Kinetics of the Displacement of Chloride in 5-Substituted-1,10-phenanthrolinedichloropalladium(II) Complexes

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The rate constants for the displacement of the first chloride by the nucleophiles Br^-, I^-, SCN^-, and $SC(NH_2)_2$ in the complexes $[Pd(L\text{–}L)Cl_2]$ (L–L = 1,10-phenanthroline, 5-chloro-1,10-phenanthroline, 5-nitro-1,10-phenanthroline, or 5-methyl-1,10-phenanthroline) have been determined in dimethylformamide at 25 °C. The rate constants, as well as the discriminating ability of the complexes, increase on decreasing pK_a of the unreplaceable ligand L–L.

In a previous paper [1] we have studied the effect of the unreplaceable ligand, L–L–L, on the rate of substitution of the group X, by different nucleophiles, in the substrates $[Pd(L\text{–}L\text{–}L)X]^+$ (L–L–L = 3-azapentane-1,5-diamine or terpyridine) in methanol at 25 °C. We have now extended our study by comparing the rates of replacement of chloride by the nucleophiles Br^-, I^-, SCN^-, and $SC(NH_2)_2$ in the closely related complexes $[Pd(L\text{–}L)Cl_2]$ [L–L = 1,10-phenanthroline (phen), 5-chloro-1,10-phenanthroline (cphen), 5-nitro-1,10-phenanthroline (nphen), and 5-methyl-1,10-phenanthroline (mphen)] in dimethylformamide at 25 °C. This comparison is interesting in that these complexes should differ in the electrophilicity of the reaction centre. The introduction of a substituent in the 5-position in the phenanthroline should change gradually the σ-donor properties of the ligand without creating steric hindrance on palladium(II).[2]

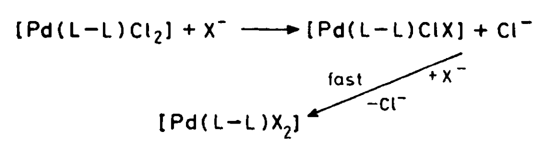
EXPERIMENTAL

Materials.—The complexes $[Pd(L\text{–}L)Cl_2]$ were prepared [3,4] by mixing methanol solutions of $K_2[PdCl_4]$ and the appropriate phenanthroline. The yellow substances which precipitated on adding water were recrystallized from dimethylformamide–water. All the complexes were characterized by elemental analysis and i.r. spectra. Dimethylformamide was distilled over calcium sulphate and then stored over molecular sieves. The nucleophiles LiBr, LiI, Na[SCN], and $SC(NH_2)_2$ were of reagent grade.

Kinetics.—The kinetics were followed spectrophotometrically in the u.v. region by the use of a Durrum D-110 stopped-flow spectrophotometer equipped with a Kel-F flow system. In order to assure pseudo-first-order conditions and to force the reactions to completion, the nucleophile concentration was at least 100 times larger than that of the complex. Four or five different concentrations were used for each nucleophile. The kinetic values were reproducible to better than ±5% [see Supplementary Publication No. SUP 22822 (4 pp.)† for values of $k_{obs.}$].

RESULTS AND DISCUSSION

Only one reaction step was observed within the lower time limit of the apparatus used (2 ms). In addition, only disubstituted complexes were obtained on isolating the reaction products between $[Pd(L\text{–}L)Cl_2]$ and the anionic reagents Br^-, I^-, and SCN^- under experimental conditions identical to the kinetic ones. These findings suggest that the reactions proceed according to the scheme shown in (1).



(1)

For all the reactions reported here, a route involving the formation of pseudo-bases [5,6] between the nucleophile and the co-ordinated phenanthroline, as reaction intermediates, is conceivable.‡ However, in no case was there evidence for the participation of such intermediates in the substitution process. Furthermore, within the time scale of the reactions studied here, no spectral change was detected on mixing large amounts of SCN^- and the complex $[Pd(nphen)(SCN)_2]$. For this particular system, the interaction between the nucleophile and the co-ordinated phenanthroline should be the greatest.[7] We assume, therefore, that the substitution reactions proceed through the usual mechanism implying attack by the nucleophile at the palladium atom.

The values of observed rate constants $k_{obs.}$ are in agreement with the usual two-term rate law, (2), where

$$k_{obs.} = k_1 + k_2[X^-] \qquad (2)$$

k_1 represents the rate constant for the solvolytic path and k_2 the rate constant for the direct bimolecular attack of the nucleophile. The values of k_1 and k_2 were obtained by least-squares analysis of the plots of $k_{obs.}$ *vs.* $[X^-]$ (Table). The values of k_1 refer to the intercepts of the plots of $k_{obs.}$ *vs.* $[Br^-]$. Only in this case could the contribution of the solvolytic rate constant to the overall rate constant be estimated without large uncertainties.

For all the complexes examined the values of k_2 conform to the sequence of nucleophilicity already observed for palladium(II) complexes.[8,9] While the solvolytic rate constants k_1 are not strongly dependent on the nature of the complex, the second-order rate constants, k_2, increase, slightly but gradually, with decreasing pK_a of the chelate phenanthroline. This

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

‡ We thank one of the referees for drawing our attention to this possibility.

Values of rate constants k_1 (s^{-1}) and k_2 ($dm^3\ mol^{-1}\ s^{-1}$) for reaction of $[Pd(L–L)Cl_2]$ with various nucleophiles in dimethylformamide at 25 °C

			$k_2/dm^3\ mol^{-1}\ s^{-1}$			
L–L	pK_a*	k_1/s^{-1}	Br^-	I^-	SCN^-	$SC(NH_2)_2$
nphen	3.6	0.020 ± 0.027	1.35 ± 0.10	17.9 ± 1.3	30.8 ± 0.4	408 ± 22
cphen	4.3	0.014 ± 0.002	1.11 ± 0.02	12.5 ± 0.5	17.1 ± 0.3	451 ± 20
phen	5.0	0.014 ± 0.001	0.54 ± 0.02	4.16 ± 0.17	7.45 ± 0.34	320 ± 10
mphen	5.2	0.013 ± 0.001	0.51 ± 0.02	3.73 ± 0.06	5.70 ± 0.25	315 ± 12

* Values from W. A. E. McBryde, ' Stability Constants of Metal Complexes,' IUPAC Chemical Data, no. 17, 1978.

indicates that the introduction of a substituent in a remote position is directly reflected in the electrophilicity of the reaction centre.

In order to estimate quantitatively the effect of the ligand, L–L, on the kinetic behaviour of our substrates, it is convenient to apply the linear free-energy relation obeyed by palladium(II) complexes (3)[8] where s is the

$$\log k_2 = s n_{Pd}^0 + \log k_1 \qquad (3)$$

nucleophilic discrimination factor and represents the effectiveness of a given substrate to discriminate among various nucleophiles; $\log k_1$ is the intrinsic reactivity, *i.e.* the logarithm of the rate constant for reaction of the complex with the poorest nucleophile, the solvent; and n_{Pd}^0 is a set of nucleophilic reactivity constants determined on the complex *trans*-$[Pd(PPr_3)_2(NO_2)_2]$ chosen as a standard.

All the complexes follow equation (3) as far as the anionic reagents are concerned. Thiourea exhibits a deviant behaviour and reacts in each case faster than expected on the basis of the linear free-energy relation (3). The deviations decrease as the pK_a of the ligand L–L decreases (see Figure). The values of intrinsic reactivity, probably due to the reduced magnitude of the effect, do not show any particular trend. The nucleophilic discrimination factor, however, shows a slight, but well above the experimental error, increase as the pK_a of the chelate phenanthroline, L–L, decreases ($s_{nphen} = 0.71 \pm 0.02$; $s_{cphen} = 0.63 \pm 0.01$; $s_{phen} = 0.58 \pm 0.01$; $s_{mphen} = 0.55 \pm 0.01$). This finding is consistent with the enhancement of electrophilicity of the reaction centre, expected on increasing σ-donor character of the nitrogen atoms of the chelate ligand L–L. In fact, the formation of a fifth bond in the transition state, and, consequently, the sensitivity of the substrate to the change in the nature of the entering group is eased as the electrophilicity of palladium increases.

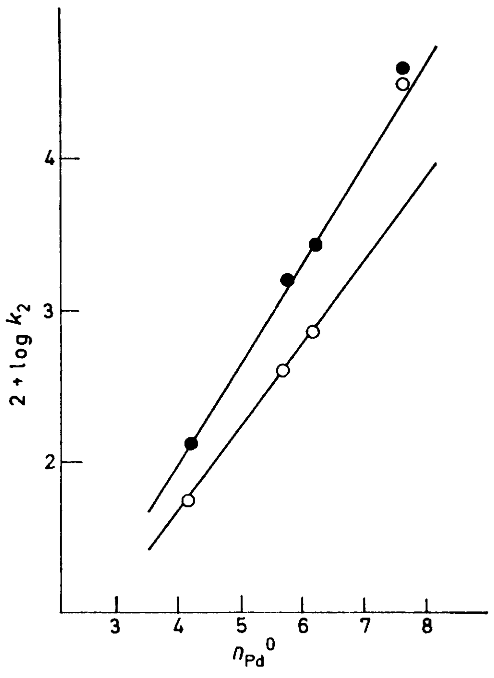

FIGURE Plots of rates of reaction of the complexes $[Pd(L–L)Cl_2]$ against n_{Pd}^0 for different nucleophiles: nphen (●) and phen (○)

The anomalous behaviour of thiourea is also not surprising. Thiourea is known to have biphilic properties;[10,11] by way of π interactions with the metal, this nucleophile is capable of binding more strongly than a normal reagent. The extent to which thiourea can behave as a biphilic reagent is obviously strictly related to the nature of the substrate. In the complexes $[Pd(L–L)Cl_2]$ thiourea can behave as a biphilic reagent to a greater extent than in the standard complex *trans*-$[Pd(PPr_3)_2(NO_2)_2]$ where three potentially biphilic groups are already present in the transition state. Likewise, along the series of complexes examined, the ability of thiourea to exert its biphilicity increases with increasing electronegativity of palladium.

Financial support from the Italian C.N.R. is acknowledged.

[9/2023 *Received*, 31*st December*, 1979]

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