Electron Rich Complexes: Rates of Halide Ion Solvolysis in $RuX(L)_2(\eta\text{-}C_5H_5)$ as a Function of Ligand

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When dissolved in DMSO-d_6, $RuCl(L)_2(\eta\text{-}C_5H_5)$ complexes ($L = PMe_3$, $PPhMe_2$, PPh_2Me, PPh_2OMe, $PMe(OMe)_2$ and L_2 = dppe) undergo slow solvolysis of chloride ion. Rates for these solvolysis reactions were measured at 67 °C, by monitoring intensities of the cyclopentadienyl proton resonances in starting material and product, $[Ru(DMSO\text{-}d_6)(L)_2(\eta\text{-}C_5H_5)]^+$. The reactions follow pseudo first order kinetics. The rates of solvolysis vary enormously with L, the fastest reaction occurring with $L = PMe_3$ ($\tau_{1/2} = 1.3$ h) and the slowest with $PMe(OMe)_2$ ($\tau_{1/2} = \sim 420$ h). In general, the rate seems most largely dependent on the donor ability of L with steric effects playing almost no role.*

Introduction

Our interest in cyclopentadienyl–ruthenium complexes is evident from papers describing syntheses of various complexes having formulas $RuX(L)_2(\eta\text{-}C_5H_5)$ and $[Ru(L)_x(L')_{3-x}(\eta\text{-}C_5H_5)]^+$ (L,L′ are phosphorus ligands) [1–3]. In the course of these studies we learned that the complexes, $RuX(L)_2(\eta\text{-}C_5H_5)$, undergo halide solvolysis when dissolved in donor solvents. In this paper we describe kinetic studies on six of these solvolysis reactions in the solvent DMSO-d_6.

Experimental

Starting Materials

Syntheses of the six complexes used in this study, $RuCl(L)_2(\eta\text{-}C_5H_5)$ ($L = PMe_3$, $PPhMe_2$, PPh_2Me, PPh_2OMe, $PMe(OMe)_2$ and L_2 = dppe), have been described elsewhere [3]. Samples of these complexes had been prepared in conjunction with our earlier studies and were judged pure by elemental analyses. The DMSO-d_6 was obtained commercially and used without further purification.

*Me = methyl, Ph = phenyl, dppe = 1,2-bis(diphenylphosphino)ethane.

Measurement of Rates of Solvolysis

A weighed sample of the complex was dissolved in DMSO-d_6 in a small volumetric flask to give a solution of known concentration (0.050 ± 0.001 *M*). A portion of this solution was transferred to an NMR tube. The tube was sealed tightly and then placed in an oil bath thermostatted at 67 ± 1 °C. Periodically the tube was removed, cooled in ice, and the ^1H NMR spectrum recorded. (Most of these reactions spanned hours or even days and the time involved in these manipulations could then be regarded as insignificant). The extent of reaction could be calculated based on the intensities of the singlet resonances for the cyclopentadienyl protons of starting material and product, both chemical shifts having been known in advance from measurements on samples of the known complexes [3]. Except as noted below, decomposition or alternative reactions were not encountered. This was judged by the constancy of the sum of cyclopentadienyl proton intensities relative to an internal standard (the residual proton resonance of the solvent).

The data obtained were analyzed by standard methods [4]. The reactions follow rigorous pseudo first order kinetics. First order rate constants and half-times for the reactions, listed in Table I, are the average of two or more kinetic runs and should be accurate to better than ±10%.

Discussion

An earlier study [5] reported that ionization of Cl^- occurs when $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ is dissolved in methanol. Presumably the same type of reaction occurs in DMSO-d_6, and we speculate that this is likely to be a general reaction when species of this formula are dissolved in donor solvents. Such reactions have been little studied however. Most synthetic procedures leading to replacement of halide ion by a neutral molecule routinely utilize a halide acceptor to promote halide loss. For example, the formation of $[Ru(PMe_3)(CO)_2(\eta\text{-}C_5H_5)]^+$ from $RuCl(CO)_2(\eta\text{-}C_5H_5)$ and PMe_3 requires the addition of a halide

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TABLE I. Solvolysis of $RuCl(L)_2(\eta\text{-}C_5H_5)$ in DMSO-d_6 (67 °C)[a].

Compound	k(sec^{-1})	$\tau_{1/2}$ (h)
$RuCl(L)_2(\eta\text{-}C_5H_5)$		
$L = PMe_3$	2000	1.3
$L = PPhMe_2$	860	2.9
$L = PPh_2Me$[b]	400	6.3
L_2 = dppe	110	22.4
$L = PPh_2OMe$	21	120
$L = PMe(OMe)_2$[c]	2.6	~420

[a]Pseudo first-order reactions, monitored by following intensities of cyclopentadienyl proton resonances. Values of k and $\tau_{1/2}$ are estimated to be accurate to ±10%. [b]Decomposition detected after about 60% conversion to product. [c]Decomposition detected after 13% conversion.

acceptor such as $AgPF_6$ [1]; in the absence of a halide acceptor, halide displacement by an added ligand does not occur, and carbonyl substitution takes precedence, in this system.

We first detected the halide solvolysis reaction when recording the ^1H NMR spectra of these $RuCl(L)_2(\eta\text{-}C_5H_5)$ compounds, peaks associated with the complexes $[Ru(DMSO\text{-}d_6)(L)_2(\eta\text{-}C_5H_5)]^+$ appearing over a period of time. Subsequently we carried out these reactions on a synthetic scale and isolated the cationic complexes as chloride salts or more conveniently as PF_6^- salts after metathesis with NH_4PF_6. The characterization of the cationic complexes could be carried out by standard procedures [3]. The fact that most of these reactions reached completion was significant; the earlier work on methanol solvolysis did not assess this point. A later study in our laboratories, to be reported elsewhere [6], has shown that partial solvolysis occurs to give an equilibrium between starting material and the ionic product in acetonitrile.

The most significant result in this study, however, concerns the extraordinary differences in the rates of solvolysis of the different complexes. The PMe_3 compound, $RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$, undergoes solvolysis at the fastest rate; this reaction has a half-time of 1.3 h at 67 °C and is complete in only a few hours. In contrast $RuCl(PPh_2OMe)_2(\eta\text{-}C_5H_5)$ solvolysis requires many days to reach completion; $\tau_{1/2}$ is 120 h so the rate of solvolysis is about one-hundredth of the rate of the PMe_3 complex. The rate of solvolysis of $RuCl[PMe(OMe)_2]_2(\eta\text{-}C_5H_5)$ is even slower but the onset of decomposition did not permit us to carry this reaction to completion.

It is at once apparent from the data that the donor ability of the ligand L has a dominant influence on the rates of these ractions. The progression of rates of solvolysis of complexes with monodentate ligands ($PMe_3 > PPhMe_2 > PPh_2Me > PPh_2OMe > PMe(OMe)_2$) is also the order of donor ability of L as assessed by $\nu(CO)$ values in various phosphine substituted metal carbonyls [7]. (The rate of solvolysis of the $RuCl(dppe)(\eta\text{-}C_5H_5)$ is in its proper position; however we do not have precise data concerning its donor properties). The influence of steric effects on these rates appears secondary at best. To illustrate this it is noted that the rate of solvolysis in the series of complexes with $L = PMe_3$, $PPhMe_2$, and PPh_2Me decrease with increased ligand size, while the opposite is true for the series with $L = PPh_2Me$, PPh_2OMe and $PMe(OMe)_2$.

About 10 years ago we suggested that facile halide solvolysis should be a typical reaction for electron rich complexes [8, 9]. This conjecture is strongly affirmed in this study. Neither $RuCl(CO)_2(\eta\text{-}C_5H_5)$ or $RuCl(CO)(L)(\eta\text{-}C_5H_5)$ undergo halide solvolysis whereas this reaction is observed for the more electron rich species $RuCl(L)_2(\eta\text{-}C_5H_5)$, (L = phosphorus ligands). More significantly, the greater electron richness of the complex (*i.e.*, the greater the donor ability of L), the more rapid the solvolysis. It seems logical that this is so. Donation of negative charge to the metal would be expected to weaken the metal halogen bond, diminishing the ionic resonance contribution ($M^{\delta+}$–$Cl^{\delta-}$) in the electron rich species, and make this bond more susceptible to heterolytic cleavage.

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