Fast Reactions at Planar Four-co-ordinate Complexes. Part 4.[1] The Reaction of Chelate Dichloropalladium(II) Complexes with Some Bidentate Ligands

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The reaction between the square-planar complexes [Pd(L–L)Cl_2] [L–L = 1,2-bis(diphenylphosphino)ethane, *o*-phenylenebis(dimethylarsine), ethylenediamine, 1,10-phenanthroline, 2,2′-bipyridine, or 1,2-bis(phenylthio)ethane] and ethylenediamine proceeds in two consecutive stages yielding [Pd$(en)_2$]Cl_2 as a final product. The intermediate species is [Pd(L–L)(en)]Cl_2 or [Pd(en)Cl_2] when L–L is 1,2-bis(phenylthio)ethane. The rate of replacement of the first chloride co-ordinated to palladium(II) in the substrates [Pd(L–L)Cl_2] at 25 °C in dimethylformamide is strongly dependent on the nature of the ligand L–L, covering four orders of magnitude. The reaction between the substrates [M(bipy)Cl_2] (M = Pd or Pt, bipy = 2,2′-bipyridine) and the bidentate nucleophiles ethylenediamine and dithio-oxamide proceeds according to an analogous two-stage reaction scheme when M is palladium; in the platinum derivatives, however, the chelate bipyridine is inert towards substitution. In the solvent dimethylformamide the entering group ethylenediamine behaves as a very effective nucleophile.

OVER the last few years we have been concerned with a study of the effect of nitrogen chelate ligands on the rate of substitution of unidentate groups in palladium(II) complexes.[2,3] In particular, we have (*i*) compared the lability of the group X co-ordinated to palladium(II) in the cationic substrates [Pd(N–N–N)X]$^{2+}$ containing the tridentate ligands 3-azapentane-1,5-diamine or terpyridine differing in steric properties and in the nature of interaction with the metal, and (*ii*) related the decrease in rate constants and in the discrimination ability for the replacement of the first chloride in the complexes [Pd(5-substituted-phenanthroline)Cl_2] [3] to the increasing σ-donor power of the phenanthroline ligand. We have now extended our study by considering a series of substrates of the type [Pd(L–L)Cl_2] where the chelate ligands all form five-membered rings with palladium(II) but differ widely in the nature of the co-ordinated atoms and in the type of interaction with the reaction centre. In this paper we report kinetic data for the reaction between the complexes [Pd(L–L)Cl_2] [L–L = 1,2-bis(diphenylphosphino)ethane (dppe), *o*-phenylenebis(dimethylarsine) (pdma), ethylenediamine (en), 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), or 1,2-bis(phenylthio)ethane (dpse)] and ethylenediamine in dimethylformamide (dmf) at 25 °C, and for the reaction between [M(bipy)Cl_2] (M = Pd or Pt) and the ligands dithio-oxamide (dtoa) and en in the solvents dimethylformamide and methanol (MeOH) at the same temperature. The rate constants relative to the replacement of the first chloride by bromide in the substrates [Pd(bipy)Cl_2] and [Pd(en)Cl_2] in dmf at 25 °C have also been determined.

EXPERIMENTAL

Materials.—The complexes [Pd(L–L)Cl_2] and [Pt(bipy)Cl_2] were prepared according to the methods reported in the literature.[4-7] The complexes [Pd(L–L)(en)]Cl_2 (L–L = phen or bipy) were prepared by mixing concentrated dmf solutions of the appropriate dichloro-complex and en in a ratio 1 : 1. The microcrystalline precipitates formed upon mixing were washed with cold dmf and dried with diethyl ether. The substances were then recrystallized from MeOH–dmf. [Pd(bipy)(dtoa)]Cl_2 was prepared following substantially the same procedure. All the complexes were characterized by elemental analysis and i.r. spectra. Dimethylformamide was distilled over calcium sulphate and then stored over molecular sieves. Methanol was distilled over magnesium methoxide. Ethylenediamine was distilled over potassium hydroxide pellets. The compounds dtoa and LiBr were of reagent grade.

Kinetics.—In order to assure pseudo-first-order conditions and to force the reactions to completion, all the kinetics were performed in the presence of an excess of nucleophile with respect to the complex. The reactions were followed either spectrophotometrically or conductometrically. In the former case the kinetic course was monitored, at a suitable wavelength in the u.v. region, by the absorbance variations associated with the reactions. The values of observed rate constants $k_{obs.}$ were evaluated from the gradients of the plots of $\ln(A_\infty - A_t)$ against time; A_∞ represents the absorbance after seven to eight half-lives and A_t the absorbance at time *t*. Slower reactions were followed using a Beckman D.U. spectrophotometer equipped with a Servogor S potentiometric recorder. Faster reactions were followed by the use of a stopped-flow Durrum D-110 equipped with a Kel-F flow system and a storage oscilloscope. The conductimetric kinetics were followed by the increase in conductivity of the reacting solutions due to the formation of ionic products from neutral reactants. A Radiometer CDM 3 conductivity bridge equipped with a Rec 61 Servograph recorder was used to monitor the reaction course. A sample of the complex (25 cm^3) was placed in a vessel in which was immersed a conductivity cell. To this solution, thermostatted at 25 °C, and under magnetic stirring, was injected the nucleophile (0.5 cm^3) at a suitable concentration. The stirring was then suspended and the increase in conductivity was monitored on the recorder. The exponential curves *C*/*t* were linearized by plotting $\ln(C_\infty - C_t)$ against time. C_∞ is the final value of conductivity of the solution and C_t the value of conductivity at time *t*. All the kinetic data, deposited as Supplementary Publication No. SUP 23014 (6 pp.),† were reproducible to better than ±5%.

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

RESULTS

When an excess of en is added to a dmf solution of the complexes $[Pd(L{-}L)Cl_2]$ an immediate spectral variation is observed. The reaction is associated with a well defined conductivity increase and, in all cases, the final value of conductivity of the solution is that expected for a 2 : 1 electrolyte in dmf [8] (140—160 S cm^2 mol^{-1}). When L–L is en, phen, or bipy, the only reaction product which can be isolated, immediately after the mixing of the complex and the ligand, is $[Pd(en)_2]Cl_2$. Isolation of the reaction product between $[Pd(L{-}L)Cl_2]$ (L–L = dppe or pdma) and en, under the same experimental conditions, yields the monosubstituted complexes $[Pd(L{-}L)(en)]Cl_2$; these substances, however, are unstable and undergo further very slow substitution by a second molecule of ethylenediamine to give $[Pd(en)_2]Cl_2$. In addition, when dealing with the complexes $[Pd(phen)Cl_2]$ or $[Pd(bipy)Cl_2]$, if the stoicheiometric ratio en : complex is unitary it is possible to isolate from the reaction mixture the monosubstituted complexes $[Pd(phen)(en)]Cl_2$ and $[Pd(bipy)(en)]Cl_2$. These findings suggest that the reaction between the substrates $[Pd(L{-}L)Cl_2]$ (L–L = dppe, pdma, phen, bipy, or en) and en in dmf proceeds according to the general scheme (1).

$$[Pd(L{-}L)Cl_2] + en \xrightarrow{k_a} [Pd(L{-}L)(en)]Cl_2 \xrightarrow[en,\ -L{-}L]{k_b} [Pd(en)_2]Cl_2 \qquad (1)$$

The reaction between the complexes $[M(bipy)Cl_2]$ (M = Pd or Pt) and the bidentate ligands, A–A, en, and dtoa in the solvent dmf and MeOH, proceeds according to an analogous two-stage scheme (2). However, in the platinum derivatives $[Pt(bipy)(A{-}A)]Cl_2$, the chelate ligand bipy is inert towards substitution by A–A.

$$[M(bipy)Cl_2] + A{-}A \xrightarrow{k_a'} [M(bipy)(A{-}A)]Cl_2 \xrightarrow[+A{-}A,\ -bipy]{k_b'} [M(A{-}A)_2]Cl_2 \qquad (2)$$

The complex $[Pd(dpse)Cl_2]$ also reacts in two steps to give $[Pd(en)_2]Cl_2$ as a final product according to reaction (3).

$$[Pd(dpse)Cl_2] + en \xrightarrow[-dpse]{k_a''} [Pd(en)Cl_2] \xrightarrow[en]{k_b''} [Pd(en)_2]Cl_2 \qquad (3)$$

The rate law for reactions (1), (2), and (3), under pseudo-first-order conditions, was the usual one followed by the square-planar complexes [equation (4)]. The ring-closure of en and dtoa is expected to be fast and, consequently, k_2 represents in all cases the rate constant for the bimolecular

$$k_{obs.} = k_1 + k_2[A{-}A] \qquad (4)$$

attack of the first end of the ligand at the palladium atom. The term k_1, *i.e.* the contribution of the solvolytic path to the overall rate constant, could be estimated only in few cases.

It was found that, as the dmf solutions of en aged, a white precipitate appeared in the volumetric flasks and the observed rates of reaction between this ligand and a given complex decreased. For this reason all the solutions of en in dmf were prepared immediately prior to use. With these solutions the $k_{obs.}$ values were reproducible to within about ±3%.

The values of k_2 relative to the two consecutive steps of the reaction of $[Pd(L{-}L)Cl_2]$ (L–L = phen or bipy) with en and dtoa in the solvent dmf were not sufficiently different to be determined without large uncertainty. It was found preferable, therefore, to obtain the values of k_b and k_b' directly from the kinetic data for the reaction of the intermediates $[Pd(L{-}L)(en)]Cl_2$ and $[Pd(L{-}L)(dtoa)]Cl_2$ with the ligands en and dtoa respectively. The values of k_a and k_a' were determined by the conductivity changes associated with the first step of reaction.

The rate constants relative to the replacement of the first chloride by bromide in the complexes $[Pd(bipy)Cl_2]$ and $[Pd(en)Cl_2]$ in dmf at 25 °C conformed to the two-terms rate law.

The values of k_1 and k_2, obtained by least-squares analysis of the plots of $k_{obs.}$ against [entering nucleophile], are reported in Tables 1—3.

TABLE 1

Second-order rate constants, $k_{2,a}$ and $k_{2,b}$, for reaction (1) in dmf at 25 °C

L–L	$10^{-2}k_{2,a}$ / dm^3 mol^{-1} s^{-1}	$10^{-2}k_{2,b}$ / dm^3 mol^{-1} s^{-1}
dppe	$1.21 \pm 0.06 \times 10^3$	
pdma	$4.76 \pm 0.19 \times 10^2$	
bipy	2.66 ± 0.13	1.09 ± 0.04
phen	2.09 ± 0.08	0.84 ± 0.03
en	0.14 ± 0.00	

The value of rate constant $k_{2,a}''$, obtained by spectrophotometry, is $1.26 \pm 0.08 \times 10^3$ dm^3 mol^{-1} s^{-1}. The value of rate constant $k_{2,b}''$ for the second step of reaction

TABLE 2

Rate constants for reaction (2) in MeOH and in dmf at 25 °C

M	A–A	Solvent	$10k_{1,a}'$ / s^{-1}	$10^4k_{2,a}'$ / dm^3 mol^{-1} s^{-1}	$k_{1,b}'$ / s^{-1}	$10k_{2,b}'$ / dm^3 mol^{-1} s^{-1}
Pd	en	MeOH	3.31 ± 0.11	$3.19 \pm 0.13 \times 10^6$	$4.16 \pm 0.21 \times 10^{-4}$	6.96 ± 0.03
	dtoa		2.49 ± 0.11	$3.03 \pm 0.12 \times 10^7$	$2.18 \pm 0.12 \times 10^{-4}$	6.86 ± 0.37
Pt	en	MeOH		$5.95 \pm 0.21 \times 10^2$ [a]		
	dtoa		$2.78 \pm 0.14 \times 10^{-3}$ [b]	$1.57 \pm 0.06 \times 10^3$ [b]		
Pd	en	dmf		$2.66 \pm 0.13 \times 10^6$		$1.09 \pm 0.04 \times 10^3$
	dtoa		$9.57 \pm 0.41 \times 10^{-2}$	$3.43 \pm 0.15 \times 10^5$	$3.36 \pm 0.12 \times 10^{-4}$	1.84 ± 0.07
Pt	en	dmf		$8.55 \pm 0.34 \times 10^2$		
	dtoa			$1.13 \pm 0.07 \times 10^2$		

[a] Data from L. Baracco, L. Cattalini, J. S. Coe, and E. Rotondo, *J. Chem. Soc. A*, 1971, 1800. [b] Data from P. Haake and P. A. Cronin, *Inorg. Chem.*, 1963, **2**, 879.

TABLE 3

Rate constants k_1 and k_2 for the reaction [Pd(L–L)Cl_2] + Br^- ⟶ [Pd(L–L)BrCl] + Cl^- in dmf at 25 °C

L–L	$\frac{k_1}{s^{-1}}$	$\frac{k_2}{dm^3\ mol^{-1}\ s^{-1}}$
bipy	0.014 ± 0.001	4.80 ± 0.27
phen	0.014 ± 0.001 *	0.54 ± 0.02 *
en	0.010 ± 0.000	0.04 ± 0.00

* Data from ref. 3.

(3) was determined conductometrically. This value (12.18 ± 0.91 dm^3 mol^{-1} s^{-1}) agrees well with that obtained directly from the reaction of [Pd(en)Cl_2] with en (Table 1).

DISCUSSION

In the nucleophilic substitutions at square-planar complexes, the labilizing effect [9,10] of the ligands co-ordinated to the reaction centre play a major role on the reaction course. In fact, the labilizing effect determines which one of the groups undergoes substitution and acts on its rate of replacement. The circumstance that the only product of the first step of the reaction between the complexes [Pd(L–L)Cl_2] (L–L = dppe, pdma, phen, bipy, or en) and en is [Pd(L–L)(en)]Cl_2 is evidence that in all these substrates the labilizing effect of the ligand L–L is much larger than that of chloride. The relative labilizing effects of L–L and chloride are reversed in the complex [Pd(dpse)Cl_2]; as a matter of fact, no species other than [Pd(en)Cl_2] is formed in the reaction with en.

The influence of the ligand L–L on the rate of replacement of chloride, in the substrates studied by us, cannot be examined in terms of *trans* effect or *cis* effect [11] only, in that both the atoms co-ordinated to palladium in these positions change along the series of substrates. Nevertheless, the influence of the ligand L–L on the kinetic values can be compared as an overall labilizing effect. Inspection of Table 1 shows that the rate of substitution of chloride depends markedly on the nature of the ligand L–L. Thus, the values of k_a, which increase in the order en < bipy ≃ phen ≪ pdma < dppe, cover four orders of magnitude. Significantly, the labilizing effect of the ligand L–L on chloride is larger for those groups such as dppe and pdma which are capable of enhancing the electrophilicity of the reaction centre by way of strong π interactions with palladium in the transition state.[12] Likewise, the difference between the values of k_a relative to the substrates containing the aromatic ligands bipy and phen and that relative to the complex [Pd(en)Cl_2] is probably due to the capability of the former only to exert π interactions.[13]

The rate of replacement of the ligand L–L by a second molecule of en in the substrates [Pd(L–L)(en)]Cl_2 also ranges within wide limits. Thus, while the reaction of [Pd(dppe)(en)]Cl_2 or [Pd(pdma)(en)]Cl_2 with en (2 mol dm^{-3}) in dmf at 25 °C lasts for many hours, the half-life for the substitution of bipy or phen under the same experimental conditions is less than a few milliseconds (Table 1). Likewise, dtoa promptly replaces bipyridine (Table 2) in the complex [Pd(bipy)(dtoa)]Cl_2.

The rate constant for the replacement of chloride by en in the complex [Pd(phen)Cl_2] in dmf is comparable to the rate constant for the same process using a strong nucleophile such as thiourea [14] (320 ± 10 dm^3 mol^{-1} s^{-1}).[3] Likewise, in dmf, en is much more effective than bromide (Table 3) in replacing the first chloride co-ordinated to palladium in the substrates [Pd(L–L)Cl_2] (L–L = bipy, en, or phen). This is an interesting point in that amines are known to behave as poor nucleophiles toward square-planar complexes.[15] The enhanced reactivity of en in dmf is shown also by the comparison of the relative reactivities of the bidentate ligands en and dtoa, toward the substrates [M(bipy)Cl_2] (M = Pd or Pt), in the solvents MeOH and dmf (Table 2). In fact, while in MeOH en is less nucleophilic than dtoa with respect to both complexes, in dmf the reactivity of en overcomes that of dtoa. The enhanced reactivity of en in dmf can be due to an interaction of the ligand with the solvent; more specifically, hydrogen bonding of the basic moiety of dmf with the amine protons could account for the higher nucleophilicity of en in this solvent. The formation of hydrogen bonds between amine protons, and also weakly basic solvents, has been established spectroscopically [16] and attack by hydrogen-bonded primary amines at several substrates has already been postulated [17,18] in order to rationalize the abnormally high reactivity of these compounds.

Finally one can observe (Table 2) that in agreement with the higher lability of palladium substrates with respect to the platinum ones,[19] the rate of replacement of chloride in the complexes [Pd(bipy)Cl_2] and [Pt(bipy)Cl_2] decreases by a factor of 10^3—10^4 on going from the former to the latter. Moreover, in the complex [Pd(bipy)(en)]Cl_2, bipy is replaced by en (0.5 mol dm^{-3}) in MeOH at 25 °C within a few seconds, but in the platinum derivative bipy is totally inert toward substitution within a period of several weeks, also using larger en concentrations.

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