228 *Inorg. Chem.* **1985**, *24*, 228–230

Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706

Rates and Equilibrium Constants for CD_3CN Solvolysis of the Halide Ion in $RuX(L)_2(\eta\text{-}C_5H_5)$ Complexes

PAUL M. TREICHEL* and PAUL J. VINCENTI

Received March 28, 1984

When dissolved in CD_3CN, the complexes $RuCl(L)_2(\eta\text{-}C_5H_5)$ (L = PMe_3, $PPhMe_2$, PPh_2Me, PPh_2OMe, $P(OEt)_3$, $PMe(OMe)_2$; $(L)_2$ = dppe) undergo partial solvolysis of chloride ion. At equilibrium the starting materials, $[Ru(CD_3CN)(L)_2(\eta\text{-}C_5H_5)]^+$ and Cl^-, are present, usually with ion pairing of the latter species. Kinetic information was obtained for these reactions (67 °C) by monitoring the singlet cyclopentadienyl proton resonances of starting material and product. Pseudo-first-order rate constants for the forward reactions were obtained that show that the solvolysis rate is strongly influenced by the donor capacity of L. The time required to reach equilibrium and the extent of conversion at equilibrium are dependent on L in the same manner. Solvolysis rates for $RuX(L)_2(\eta\text{-}C_5H_5)$ (X = Cl, Br, I; L = PPh_2OMe or $(L)_2$ = dppe) are minimally dependent on X when this ligand is a halide ion; solvolysis does not occur with anionic π acceptor ligands such as CN^- or $SnCl_3^-$. Addition of small increments of water (with $RuCl(L)_2(\eta\text{-}C_5H_5)$, L = PPh_2OMe or $(L)_2$ = dppe) causes enhancement of the rate of solvolysis and increases the extent of solvolysis. Addition of halide acceptors ($AgPF_6$, $NaPF_6$, NH_4PF_6) causes these reactions to proceed faster and reach completion; however, the halide acceptors vary substantially in their effect on the rates of reaction.

Introduction

Most reactions of metal carbonyl halides, $MX(CO)_{m+n}$, or partially substituted derivatives, $MX(CO)_n(L)_m$, with species that can serve as ligands (PR_3, CNR, X^-, etc.) occur with carbonyl replacement. Halide replacement with these complexes is rarely seen, although halide substitution can easily be accomplished if a halide acceptor is added. In contrast, halide replacement is often the preferred mode of substitution in homologous species in which most of the carbonyl groups have been replaced by ligands that are better donors than CO. For example, the reaction of $MnBr(CO)(CNMe)_4$ with CNMe produces $[Mn(CO)(CNMe)_5]Br$, replacement of Br^- rather than CO occurring.[1] The preference for bromide ion substitution over carbonyl substitution in electron-rich $MnBr(CO)(CNMe)_4$ (along with other examples) led us to suggest that halide ion substitution should be a common occurrence for electron-rich complexes.[2,3] However, experimental evidence neither is abundant nor is carefully developed to support this suggestion.

The premise that halide ion displacement should be favored in electron-rich complexes seems logical. The presence of good donor ligands rather than CO in the metal coordination sphere, leading to an increase of negative charge on the metal center, ought to weaken a metal–halogen bond by decreasing the ionic resonance contribution ($M^{\delta+}\text{–}X^{\delta-}$) to the bond strength. Thus, enhanced halide substitution rates might reasonably be anticipated for such species. In contrast, substitution of good donor ligands generally strengthens the metal–carbonyl bond and slows the rate of substitution of carbonyl groups.

In this paper we describe solvolyses of a series of ruthenium complexes having formulas $RuCl(L)_2(\eta\text{-}C_5H_5)$ (L = phosphorus ligands) that were prepared in our laboratories as part of a broader study.[4–7] Slow displacement of halide ion occurs upon dissolution of these compounds in polar solvents. The rate of this process and the extent of conversion to an ionic product, $[Ru(solv)(L)_2(\eta\text{-}C_5H_5)]^+Cl^-$, have been found to depend on the identity of the phosphorus ligand.

Solvolysis of halide ion in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ has previously been shown to occur in methanol.[8] We have reported the solvolysis of $RuCl(L)_2(\eta\text{-}C_5H_5)$ species in $Me_2SO\text{-}d_6$ elsewhere,[9] speculating that this type of reaction may be encountered for these species in most or all donor solvents. In contrast, such reactions do not occur for $RuCl(CO)_2(\eta\text{-}C_5H_5)$; with donor solvents or with molecules capable of functioning as ligands, CO displacement occurs in preference.[4] Analogous reactions have not been studied for the corresponding iron systems, although the reaction of $[Fe(CH_3CN)(PMe_3)_2(\eta\text{-}C_5H_5)]BF_4$ and $[Bu_4N]I$ is known to occur in a different solvent (THF) to give $FeI(PMe_3)_2(\eta\text{-}C_5H_5)$.[10] No similar studies have been reported for the osmium complexes.

In conjunction with this study, we have also investigated the effect of various halide acceptors including water on the rate and conversion of starting material to product. Though qualitative, these data suggest that the traditional halide acceptor species used routinely in synthesis have quite different effects on both thermodynamics and kinetic parameters for these reactions.

Experimental Section

Starting Materials. Syntheses of the $RuCl(L)_2(\eta\text{-}C_5H_5)$ complexes used in this study were accomplished by the reaction of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and the ligand in toluene. Details of this procedure have been reported in the literature.[7] Purity of the samples was verified by elemental analysis, spectroscopic data, and by melting point. The deuterated solvent, CD_3CN, was obtained from Stohler Isotope Chemicals, Rutherford, NJ. It was used without purification; opened vials were kept in a drybag under nitrogen, however, and this solvent was not stored for prolonged periods because of the potential for uptake of water.

Measurement of Solvolysis Rates. A weighed sample of the starting material was dissolved in CD_3CN in a small volumetric flask to give a solution of accurately known concentration (usually 0.050 ± 0.001 M). A portion of this solution was transferred to a NMR tube; the tube was then sealed and placed in an oil bath thermostated at 67 ± 1 °C. Periodically the tube was removed from the bath and cooled to 0 °C and the ^1H NMR spectrum recorded. (In reactions spanning periods of many hours or days, the time involved in these manipulations was considered to be negligible; otherwise, corrections were included for the time used in this procedure.) The extent of reaction was calculated from the intensities of the singlet cyclopentadienyl proton resonances of starting material, $RuCl(L)_2(\eta\text{-}C_5H_5)$, and product, $[Ru(CD_3CN)(L)_2(\eta\text{-}C_5H_5)]Cl$, the chemical shifts of both resonances being available from previous work.[7] Neither decomposition nor other reactions occurred in most instances; this fact was ascertained by the relative constancy of the intensities of the cyclopentadienyl proton resonances vs. the residual proton resonances of the solvent, the latter serving as an internal standard. Two or more kinetic runs were carried out on each sample.

The mathematical reactionship appropriate for a reversible reaction that is first order in the forward direction and second order in the reverse direction ($A \rightleftarrows B + C$) is

$$\ln \frac{a_0x_e + x(a_0 - x_e)}{a_0(x_e - x)} = k_f(2a - x_e/x_e)t$$

for which a_0 is the initial concentration of A, x is the extent of reaction of reaction at time t (i.e., $a_0 - a_t$), and x_e is the extent of reaction at

---

(1) Treichel, P. M.; Dirreen, G. E.; Mueh, H. J. *J. Organomet. Chem.* **1972**, *44*, 339–352.

(2) Treichel, P. M.; Wagner, K. P.; Mueh, H. J. *J. Organomet. Chem.* **1975**, *86*, C13–C16.

(3) Treichel, P. M.; Mueh, H. J. *J. Organomet. Chem.* **1976**, *122*, 229–240.

(4) Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 205–218.

(5) Treichel, P. M.; Komar, D. A. *Inorg. Chim. Acta* **1980**, *42*, 277–280.

(6) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* **1981**, *206*, 77–88.

(7) Treichel, P. M.; Komar, D. A.; Vincenti, P. J. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 383–400.

(8) Haines, R. J.; DuPreez, A. L. *J. Organomet. Chem.* **1975**, *84*, 357–367.

(9) Treichel, P. M.; Komar, D. A.; Vincenti, P. J. *Inorg. Chim. Acta* **1984**, *88*, 151–152.

(10) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* **1981**, *206*, 77–88.

Table I. Values of k_f, k_r, and K_e[a]

$[H_2O]$, M	k_f, $s^{-1} \times 10^6$	k_r, $s^{-1} \times 10^{-6}$	K_{eq}
	$RuCl(PPh_2OMe)_2(\eta\text{-}C_5H_5)$		
0.07	4.8	240	0.020
0.17	6.7	270	0.025
0.35	9.9	290	0.034
0.52	13.5	300	0.045
0.66	19.7	290	0.068
	$RuBr(PPh_2OMe)_2(\eta\text{-}C_5H_5)$		
0.07	4.4	69	0.064
	$RuCl(dppe)(\eta\text{-}C_5H_5)$		
0.07	15	290	0.051
0.23	18	240	0.975
0.39	27	225	0.12
0.95	53	182	0.29

[a] $K_e = k_f/k_r = [MNCCH_3^+][Cl^-]/[MCl]$.

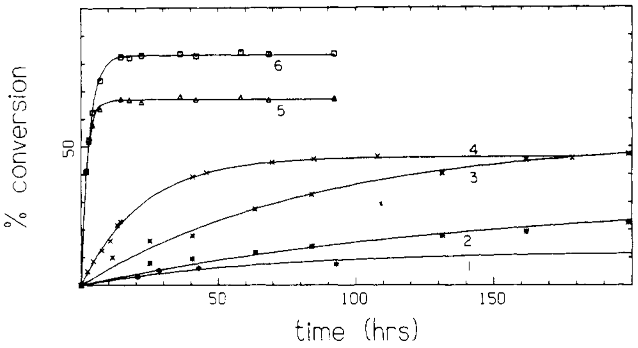

Figure 1. Effect of various ligands on the solvolysis of chloride ion in $RuCl(L)_2(\eta\text{-}C_5H_5)$ by CD_3CN (67 °C): (1) $P(OMe)_3$; (2) $PMe(OMe)_2$; (3) $P(OEt)_3$; (4) PPh_2OMe; (5) $PPhMe_2$; (6) PMe_3.

equilibrium ($a_0 - a_e$).[11] Data obtained for the complexes $RuX(PPh_2OMe)_2(\eta\text{-}C_5H_5)$ (X = Cl, Br) and $RuCl(dppe)(\eta\text{-}C_5H_5)$ fit this equation and were analyzed to obtain values of k_f, k_r, and K_{eq} (Table I). In several instances, values for K_{eq} were obtained from different initial concentrations of starting material; consistency of these values further confirmed the kinetic scheme chosen for these systems.

Small amounts of water in CD_3CN significantly influenced the rates of these reactions. This fact was probed with these metal complexes by carrying out kinetic runs on solutions containing known amounts of water. The amount of H_2O present was determined by integration of its proton resonance. This resonance is seen as a broad singlet whose position and intensity vary somewhat with its concentration. The analysis of these data also gave rate constants and the equilibrium constants (Table I) appropriate to this kinetic scheme.

Data were also collected for the solvolyses of a number of other complexes: $RuCl(L)_2(\eta\text{-}C_5H_5)$ (L = PMe_3, $PPhMe_2$, PPh_2Me, $P(OEt)_3$, $PMe(OMe)_2$, $RuX(dppe)(\eta\text{-}C_5H_5)$ (X = Br, I), $RuI(PPh_2OMe)_2(\eta\text{-}C_5H_5)$). The fit of these data to the equation given above was very good over several half-lives, but a small systematic deviation was seen as the reaction approached the final equilibrium position. We emphasize that the deviation was small, noting also that the uncertainty associated with the mathematical analysis becomes quite large as the denominator in the logarithmic term ($x - x_0$) approaches zero. We suspect that the problem here is that there is a small amount of ion pairing at higher concentrations, which compromises the validity of the simple $A \rightleftarrows B + C$ kinetic scheme. The data were unfortunately not accurate enough to test this hypothesis with a more complex kinetic scheme. For these compounds, we chose to use the data from the early part of the reaction in the equation above, accepting the possibility of a somewhat greater error, to obtain a value for k_f (Table II). (The compromise here is that the mathematical expression contains a value of x_e that would not be accurate if ion pairing occurs.) The results obtained in this way were checked against values of k_f obtained by extrapolation of the slope of a graph of ln a vs. time to $t = 0$ (i.e., determining the first-order rate constant at $t = 0$, when product concentrations are zero). Values of k_f obtained by the two methods were the same within experimental error. This result further argues for the assumption that the deviations from the kinetic scheme are small.

Table II. CD_3CN Solvolysis of $RuX(L)_2(\eta\text{-}C_5H_5)$ (67 °C)

	k_f, $s^{-1} \times 10^6$	time req to attain equil,[a] h	$\tau_{1/2}$, h	% solv at equil
A. $RuCl(L)_2(\eta\text{-}C_5H_5)$ (0.05 M Except As Noted)				
L = PMe_3	78	13	2	83
L = $PPhMe_2$	80	14	2	67
L = PPh_2Me	67	14	2	77
$(L)_2$ = dppe (0.02 M)	15	75	15	77
L = PPh_2OMe	4.8	60	14	46
L = $P(OEt)_3$	3.3	~200	60	50
L = $PMe(OMe)_2$	0.4	~250	65	5
L = CO	no reaction			
L = PPh_2OMe (0.04 M)	5.4	60	14	50
L = PPh_2OMe (0.03 M)	4.8	50	14	55
$(L)_2$ = dppe (0.015 M)	13	90	15	81
B1. $RuX(PPh_2OMe)_2(\eta\text{-}C_5H_5)$				
X = Br (0.021 M)	4.4	50	12	66
X = I (0.012 M)	5.4	120	25	60
B2. $RuX(dppe)(\eta\text{-}C_5H_5)$				
X = Br (0.025 M)	22	30	6	85
X = I (0.036 M)	11	45	13	67
C. $RuCl(PPhMe_2)_2(\eta\text{-}C_5H_5)$				
T = 42 °C	5.7	200	25	81
T = 53 °C	16	48	9	75
T = 67 °C	80	14	2	67
D1. $RuCl(PPh_2OMe)_2(\eta\text{-}C_5H_5) + H_2O$				
$[H_2O]$ = 0.07 M	4.8	60	14	45
$[H_2O]$ = 0.17 M	6.7	50	13	50
$[H_2O]$ = 0.35 M	9.9	40	10.5	55
$[H_2O]$ = 0.52 M	13.5	40	7	60
$[H_2O]$ = 0.66 M	19.7	40	6	67
D2. $RuCl(dppe)(\eta\text{-}C_5H_5)$ (0.02 M) + H_2O				
$[H_2O]$ = 0.07 M	15	75	15	77
$[H_2O]$ = 0.23 M	18	42	8	82
$[H_2O]$ = 0.39 M	27	27	5	87
$[H_2O]$ = 0.95 M	53	20	2.5	94
E. $RuCl(PPh_2OMe)_2(\eta\text{-}C_5H_5)$ + Halide Acceptor				
$AgPF_6$		fast		100
$NaPF_6$		27		100
NH_4PF_6		80		100
Me_4NPF_6		85		60

[a] For reactions taking more than 100 h it was difficult to identify the exact time when equilibrium was reached.

For these systems, qualitative information is also provided (Table II; Figure 1) on the half-time of the reaction and the approximate time required to reach equilibrium. Also included is the extent of conversion to products at equilibrium. We believe these numbers are comparable at a qualitative level. Small deviations due to ion pairing cause rather large errors in K_{eq} so it did not seem worthwhile to determine these values.

Solvolysis reactions in the presence of approximately equimolar amounts of a halide acceptor ($NaPF_6$, NH_4PF_6, Me_4NPF_6, $AgPF_6$) were followed in a similar manner by ^1H NMR. The data in Table II were generally reproducible in several determinations. No attempt was made to fit these data to a kinetic scheme, however, since it was felt that the chemical system was too complicated to permit development of a simple model for this type of reaction.

Results and Discussion

When dissolved in acetonitrile-d_3, the complexes $RuCl(L)_2(\eta\text{-}C_5H_5)$ undergo a slow solvolysis of chloride ion. Eventually, equilibrium is reached between the starting material and the ion $[Ru(CD_3CN)(L)_2(\eta\text{-}C_5H_5)]^+$ and Cl^-. We have measured rates of these reactions (at 67 °C) with seven different precursors in which the ligands L are aryl- and alkylphosphines, phosphonate and phosphinate esters, and phosphites (eq 1). A similar study was accorded to the solvolysis of bromide and iodide analogues.

$$RuCl(L)_2(\eta\text{-}C_5H_5) + CD_3CN \rightleftarrows [Ru(CD_3CN)(L)_2(\eta\text{-}C_5H_5)]^+ + Cl^- \quad (1)$$

---

[11] Moore, J. W.; Pearson, R. G. "Kinetics and Mechanisms", 3rd ed.; Wiley-Interscience: New York, 1982; p 304.

Data on the complexes $\mathrm{RuX(PPh_2OMe)_2(\eta\text{-}C_5H_5)}$ (X = Cl, Br) and $\mathrm{RuCl(dppe)(\eta\text{-}C_5H_5)}$ fit the kinetic scheme

$$\mathrm{A} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{B} + \mathrm{C}$$

where A, B, and C refer to starting complex, cationic product, and halide ion. Values of k_f, k_r, and K_e were derived from the concentration–time data (Table I). Values of K_e of 0.02 and 0.05 were obtained for the systems $\mathrm{RuCl(L)_2(\eta\text{-}C_5H_5) \rightleftharpoons [Ru(solv)(L)_2(\eta\text{-}C_5H_5)]^+ + Cl^-}$ for L = $\mathrm{PPh_2OMe}$ and $\mathrm{(L)_2}$ = dppe. Values of K_e in these systems were calculated from the expression $K_e = \mathrm{[Ru(solv)(L)_2(\eta\text{-}C_5H_5)^+][Cl^-]/[RuCl(L)_2(\eta\text{-}C_5H_5)]}$. The equilibrium constants are consistent in several runs in which different initial concentrations of starting complex were used.

For other complexes, small deviations were encountered at the latter stages of the reactions in the fit of data to this kinetic scheme. This is probably a result of ion pairing at the higher ionic concentrations. Forward rate constants were obtained from data over the first several half-lives as described in the Experimental Section (Table II). The variation in rate constants of these solvolysis reactions over a range that is several orders of magnitude with the identity of L is most striking. In general, the rates are related to the donor ability of the ligand L in $\mathrm{RuCl(L)_2(\eta\text{-}C_5H_5)}$. Solvolysis is most rapid if L is a phosphine and is slower for complexes with phosphite or phosphinate ligands. There is little difference among k_f values of the various phosphine complexes; however, the two complexes $\mathrm{RuCl(L)_2(\eta\text{-}C_5H_5)}$ (L = $\mathrm{PMe_3}$, $\mathrm{PPhMe_2}$) undergo solvolysis at essentially the same rate, and for $\mathrm{RuCl(PPh_2Me)_2(\eta\text{-}C_5H_5)}$, solvolysis is only slightly slower. Likewise, the rates of solvolysis of the complexes $\mathrm{RuCl(L)_2(\eta\text{-}C_5H_5)}$ in which L = $\mathrm{PPh_2OMe}$, $\mathrm{PMe(OMe)_2}$, and $\mathrm{P(OEt)_3}$ are not much different. In the solvolysis of these ruthenium complexes in $\mathrm{Me_2SO}$, a greater degree of discrimination as a function of ligand was observed.[9]

Rates of solvolysis for $\mathrm{RuX(PPh_2OMe)_2(\eta\text{-}C_5H_5)}$ and $\mathrm{RuX(dppe)(\eta\text{-}C_5H_5)}$ complexes as a function of halide ion are different, but not to a major extent (Table IIA,B). The order of rates based on halide in the second series was Cl > Br > I, and in the first series, Cl ~ I > Br.

The percent conversion to product at equilibrium varies with respect to L in much the same fashion as do the forward rate constants. Those compounds in which L is a phosphine are converted to ionic product to the extent of about 70–80%, again with only small differences between members of this group. The solvolyses of $\mathrm{RuCl(L)_2(\eta\text{-}C_5H_5)}$ (L = $\mathrm{PPh_2OMe}$, $\mathrm{P(OEt)_3}$, $\mathrm{PMe(OMe)_2}$) occur to the extent of 46%, 50%, and 25%, respectively. It was possible only to obtain a qualitative comparison of the extent of reaction. Equilibrium constant values were unavailable for most systems because the data suggested that ion pairing often is a factor in the later stages of the reaction.

The solvolysis of $\mathrm{RuCl(PPhMe_2)_2(\eta\text{-}C_5H_5)}$ in $\mathrm{CD_3CN}$ was investigated at several different temperatures (Table IIC). Graphs of log k_f vs. $1/T$ and log k_f/T vs. $1/T$ were used to calculate the values of the activation parameters ΔH^{*} (=+23.4 kcal/mol) and ΔS^{*} (=−8.6 eu).

Rate data for the forward reaction are appropriate for a dissociative interchange ($\mathrm{I_d}$) mechanism. In such a mechanism, the major contribution to the activation energy is the breaking (heterolytically) of the metal–halide bond.

Initial difficulties were encountered in obtaining reproducible data from these reactions due to traces of water in the solvent. It was found that water speeded up the reactions and shifted the equilibrium position to favor the ionic product. The latter effect is expected since solvation energies obviously contribute to the favorability of these reactions. Water, we believe, should solvate the halide ion more effectively than does $\mathrm{CD_3CN}$, and this should further stabilize the ionic product. In its effect on rate, water can be considered to act as a halide acceptor. Water is presumably attracted to the chloride ligand in the starting material via a dipolar or hydrogen-bonding interaction, the chloride ligand in the starting material bearing a partially negative charge. The heterolytic breaking of the ruthenium–chloride bond can occur in a solvent-assisted process, the energy of the bond breaking being somewhat compensated by the gain in solvation energy of the anion.

The discovery that water acts as a halide acceptor led to the final part of this study. Various halide acceptors have been used to promote replacement of a halide, including metal halides (primarily $\mathrm{AlCl_3}$), silver salts ($\mathrm{AgPF_6}$, $\mathrm{AgBF_4}$, $\mathrm{AgClO_4}$), $\mathrm{NOPF_6}$, $\mathrm{NH_4PF_6}$, $\mathrm{TlPF_6}$, $\mathrm{HPF_6}$, $\mathrm{NaPF_6}$, and a few other species. The possibility that there might be differences between halide acceptors has apparently not been considered. We thought that this question might be addressed directly in these studies and, to this end, elected to follow the solvolysis reactions of $\mathrm{RuCl(PPh_2OMe)_2(\eta\text{-}C_5H_5)}$ in $\mathrm{CD_3CN}$ solutions, to which an approximately equimolar quantity of a halide acceptor was added.

The addition of a hexafluorophosphate salt ($\mathrm{NaPF_6}$, $\mathrm{NH_4PF_6}$, $\mathrm{AgPF_6}$) changes the overall reaction (eq 2). Precipitation of an insoluble chloride salt accompanies these reactions; that the reactions reach completion may be a consequence of this fact. The rates of reaction are also greater, but to a different extent for each of the examples chosen. Silver hexafluorophosphate was the most effective in this regard, with the reaction being mostly complete at room temperature by the time an NMR spectrum could be taken. All other reactions were slow enough at 67 °C to be conveniently followed by NMR. The reaction with $\mathrm{NaPF_6}$ reached completion at 67 °C in 27 h, while the $\mathrm{NH_4PF_6}$ reaction occurred at about one-third of this rate. Both reactions were considerably faster than a reaction without a halide acceptor.

$$\mathrm{RuCl(L)_2(\eta\text{-}C_5H_5) + CD_3CN + MPF_6 \rightleftharpoons [Ru(CD_3CN)(L)_2(\eta\text{-}C_5H_5)]^+ + PF_6^- + MCl} \quad (2)$$

$$\mathrm{L = PPh_2OMe;\ M^+ = Ag^+, Na^+, NH_4^+, Me_4N^+}$$

A reaction was also attempted with $\mathrm{Me_4NPF_6}$. This species, not previously used as a halide acceptor, enhanced the rate to only a small extent. This reaction did not reach completion, although some $\mathrm{Me_4NCl}$ was seen to precipitate.

The mechanism for rate enhancement by a halide acceptor in these reactions is probably similar to that proposed above to explain the effect of water on rates. There is an attractive force between the cation ($\mathrm{NH_4^+}$, $\mathrm{Ag^+}$, $\mathrm{Na^+}$) and the chloride ligand, with a concurrent compensation of the energy expended to separate the chloride ligand from ruthenium.

Registry No. $\mathrm{RuCl(PPh_2OMe)_2(\eta\text{-}C_5H_5)}$, 92361-51-8; $\mathrm{RuBr(PPh_2OMe)_2(\eta\text{-}C_5H_5)}$, 92361-66-5; $\mathrm{RuCl(dppe)(\eta\text{-}C_5H_5)}$, 71397-10-9; $\mathrm{RuCl(PMe_3)_2(\eta\text{-}C_5H_5)}$, 74558-74-0; $\mathrm{RuCl(PPhMe_2)_2(\eta\text{-}C_5H_5)}$, 76256-41-2; $\mathrm{RuCl(PPh_2Me)_2(\eta\text{-}C_5H_5)}$, 34692-07-4; $\mathrm{RuCl(P(OEt)_3)_2(\eta\text{-}C_5H_5)}$, 92361-53-0; $\mathrm{RuCl(PMe(OMe)_2)_2(\eta\text{-}C_5H_5)}$, 92361-55-2; $\mathrm{RuCl(CO)_2(\eta\text{-}C_5H_5)}$, 32611-12-4; $\mathrm{RuI(PPh_2OMe)_2(\eta\text{-}C_5H_5)}$, 92361-67-6; $\mathrm{RuBr(dppe)(\eta\text{-}C_5H_5)}$, 92361-61-0; $\mathrm{RuI(dppe)(\eta\text{-}C_5H_5)}$, 92361-62-1; $\mathrm{RuCl(P(OMe)_3)_2(\eta\text{-}C_5H_5)}$, 34822-87-2; $\mathrm{AgPF_6}$, 26042-63-7; $\mathrm{NaPF_6}$, 21324-39-0; $\mathrm{NH_4PF_6}$, 16941-11-0; $\mathrm{Me_4NPF_6}$, 558-32-7; $\mathrm{CD_3CN}$, 2206-26-0.