2$	34.5	4.48 ± 0.22	22.8 ± 1.52	196 ± 16
$RhBr(CO)(PPh_3)_2$	25.0	0.88 ± 0.08	15.8 ± 0.6	56 ± 5
$Rh(NCS)(CO)(PPh_3)_2$	25.0	0.81 ± 0.05	8.19 ± 0.39	99 ± 7
$Rh(NCO)(CO)(PPh_3)_2$	25.0	2.98 ± 0.10	5.27 ± 0.81	560 ± 90
$RhCl(CO)(AsPh_3)_2$	25.0	146 ± 14^d		
$RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2$	25.0	27.7 ± 1.3	(2.11 ± 0.22)^e	(13 100 ± 1400)^c
$RhCl(CO)(P(p\text{-}CH_3C_6H_4)_3)_2$	25.0	11.4 ± 0.2	(3.48 ± 0.39)^e	3 280 ± 400)^c
$RhCl(CO)(P(p\text{-}ClC_6H_4)_3)_2$	25.0	1.66 ± 0.17	23.9 ± 2.9	69 ± 10
$RhCl(CO)(P(OPh)_3)_2$	25.0	9.37 ± 0.66	81.4 ± 6.6	115 ± 12
$RhCl(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)_2$	25.0	0.92 ± 0.01	26.7 ± 2.3	34 ± 4
$RhCl(CS)(PPh_3)_2$	25.0	3.01 ± 0.12	6.20 ± 0.77	480 ± 62
$IrCl(CO)(PPh_3)_2$	15.2	22.5 ± 0.8^d		
$IrCl(CO)(PPh_3)_2$	25.0	25.2 ± 0.8^d		
$IrCl(CO)(PPh_3)_2$^{a}	25.0	12.2 ± 0.6^d		(140 000)^f
$IrCl(CO)(PPh_3)_2$	35.0	28.0 ± 0.3^d		

[a] In THF. [b] In C_6H_5CN. [c] Obtained spectrophotometrically by the method of N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, 81, 6138 (1959). [d] Obtained by neglecting k_{-1}, which is too small. [e] Calculated from $k_{-1} = k_2/K$. [f] In THF at 30 °C; ref 27.

organic solvents. Thus, kinetic experiments were carried out in acetone, THF, and benzonitrile.

Plots of log ($A_\infty - A_t$) vs. time, where A_t and A_∞ are absorbances at time t and infinite reaction time, showed a good linearity for at least 4 half-lives, and the pseudo-first-order rate constants, k_{obsd}, were calculated by the method of least squares. The rate constants were reproducible within ±5%.

In the interaction of TCNE with $RhCl(CO)(PPh_3)_2$ in benzonitrile and with $RhBr(CO)(PPh_3)_2$ or $RhI(CO)(PPh_3)_2$ in acetone we observed the second reaction, whose rate constants in most cases were 40–200 times smaller than those of the first reaction. The reaction of TCNE with $RhI(CO)(PPh_3)_2$ in acetone was followed between 350 and 500 nm by a Union RA-1300 stopped-flow/rapid-scan spectrophotometer. The result showed that the initial stage of the reaction was dominated by the addition reaction, followed by the formation of the TCNE anion radical, which was confirmed by the occurrence of weak characteristic hyperfine structures of the absorption in the vicinity of 420 nm: 404, 417, 425, 435, 445, 459, 470 nm (the five peaks at the shortest wavelengths were too weak to be observed; lit.[14a] 366, 374, 382, 390, 398, 407, 416, 425, 435, 445, 457, 468 nm). In addition, ESR signals due to the TCNE anion radical ($\langle a_N \rangle$ = 1.56 G; lit.[14b] 1.574 G) were observed in the quick mixing of TCNE with $RhCl(CO)(PPh_3)_2$ in benzonitrile at room temperature. The Guggenheim method was used to determine the rate constants for the initial reaction. In the case of $RhI(CO)(PPh_3)_2$, however, the two consecutive first-order reactions could not completely be separated, because the second reaction was as fast as the first reaction. The formation reaction of the anion radical was not further pursued, since we have been interested in the initial addition reaction.

Results and Discussion

Kinetics. Electronic spectra of $RhCl(CO)(PPh_3)_2$ in acetone with varying amounts of TCNE are shown in Figure 1. A similar equilibrium was found in the systems of $RhCl(CO)L_2$–TCNE (L = $P(p\text{-}CH_3OC_6H_4)_3$ or $P(p\text{-}CH_3C_6H_4)_3$). Thus, the reaction of *trans*-$MX(CO)L_2$ with TCNE is considered to be reversible (eq 1). Plots of the observed rate

$$trans\text{-}MX(CO)L_2 + TCNE \rightleftharpoons [(TCNE)MX(CO)L_2] \quad (1)$$

constants (k_{obsd}) vs. the concentration of TCNE gave straight lines with nonzero intercepts; a representative result for the reaction of $RhCl(CO)(PPh_3)_2$ with TCNE at various temperatures is depicted in Figure 2.

The addition of free triphenylphosphine in the reaction of $RhCl(CO)(PPh_3)_2$ with TCNE, up to 100 times the concentration of the complex in acetone, has little effect on the rate in the low TCNE concentration range. Therefore, it is considered that the dissociation of the phosphine may not participate in the reaction. However, for the high TCNE concentrations (>8.4 × 10^{-3} M) the reaction was dominated by the fast reaction between TCNE and free triphenylphosphine.[15] For the reversible reaction of the eq 1 the rate law can be written

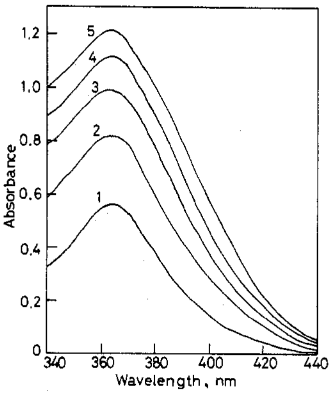


Figure 1. Electronic spectra of $RhCl(CO)(PPh_3)_2$ (1.98 × 10^{-4} M) in acetone with varying amounts of TCNE: (1) 0, (2) 4.25 × 10^{-4} M, (3) 8.50 × 10^{-4} M, (4) 1.27 × 10^{-3} M, (5) 2.12 × 10^{-3} M.

$$-\frac{d[MX(CO)L_2]}{dt} = k_2[MX(CO)L_2][TCNE] - k_{-1}[(TCNE)MX(CO)L_2] \quad (2)$$

where k_2 and k_{-1} are the forward second-order and the backward first-order rate constants, respectively. In the presence of a large excess of TCNE, the observed rate constants k_{obsd} are written[16]

$$k_{obsd} = k_2[TCNE] + k_{-1} \quad (3)$$

Table II lists the k_2 and k_{-1} values obtained from the slope and intercept of the linear relationship between k_{obsd} and [TCNE]. For the reaction of $RhCl(CO)(PPh_3)_2$ with TCNE in acetone the equilibrium constant evaluated from the kinetic results (as $K = k_2/k_{-1}$) is consistent with that obtained by the spectrophotometric method (see Table II). Table II also contains rate data at various temperatures for the two representative reactions of $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$ with TCNE in acetone. The plots of log k_2, log k_{-1}, or log K vs. $1/T(K)$ gave straight lines, from which the activation parameters or thermodynamic parameters were calculated (Table III).

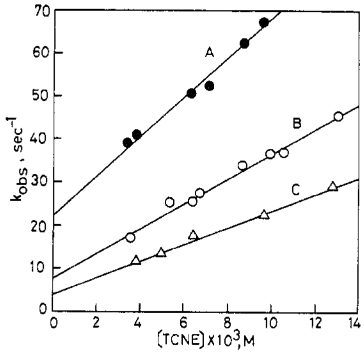


Figure 2. Plots of k_{obsd} vs. [TCNE] for the reactions of RhCl(CO)$(PPh_3)_2$ (3.1×10^{-4} M) with TCNE in acetone at different temperatures: A, 34.5 °C; B 25.0 °C; C, 15.5 °C.

Table III. Activation Parameters for the Reaction of the Metal Substrates with TCNE in Acetone at 25 °C

Compd	$\Delta H_2{}^*$,[a] kcal/mol	$\Delta S_2{}^*$,[a] eu
$RhCl(CO)(PPh_3)_2$[b]	7.0 ± 0.3	-19.4 ± 1.0
$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]^+$[c]	3.5 ± 0.2	-27.7 ± 3.4
$IrCl(CO)(PPh_3)_2$	1.4 ± 0.1	-33.8 ± 0.1

[a] The subscript 2 stands for the forward reaction. [b] $\Delta H_{-1}{}^* = 15.8 \pm 1.5$ kcal/mol; $\Delta S_{-1}{}^* = -1.4 \pm 3.0$ eu; $\Delta H° = -8.8 \pm 1.0$ kcal/mol; $\Delta S° = -18.0 \pm 3.0$ eu; subscript −1 stands for the reverse reaction. [c] $k_2 = 1.36 \times 10^4$ M^{-1} s^{-1}; ref 5.

Dependence on Ligands, Metals, and Solvents. The rate constant k_2 in the reaction of *trans*-$RhX(CO)(PPh_3)_2$ with TCNE increases in the order X = NCS $\simeq$ Br < Cl $\simeq$ NCO. On the other hand, in the $RhCl(CO)L_2$ complex k_2 increases in the order L = $P(O\text{-}o\text{-}CH_3C_6H_4)_3$ < $P(p\text{-}ClC_6H_4)_3$ < PPh_3 < $P(OPh)_3$ < $P(p\text{-}CH_3C_6H_4)_3$ < $P(p\text{-}CH_3OC_6H_4)_3$ < $AsPh_3$ << PPh_2Me (too fast to measure). By plotting log k_2 against the Hammett σ_p constants of the para substituents, a straight line with the slope $\rho = -2.5$ is obtained. This negative ρ value indicates that the reaction is accelerated by electron-releasing substituents, which increase the nucleophilicity of the metal substrate.

The difference in the reaction rate between RhCl(CO)$(PPh_3)_2$ and RhCl(CS)$(PPh_3)_2$ is very small, but IrCl(CO)$(PPh_3)_2$ reacts with TCNE about 9 times faster than RhCl(CO)$(PPh_3)_2$ in acetone at 25 °C (Table II).

The reaction rate are strongly dependent on the solvent; k_2 of the reaction between $MCl(CO)(PPh_3)_2$(M = Rh, Ir) and TCNE increases in the order THF < $(CH_3)_2CO$ < C_6H_5CN, and k_{-1} varies inversely (Table II). In addition, the K value in the Rh(I) complex undergoes the larger solvent effect than k_2. The final product is therefore suggested to be more polar than the activated complex.

Mechanistic Consideration. The entropies of activation $\Delta S_2{}^*$ for the reaction of *trans*-$MCl(CO)(PPh_3)_2$ (M = Rh, Ir) with TCNE are large negative values (Table III), which indicate that the reaction undergoes stereochemical restrictions in the transition state. The metal complex may be possible to interact with TCNE at three different sites:[2] (1) the carbon–carbon double bond, (2) the carbon–nitrogen triple bond, and (3) the nitrile nitrogen.[17] In view of the low oxidation state of Rh(I) and Ir(I), the present metal complexes are likely to prefer soft–soft interaction with TCNE.[18] Thus, site 1 or 2 is more favorable than site 3. No rhodium and iridium complexes of TCNE with the bonding mode of site 2, however, are known up to the present. Thus, the C≡N bond is less likely to be the reaction site, although it cannot completely be ruled out from the present results.

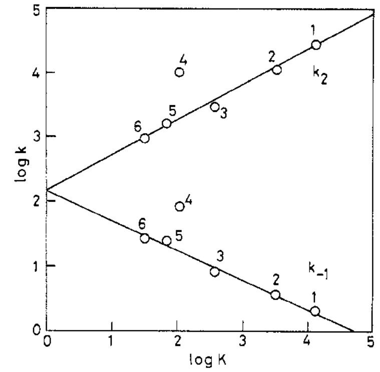
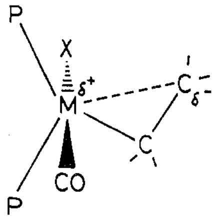
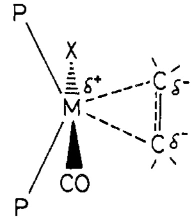


Figure 3. Linear free energy relationships for the reversible reaction $RhCl(CO)L_2$ + TCNE $\rightleftharpoons$ $[(TCNE)RhCl(CO)L_2]$ in acetone at 25 °C; L = $P(p\text{-}CH_3OC_6H_4)_3$ (1), $P(p\text{-}CH_3C_6H_4)_3$ (2), PPh_3 (3), $P(OPh)_3$ (4), $P(p\text{-}ClC_6H_4)_3$ (5), $P(O\text{-}o\text{-}CH_3C_6H_4)_3$ (6).

In the case of the reaction site being the C=C bond, there are two possible mechanisms in the nucleophilic attack of the metal complexes toward TCNE: (1a) an asymmetric interaction in a nonconcerted fashion and (1b) a symmetric coordination in a concerted manner. In the previous paper on the reaction of $[Rh(RNC)_2(PR'_3)_2]^+$ with TCNE,[5] we have assumed that there is little charge separation in 1b, leading to the choice of mechanism 1a, on the basis of the solvent effect on the reaction rate and the activation parameters. This assumption, however, should be revised, since it is possible for the Rh(I) center to interact with TCNE through considerable electron transfer toward TCNE in a three-centered manner.[19] Thus, both proposed transition states (1a and 1b) are considered to be dipolar. This is consistent with a negative ρ value and a large solvent effect on the reaction rate or the activation parameters. The solvent effect can be interpreted as a result of an induced dipole by electron transfer from the metal complex to TCNE, accompanied by the prerequisite deformation of the square-planar complex.[20]



(1a)



(1b)

The appearance of TCNE anion radical is remarkably dependent on the nature of halide ligands. Thus, RhCl(CO)$(PPh_3)_2$ forms the radical only in a very polar solvent benzonitrile, while the bromo and iodo analogues produce it even in acetone. In view of the fact that bromide and iodide are more polarizable than chloride,[21] the appearance of the anion radical seems to suggest a complete charge separation induced on the asymmetric dipolar intermediate in mechanism 1a. However, the radical formation might be a side reaction.[22] Thus, the present results will equally be interpreted by either of the transition states 1a or 1b. On the other hand, it was recently reported that the reaction of *cis*- and *trans*-$CF_3(CN)C{=}C(CF_3)CN$ with IrCl(CO)$(PPh_3)_2$ gave only $[(\textit{trans}\text{-}CF_3(CN)C{=}C(CF_3)CN)IrCl(CO)(PPh_3)_2]$ and this was interpreted in terms of transition state 1a.[3]

Figure 3 shows the LFER plots[23] of log k_2 vs. log K and log k_{-1} vs. log K for a series of reactions of $RhCl(CO)L_2$ (L = phosphorus ligands) with TCNE. The linear relations except for $P(OPh)_3$[24] are indicative of a single mechanism for these reactions. It has previously been proposed that a value of β (the slope of the plot) near zero or unity implies the structure of an activated complex resembling that of the reactant or of the product.[26] The LFER plots gave the values of $\beta_2 = 0.55$

(for log k_2 vs. log K) and $\beta_{-1} = -0.45$ (for log k_{-1} vs. log K). Therefore, in the transition state the configuration around the rhodium would be in the middle of those of the reactant and product. Thus, in the activated complex the two trans phosphorus or arsenic ligands may be moderately bent back and considerable electron transfer from the metal to TCNE may take place.

Finally, it can be concluded from the ΔH_2^* values and the k_2 values at 25 °C (Tables II and III) that the nucleophilicity of the metal substrate increases in the order of $RhCl(CO)(PPh_3)_2 < [Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]^+ < IrCl(CO)(PPh_3)_2$.

Registry No. *trans*-$RhCl(CO)(PPh_3)_2$, 15318-33-9; *trans*-$RhCl(CO)(PPh_2Me)_2$, 19552-34-2; *trans*-$RhCl(CO)(AsPh_3)_2$, 16970-35-7; *trans*-$RhCl(CO)(P(OPh)_3)_2$, 53275-15-3; *trans*-$RhCl(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)_2$, 59349-69-8; *trans*-$RhCl(CO)(P(p\text{-}ClC_6H_4)_3)_2$, 17966-82-4; *trans*-$RhCl(CO)(P(p\text{-}CH_3C_6H_4)_3)_2$, 17070-18-7; *trans*-$RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2$, 16970-33-5; *trans*-$RhCl(CS)(PPh_3)_2$, 59349-68-7; *trans*-$Rh(NCO)(CO)(PPh_3)_2$, 23028-37-7; *trans*-$Rh(NCS)(CO)(PPh_3)_2$, 17966-78-8; *trans*-$RhBr(CO)(PPh_3)_2$, 17070-17-6; *trans*-$RhI(CO)(PPh_3)_2$, 21006-49-5; *trans*-$IrCl(CO)(PPh_3)_2$, 15318-31-7; $[Rh(C_8H_{12})Cl]_2$, 12092-47-6; $RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2(TCNE)$, 59389-60-5; $RhCl(CO)(PPh_3)_2(TCNE)$, 32613-67-5; $RhCl(CO)(PPh_2Me)_2(TCNE)$, 59389-66-1; $RhCl(CO)(AsPh_3)_2(TCNE)$, 59389-65-0; $RhCl(CO)(P(OPh)_3)_2(TCNE)$, 59389-64-9; $RhCl(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)_2(TCNE)$, 59389-70-7; $RhCl(CO)(P(p\text{-}ClC_6H_4)_3)_2(TCNE)$, 59389-68-3; $RhCl(CO)(P(p\text{-}CH_3C_6H_4)_3)_2(TCNE)$, 59389-67-2; $RhCl(CS)(PPh_3)_2(TCNE)$, 59389-63-8; $Rh(NCO)(CO)(PPh_3)_2(TCNE)$, 59389-62-7; $Rh(NCS)(CO)(PPh_3)_2(TCNE)$, 59389-61-6; $RhBr(CO)(PPh_3)_2(TCNE)$, 30103-58-3; $RhI(CO)(PPh_3)_2(TCNE)$, 30103-59-4; $IrCl(CO)(PPh_3)_2(TCNE)$, 20741-47-3; TCNE, 670-54-2.

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Structural and Mechanistic Studies of Coordination Compounds. 15.[1] Evidence of an SN1cB Mechanism for the Base Hydrolysis of Some *trans*-Chloro- and -Bromoisothiocyanato Macrocyclic Quadridentate Amine Complexes of Cobalt(III)

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Received January 22, 1976 AIC60058W

The kinetics of base hydrolysis of *trans*-$[CoL(NCS)X]^+$ [L = cyclam (1,4,8,11-tetraazacyclotetradecane), teta (*meso*-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane), and trans[14]diene (1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradeca-1,7-diene); X = Cl and Br] have been studied in buffer solutions. Steric acceleration has been observed which strongly supports a dissociative mechanism for these reactions. In the teta and trans[14]diene systems, general base catalysis has been detected and the second-order rate constant with respect to hydroxide ion concentration is virtually independent of the nature of both orienting (NCS^- and Cl^-) and leaving (Cl^- and Br^-) groups. These together with the observations that the activation enthalpies fall within 12–16 kcal mol^{-1} and activation entropies fall within 8–16 cal mol^{-1} deg^{-1} are good evidence for a "limiting" SN1cB mechanism, in which the deprotonation of an amine ligand becomes the rate-determining step, for the base hydrolysis of these two systems of complexes. For the cyclam complexes, the base hydrolysis is "normal" (nonlimiting) and the rate constant then depends on the nature of both orienting (NCS^- and Cl^-) and leaving (Cl^- and Br^-) groups.

Introduction

The base hydrolysis of amine complexes of cobalt(III) has been extensively investigated and a number of mechanisms have been proposed.[2] Much evidence has now been accumulated to support the SN1cB mechanism,[2] as represented in general terms by