Contribution from the [a] Facoltà di Chimica Industriale, Università di Venezia,, [c] Istituto di Chimica Generale, Università di Messina, Italy, and [b] Department of Chemistry, Kings College, London, WC2R 2LS, United Kingdom

Kinetic Studies on the Reactions of Dichloro1,2-bis(phenylselenoethane)palladium(II) with Amines

L. Cattalini [a], **J.S. Coe** [b], **F. Faraone** [c], **V. Marsala** [c], **E. Rotondo** [c]

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Kinetic studies are reported for the displacement of the chelate group from $Pd(C_6H_5SeC_2H_4SeC_6H_5)Cl_2$ by several substituted pyridines. Also reported are further studies on reactions of the corresponding thioether complex with these amines. Values of activation parameters for the reactions have been determined and the results interpreted in terms of differences in size and π-bonding capacities of Se and S.

Introduction

Earlier kinetic studies on the displacement by amines of the chelate ligand from complexes of the type $Pd(S\text{–}S)X_2$ ($S\text{–}S = C_6H_5SC_2H_4SC_6H_5$) have elucidated the basic mechanism of the reaction[1-3] and some effects of the anionic group X.[4] The present work extends these studies to the reactions of some amines with the selenoether complex $Pd(Se\text{–}Se)Cl_2$ ($Se\text{–}Se = C_6H_5SeC_2H_4SeC_6H_5$) and was undertaken with the object of providing some kinetic evidence for the nature of the differences between the Pd–Se and Pd–S bonds.

Experimental

Materials. $C_6H_5SeC_2H_4SeC_6H_5$: 1.12 g of 1,2-dibromoethane was added dropwise under nitrogen to a solution of C_6H_5SeH (2 g) in methanol (100 cm^3). The mixture was allowed to stand 2 hr and was then treated with aqueous sodium carbonate to remove excess C_6H_5SeH. Extraction with petroleum ether and evaporation of the solvent yielded the solid product.

$Pd(C_6H_5SeC_2H_4SeC_6H_5)Cl_2$: 1.5 g of the organic ligand was added in small quantities to a stirred aqueous solution of Na_2PdCl_4 (1.3 g). The product was precipitated as a red-brown solid that decomposed on heating above 290°C.

(*Anal.* %: Found: C 31.9, H 2.5, Cl 12.7. Calcd: C 32.50, H 2.72, Cl 13.70).

The complex $Pd(C_6H_5SC_2H_4C_6H_5)Cl_2$ was obtained as described previously.[1]

Reaction Product. This was isolated in the case of the reaction of $Pd(Se\text{–}Se)Cl_2$ with pyridine.

Anal. %: C 24.2, H 2.26, N 6.5, Cl 16.1. Calcd for $Pd(py)_2Cl_2$: C 24.40, H 2.36, N 6.61, Cl 16.80.

The infrared spectrum of the product (in the region 400-250 cm^{-1}) showed a single band at 357 cm^{-1}. Its spectrum in the UV region was identical to that observed for the final reaction mixtures in the kinetic experiments.

Kinetic Experiments. The procedure was as described previously[1] for the reactions of the sulphur complex.

Results

The general pattern of changes of spectra with time for the reactions of $Pd(Se\text{–}Se)Cl_2$ with amines was as observed previously[1] for $Pd(S\text{–}S)Cl_2$. Rate constants for individual runs (k_{obs}) were obtained from the linear plots of log (D_t–D_∞) against time, where D_t and D_∞ are, respectively, the absorbances of the solution at time t and at the end of the reaction. Values of k_{obs} for the reactions of amines with $Pd(Se\text{–}Se)Cl_2$ and with $Pd(S\text{–}S)Cl_2$ are given in Table I. For a particular reaction a plot of k_{obs} against amine concentration gave a straight line with, in some cases, departure from linearity at low amine concentrations. The gradients of these straight lines are given as k_2 values in Table II together with activation parameters calculated from them and the pK_a values of the amines at 25°C.

Discussion

The general pattern of the results for the reactions of $Pd(Se\text{–}Se)Cl_2$ with amines is similar to that observed earlier[1] for the corresponding reactions of $Pd(S\text{–}S)Cl_2$ at 25°C except that, for the reactions of the selenium complex with doubly hindered amines (2,6-dimethylpyridine and 2,4,6-trimethylpyridine), the plots of k_{obs} against [am] were linear. It seems likely, therefore, that the same reaction scheme[1] is applicable in the case of both substrates. Thus, for all the reactions reported here, the gradients of the straight lines obtained on plotting k_{obs} against amine concentration are interpreted as values of k_2, the rate con-

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Table I. Rate constants (k_{obs}) for the reactions of Pd(Se-Se)Cl_2 and of Pd(S-S)Cl_2 with amines (am) in 1,2-dimethoxyethane.

Temp. (°C)	16		25		40	
Amine	10^2[am] (M)	10^2k_{obs} (s^{-1})	10^2[am] (M)	10^2k_{obs} (s^{-1})	10^2[am] (M)	10^2k_{obs} (s^{-1})
(A). Pd(Se-Se)Cl_2.						
Pyridine	62.2	15.8	4.18	15.9	3.51	27.7
	46.8	11.1	3.0	10.5	2.63	19.4
	31.0	6.75	2.66	9.1	1.75	11.1
	20.7	3.5	2.1	6.9	1.16	5.0
3-Chloro-pyridine	32.4	16.8	31.4	20.7	11.3	13.6
	24.2	11.1	21.8	13.5	8.5	9.0
	16.2	6.5	14.6	8.4	5.65	4.94
	10.7	2.7	10.9	4.6	3.8	2.13
			5.46	1.5		
3-Cyano-pyridine	52.2	6.55	20.0	4.36	36.2	19.5
	36.5	4.30	10.0	1.20	30.2	15.0
	26.1	2.72	9.8	1.13	25.2	10.9
	14.4	1.30	7.5	0.65	21.8	10.2
					15.2	5.6
					11.0	2.6
3-Methyl-pyridine	3.82	11.9	2.8	13.4	3.82	34.1
	2.86	9.0	2.1	8.96	2.86	25.5
	1.91	4.79	1.87	7.66	1.91	15.4
	0.955	1.31	1.4	5.46	0.955	4.96
			0.935	2.8		
3,5-Dimethyl-pyridine	4.28	17.2	4.26	28.0	3.14	38.2
	3.20	10.8	2.85	17.4	2.35	25.0
	2.14	6.45	1.9	10.5	1.57	15.5
	1.42	1.97	1.42	6.5	1.05	7.5
			1.14	4.7		
2,4-Dimethyl-pyridine	40.5	3.94	8.1	1.51	33.8	13.9
	33.8	3.20	6.7	1.17	27.0	11.1
	27.0	2.47	6.08	1.09	23.0	8.0
	20.3	1.90	4.05	0.70	13.5	5.0
	13.5	1.23	3.35	0.57	8.0	3.08
	8.1	0.70	2.7	0.44		
2,5-Dimethyl-pyridine	45.5	3.75	47.9	7.50	34.7	12.1
	34.1	2.87	35.8	5.55	26.0	8.4
	22.8	1.88	27.0	4.30	17.3	5.6
	11.4	0.88	17.7	2.75	8.7	2.58
	4.55	0.40	9.0	1.25	3.5	0.84
2,6-Dimethyl-pyridine	23.1	0.45	78.0	4.18	55.8	6.45
	13.8	0.38	57.6	3.15	41.6	4.80
	11.7	0.31	39.0	2.10	31.0	3.84
	8.5	0.23	26.0	1.50	20.8	2.30
	5.0	0.14				
2,4,6-Trimethylpyridine	105	4.99	113	8.45	75.3	12.90
	79.5	2.65	75.3	5.25	64.3	11.0
	59.5	2.02	51.0	3.70	53.0	9.20
	39.7	1.30	38.2	2.77	48.2	8.50
	19.7	0.61	25.5	1.86	35.3	6.31
			17.0	1.27	32.2	5.50
					21.5	4.20
					17.7	2.88
					7.06	1.31

	15		40	
	10^2[am] (M)	10^2k_{obs} (s^{-1})	10^2[am] (M)	10^2k_{obs} (s^{-1})
(B). Pd(S-S)Cl_2.				
Pyridine	3.72	15.5	2.79	41.5
	2.79	11.5	1.86	26.6
	1.86	8.0	1.24	17.1
	0.93	4.55	0.764	9.5
			0.372	4.05
3-Methylpyridine	4.99	24.8	1.82	36.2
	3.42	17.9	1.37	24.8
	2.50	12.0	0.91	16.0
	1.25	4.85	0.27	3.72
	0.67	3.0	0.14	1.46

Table I. (Continued)

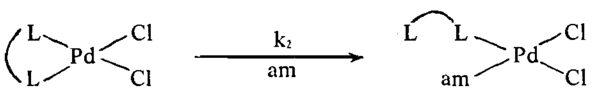
3,5-Dimethylpyridine	2.82	18.4	1.0	24.2
	2.20	14.4	0.75	18.3
	1.40	9.3	0.50	12.0
	0.75	4.9	0.25	6.0
			0.10	1.4
2-Methyl-pyridine	75.0	1.94	75.0	14.8
	56.3	1.40	56.3	10.6
	37.5	1.02	37.5	7.6
	18.7	0.52	18.7	3.8
2,4-Dimetryl-pyridine	67.5	2.87	67.5	21.9
	50.6	2.05	50.6	15.6
	33.7	1.50	33.7	11.3
	16.9	0.74	16.9	5.6
2,5-Dimethyl-pyridine	71.5	2.44	71.5	19.7
	53.6	1.83	53.6	14.6
	35.7	1.26	35.7	10.2
	17.8	0.59	17.8	5.6

Table II. Values of k_2 and activation parameters for the reactions of $Pd(Se\text{-}Se)Cl_2$ and of $Pd(S\text{-}S)Cl_2$ with amines.

Amine	pK_a (25°)	$Pd(Se\text{-}Se)Cl^2$ $k_2(M^{-1}s^{-1})$ 16°C	25°C	40°C	ΔH* kcal mol^{-1}	ΔS* e.u.	$Pd(S\text{-}S)Cl_2$ $k_2(M^{-1}s^{-1})$ 15°C	25°C	40°C	ΔH* kcal mol^{-1}	ΔS* e.u.
Pyridine	5.17	2.85	4.3	8.6	7.6	—30.1	4.0	6.8[a]	15.2	8.9	—24.8
3-Chloropyridine	2.84	0.53	0.81	1.68	7.9	—32.2	—	—	—	—	—
3-Cyano-pyridine	1.38	0.19	0.32	0.65	8.4	—32.4	—	—	—	—	—
3-Methylpyridine	5.68	3.8	5.8	10.4	7.0	—31.5	5.0	8.5	20.0	9.3	—23.1
3,5-Dimethylpyridine	6.34	5.5	8.5	15.2	7.0	—30.7	6.5	10.6[a]	24.2	8.8	—24.3
2-Methylpyridine	6.1	—	—	—	—	—	0.025	0.06[a]	0.19	14.0	—17.0
2,4-Dimethylpyridine	6.9	0.10	0.18	0.43	10.4	—26.9	0.04	0.092[a]	0.31	14.0	—16.4
2,5-Dimethylpyridine	6.6	0.081	0.156	0.35	10.5	—26.9	0.034	0.08	0.27	14.2	—16.2
2,6-Dimethylpyridine	6.7	0.0028	0.0052	0.012	10.7	—33.1	—	—	—	—	—
2,4,6-Trimetylpyridine	7.5	0.0038	0.007	0.018	11.1	—31.2	—	—	—	—	—

[a] Values from ref. (1).

stant for the reaction:



where L is Se or S. This rate-determining step is followed by the rapid replacement of L—L by a second amine molecule and by the isomerisation of the *cis*-$Pd(am)_2Cl_2$. The infrared spectrum of the product isolated from the reaction of $Pd(Se{-}Se)Cl_2$ with pyridine shows only a single band at 357 cm^{-1} and is probably *trans*-$Pd(py)_2Cl_2$.

The results in Table II show that for reactions involving amines with no ortho-substituent the value of ΔH* increases by 1-2 kcal mol^{-1} and ΔS* increases by 5-8 e.u. on passing from the selenium to the sulphur complex. Corresponding increases for the reactions of amines with one ortho-methyl group are 3-4 kcal mol^{-1} in ΔH* and about 10 e.u. in ΔS*. These comparisons show that for the selenium complex the bonding in the transition state is stronger and the transition state is more compact. (No direct comparison is possible for the reactions involving amines with methyl groups in both the 2- and 6-positions because in these cases values of k_2 could not be obtained with $Pd(S{-}S)Cl_2$ as substrate.[1])

With reference to the activation parameters for the reactions of a given substrate, it appears that both for the selenium and for the sulphur systems the introduction of an ortho-methyl group in the entering amine results in an increase in ΔH* and in ΔS*, the increase in ΔH* being slightly greater for the sulphur than for the selenium complex.

Plots of log k_2 for the se lenium system at each temperature against pK_a values of the amines give three parallel straight lines for the first five (unhindered) amines. On the same graph, lines drawn through the six pairs of points corresponding to the other two groups of amines are also parallel to the first set. The common gradient of these lines ($\alpha = 0.28$) is a measure of the capacity of the substrate to discriminate between the various nucleophilic entering groups.[4] The spacing along the log k_2 axis between a given pair of lines for reactions at a given temperature gives the value $\Delta = 1.8$ for the first two groups of amines. This «steric index» gives a measure of the effect of an ortho-methyl group on the reaction velocity. The corresponding values of α and Δ for the $Pd(S{-}S)Cl_2$ system are 0.22 and 2.4 respectively.[1]

It seems possible to account for most of the features of the present reactions in terms of the differences between Se and S in size and in π-bonding capacity. The lower sensitivity of the selenoether complex to steric effects is shown by the similarity in its general kinetic behaviour with all the amines studied, by the smaller changes in ΔH* accompanying changes in the nature of the entering amine, and by the smaller value of Δ. These effects (and possibly also the differences in ΔS^* for the reactions of the selenium and sulphur complexes) are understandable in terms of the difference in size of the two donor atoms. The differences in ΔH^* values for corresponding reactions of the seleno- and thio-ethers could be due to stronger π-bonding in the Pd–Se as compared with the Pd–S bond.[5] This would lead to the palladium becoming more positive and thus to stronger bonding in the transition state and also to a greater capacity of the selenium complex to discriminate between the entering nucleophiles.

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