The Mechanism of the Catalytic *cis–trans* Isomerization of Planar Diacidodiaminopalladium(II) Complexes

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Abstract: The kinetics of the second stage of the reactions of the complexes $[Pd(S\text{–}S)X_2]$ (S–S = $C_6H_5\text{–}S\text{–}CH_2CH_2\text{–}S\text{–}C_6H_5$; X = N_3, Br, I, CNS) with a variety of amines (am) have been studied in 1,2-dimethoxyethane at 25°. The results indicate that the process is the isomerization of the species $[Pd(am)_2X_2]$ from the *cis* to the *trans* form, catalyzed by the presence of excess amine. The rate shows a first-order dependence on both the concentration of complex and free amine, and the rate-determining step is the displacement of one of the anionic ligands, X, followed by the fast reentering of X^- into the intermediate complex, $[Pd(am)_3X]^+$. The effects on the kinetics of systematically changing the nature of X and am confirm this mechanism and also allow a discussion of the details of the mechanism.

A *cis–trans* isomerization in planar complexes of d^8 transition metal ions of the type $[MA_2B_2]$ has been observed in a number of cases, but quantitative investigations have been confined mainly to studies of equilibria[1] and photochemical isomerization.[2,3] These isomerizations appear to be catalyzed in solution by the presence of a free ligand in the reaction mixture. Thus, while complexes of the type *cis*- and *trans*-$[PtL_2Cl_2]$ (L = PR_3, AsR_3, SbR_3, and R_2S) are resistant to isomerization (although substitutionally labile), they rapidly achieve isomeric equilibrium in the presence of traces of the free ligand, L.[4,5] Since the ligand displacement reactions are known to occur with complete retention of the geometric configuration,[6,7] a two-step reaction scheme, which does not contradict the stereospecific behavior of the substitution processes, was proposed to explain isomerization.[4,6] However, there are no kinetic data in the literature which can provide experimental evidence for this mechanism.

We have recently studied[8] the kinetics of displacement of the chelate group, $C_6H_5\text{–}S\text{–}CH_2CH_2\text{–}S\text{–}C_6H_5$ (S–S) from the complex $[Pd(S\text{–}S)Cl_2]$ by amines in 1,2-dimethoxyethane. A parallel study[9] indicated that this reaction first produces the relatively unstable *cis* complex, *cis*-$[Pd(am)_2Cl_2]$, in accordance with the general stereochemical rule. However, it was not possible to rule out in the spectrophotometric runs a slow *cis* → *trans* isomerization, owing to the small differences in the uv spectra of the two dichloro isomers.

Preliminary experiments on the course of the reaction

$$[Pd(S\text{–}S)X_2] + 2am \longrightarrow [Pd(am)_2X_2] + S\text{–}S \qquad (1)$$

(am = amine; X = N_3, Br, I, CNS) in 1,2-dimethoxyethane showed that the final products were the *trans* isomers, but a relatively slow reaction followed the displacement of S–S by amines and could be studied spectrophotometrically. *cis–trans* equilibria do not interfere in these systems since the high stabilities of the *trans* forms in palladium(II) chemistry[6,7] cause the reaction to go to completion. The results are reported and discussed in this paper.

Results

Examination of the changing spectrum of a solution originally containing the starting complex, $[Pd(S\text{–}S)X_2]$, and excess amine shows that a two-stage process is involved. A typical kinetic run is reported in Figure 1. The first stage is the displacement of the ligand S–S by two amine molecules, and the corresponding kinetics are being investigated and will be published elsewhere. The final product is a complex of the type *trans*-$[Pd(am)_2X_2]$ since the final spectra are identical with those of original samples of the corresponding *trans*-diamino complexes. Moreover, the species *trans*-$[Pd(am)_2X_2]$ can be obtained from $[Pd(S\text{–}S)X_2]$, in almost quantitative yield, by carrying out the reactions under preparative conditions.

The second stage, which is appreciably slower than the first, can be attributed to a *cis* → *trans* isomerization by the following evidence.

(i) The use of bidentate nitrogen donors such as ethylenediamine or bipyridyl as entering reagents causes the disappearance of the second stage in the changing spectrum and the products are the complexes $[Pd(N\text{–}N)X_2]$.

(ii) The rate of the second stage is independent of the nature of the bidentate sulfur ligand, as can be seen from the reactions of the substrates containing 1,8-bis(methylthio)naphthalene, $C_6H_5\text{–}S\text{–}(CH_2)_3\text{–}S\text{–}C_6H_5$ and $C_6H_5\text{–}S\text{–}(CH_2)_2\text{–}S\text{–}C_6H_5$ (Table I).

(iii) The isomerization of an authentic sample of *cis*-$[Pd(NH_3)_2Br_2]$ in the presence of free ammonia gives the same change in the uv spectrum as that observed during the second stage of the reaction between $[Pd(S\text{–}S)Br_2]$ and ammonia. Moreover, the rate of the isomerization of *cis*-$[Pd(NH_3)_2Br_2]$ and the rate of the second stage of the reaction of $[Pd(S\text{–}S)Br_2]$, measured under the same experimental conditions, are identical (Table I).

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Table I. First- and Second-Order Rate Constants Relative to the Reactions (2) in 1,2-Dimethoxyethane at 25° [a]

Amine	pK_a[e]	X	10^2[am], M	$10^2 k_{obsd}$, sec^{-1}	k_i, M^{-1} sec^{-1}
4-Cyanopyridine	1.9	I	10.5	1.33	0.127
			24.8	3.18	0.128
			26.2	3.3	0.126
3-Chloropyridine	2.84	I	6.3	0.65	0.103
			31.5	3.14	0.099
			63	6.32	0.099
4-Formylpyridine	4.53	I	5.0	1.63	0.326
			10	3.3	0.33
			20	6.2	0.315
			50	16.4	0.328
Pyridine	5.17	I	3.2	1.23	0.384
			7.5	2.9	0.386
			11.2	4.2	0.375
			18.5	7.2	0.390
			31	12.1	0.391
			37	14.5	0.392
Pyridine[b]	5.17	I	1.45	0.54	0.374
			14.5	5.62	0.388
Pyridine[c]	5.17	I	1.45	0.545	0.386
			14.5	5.65	0.390
3-Methylpyridine	5.68	I	5.94	2.05	0.345
			11.9	4.23	0.355
			29.7	10.5	0.354
			59.4	21	0.354
4-Methylpyridine	6.02	I	3.05	1.65	0.542
			15.25	8.5	0.557
			30.5	16.8	0.551
3,5-Dimethylpyridine	6.34	I	1.87	0.60	0.324
			9.35	2.80	0.300
			18.7	5.85	0.313
3,4-Dimethylpyridine	6.46	I	1.096	0.515	0.480
			5.48	2.70	0.492
			10.96	5.3	0.483
			54.8	27.4	0.50
4-Cyanopyridine	1.9	CNS	5.3	0.68	0.128
			26.5	3.2	0.121
			53	6.7	0.126
3-Chloropyridine	2.84	CNS	13.3	1.3	0.098
			33.3	3.0	0.090
			66.6	6.2	0.093
4-Formylpyridine	4.53	CNS	5.0	2.08	0.416
			10	4.15	0.415
Pyridine	5.17	CNS	7.06	3.8	0.538
			35.8	19	0.530
			70.6	38	0.536
3-Methylpyridine	5.68	CNS	1.392	0.70	0.505
			6.96	3.75	0.538
			13.92	7.25	0.520
4-Methylpyridine	6.02	CNS	3.86	3.1	0.83
			9.65	8.2	0.85
			19.3	16.4	0.85
3,5-Dimethylpyridine	6.34	CNS	2.78	1.15	0.414
			5.56	2.3	0.413
3,4-Dimethylpyridine	6.46	CNS	2.98	2.35	0.788
			5.96	4.8	0.806
			11.9	9.8	0.823
			29.8	24	0.805
Pyridine	5.17	Br	5.68	1.4	0.244
			11.4	3.0	0.263
			22.7	5.8	0.256
			56.8	14.5	0.255
3-Methylpyridine	5.68	Br	8.2	1.98	0.242
			16.4	3.9	0.238
			41	9.9	0.242
4-Methylpyridine	6.02	Br	3.3	1.04	0.315
			6.6	2.18	0.330
			13.2	4.25	0.322
3,5-Dimethylpyridine	6.34	Br	5.5	1.15	0.209
			13.7	2.8	0.204
			27.4	5.9	0.215
3,4-Dimethylpyridine	6.46	Br	5.5	1.6	0.291
			11.0	3.4	0.309
			22	6.65	0.302
Ammonia	9.24	Br	8.42	0.98	0.116
Ammonia[d]		Br	8.42	0.97	0.115
4-Formylpyridine	4.53	N_3	20	0.59	0.0295
			50	1.5	0.03
Pyridine	5.17	N_3	18.3	0.58	0.0317
			30.3	1.03	0.034
			60.6	2.02	0.0333
3-Methylpyridine	5.68	N_3	11.55	0.38	0.0329
			23.1	0.74	0.0320
			57.3	1.84	0.0321
4-Methylpyridine	6.02	N_3	11.8	0.5	0.042
			29.5	1.24	0.042
			59	2.55	0.043
3,5-Dimethylpyridine	6.34	N_3	8.7	0.25	0.028
			21.7	0.635	0.029
			43.4	1.33	0.030
3,4-Dimethylpyridine	6.46	N_3	18.5	0.735	0.039
			46.3	1.88	0.040
			92.6	3.8	0.041

[a] Note well: The concentration of the complex in the reaction mixture was always less than 10^{-4} M. [b] Starting substrate containing 1,8-bis(methylthio)naphthalene. [c] Starting substrate containing C_6H_5–S–$(CH_2)_3$–S–C_6H_5. [d] Reaction on the complex *cis*-[Pd$(NH_3)_2Br_2$]. [e] Values relative to the acid amH$^+$ in water, from D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth & Co., Ltd., London, 1965; L. G. Sillén and A. E. Martell, "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

Thus we are confident that the rates which have been measured are those of the process

$$cis\text{-}[\mathrm{Pd(am)_2X_2}] \xrightarrow{\text{(am)}} trans\text{-}[\mathrm{Pd(am)_2X_2}] \quad (2)$$

The kinetics have been followed in the presence of a large excess of free amine, *i.e.*, under conditions where the displacement of the chelate group, S–S, in the first stage is relatively fast. The first-order rate constants, k_{obsd}, have been calculated from the slope of the plot of log $(D_t - D_\infty)$ *vs.* time, where D_t and D_∞ are the optical densities of the reaction mixture at time t (during the second stage) and at the end of the reaction, respectively. The reproducibility was excellent, and measurements carried out at different wavelengths, where there is an adequate change of optical density, give the same value for the rate constants. The values of k_{obsd} are summarized in Table I.

The best experimental conditions are achieved with the complexes containing the anionic ligands iodide and thiocyanate since the *cis* and *trans* isomers have markedly different absorption in the region of the spectrum where the amines do not absorb light. The complexes containing bromide and azide, however, only show large differences at the shorter wavelengths (see Experimental Section) and so it was not possible to follow the reactions of the latter complexes with amines having a strong absorption in the ultraviolet region of the spectrum.

Discussion

The data reported in Table I show that the pseudo-first-order rate constant of the isomerization process (2), k_{obsd}, is dependent on the concentration of the free

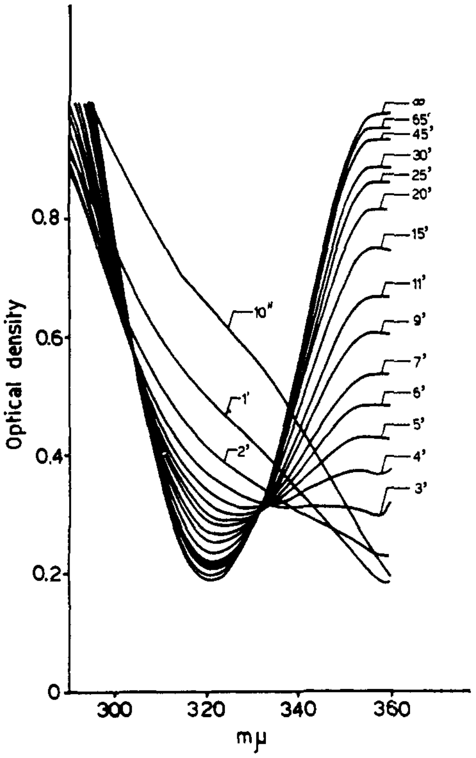

Figure 1. Spectral changes during the reaction of $[Pd(S–S)I_2]$ with 4-methylpyridine, 1.05×10^{-2} *M*, in 1,2-dimethoxyethane at 25°.

amine; the kinetics obeys the rate law

$$\text{rate} = -d[cis]/dt = k_i[cis][\text{am}]$$

The second-order rate constants, k_i, have been calculated from the linear plots of k_{obsd} against [am] and are also reported in Table I. The first-order dependence of the rate on the concentration of the amine in the reaction mixture strongly suggests that the rate-determining step is

$$cis\text{-}[Pd(am)_2X_2] + \text{am} \xrightarrow{k_i} [Pd(am)_3X]^+X^- \quad (3)$$

followed by the fast reentering of the anionic ligand

$$[Pd(am)_3X]^+X^- \xrightarrow{\text{fast}} trans\text{-}[Pd(am)_2X_2] + \text{am} \quad (4)$$

In the complexes *cis*-$[Pd(am)_2X_2]$, the *trans*-labilizing effect of X is large enough to cause the fast substitution of the amine ligands. In fact, parallel experiments carried out under the same experimental conditions show that, on starting from *cis*-$[Pd(NH_3)_2Br_2]$, the rate of isomerization in the presence of pyridine is the same as that observed on starting from $[Pd(S–S)Br_2]$ + py. This replacement, however, leads merely to exchange of am and therefore is not detected spectrophotometrically.

In other words, the *cis* complex undergoes isomerization according to the scheme shown in Figure 2, where the transition states are represented as trigonal-bipyramidal structures, as is normal for ligand substitution in planar complexes.[6,7] This mechanism is essentially that originally proposed by Drew and Wyatt[4] and reported by Basolo and Pearson.[6] It implies that the rate-determining step for the isomerization is the substitution process (3). This type of reaction is known to occur with an associative asynchronous mechanism,[7] and it will be therefore necessary to discuss the details of the mechanism in order to decide, possibly, the type of transition state which is involved. The data collected in Table I permit discussion of the effects arising from the systematic change of the nature of am and X in the reacting system on the kinetic behavior. They are both composite effects and will be discussed separately.

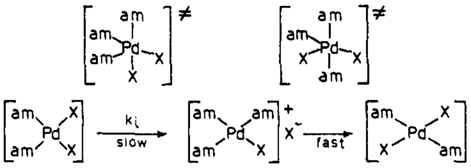

Figure 2. The mechanism of isomerization of *cis*-$[Pd(am)_2X_2]$ in the presence of excess amine.

The Role of the Acidic Ligands, X. The substitutions represented by reaction 3 occur at a substrate containing two ligands X, one of which is the replaceable group and the other the ligand *cis* to it in the ground state. As a consequence, the influence of their nature on the kinetic behavior might be discussed in terms of leaving-group effect and *cis* effect at the same time.

Studies on the effect of changing the nature of the leaving group on the rate of substitution in planar complexes have been made in the past, mainly with platinum(II) substrates. For anionic replaceable ligands data are available for the entry of neutral and anionic nucleophiles in neutral and cationic substrates in various solvents.[10–14]

It was found that the reactivity changes with the nature of the displaced ligands, but the sequence of leaving-group effect on the reactivity is strongly dependent on the nature of the reacting system. Therefore, it is pointless to compare the sequence of reactivity obtained in this work with that relative to the reactions of amines on the complexes $[Pd(dien)X]^+$ in methanol,[15] which is the only study of this type which has been made with palladium(II) complexes.

However, a common feature of all the researches reported above[10–15] was that, although the reactivity depends very much upon the nature of the leaving group, the effect of the latter on the ability of the substrate to discriminate between different reagents is almost negligible. On the other hand, the nature of the *cis* ligands influences both reactivity and discrimination. This was shown[16,17] in the study of the reactions

$$trans\text{-}[PtL_2Cl_2] + Y^- \longrightarrow trans\text{-}[PtL_2ClY] + Cl^-$$

$$[Pt(bipy)(C)Cl] + Y^- \longrightarrow [Pt(bipy)(C)Y] + Cl^-$$

The results indicate that the order of *cis* effect on the discrimination can be expressed, at least qualitatively,

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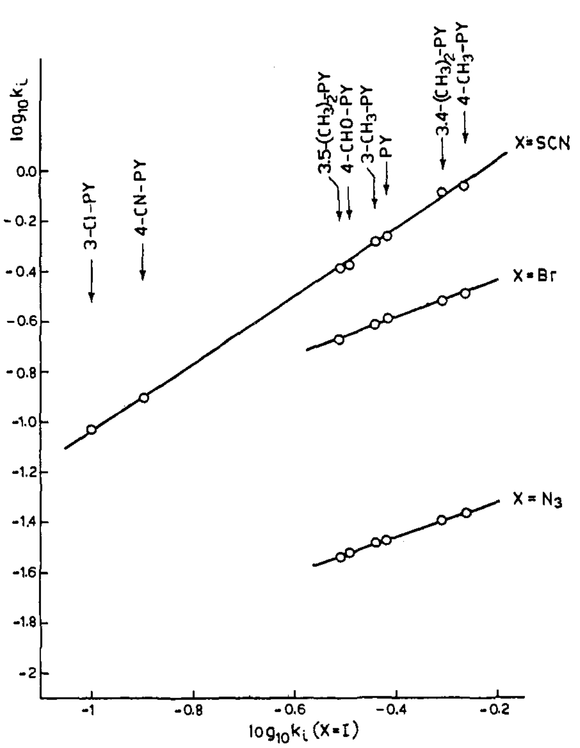

Figure 3. Plot of log k_i for the various reactions *vs.* log k_i relative to the reactions of the diiodo complexes, chosen as a reference system.

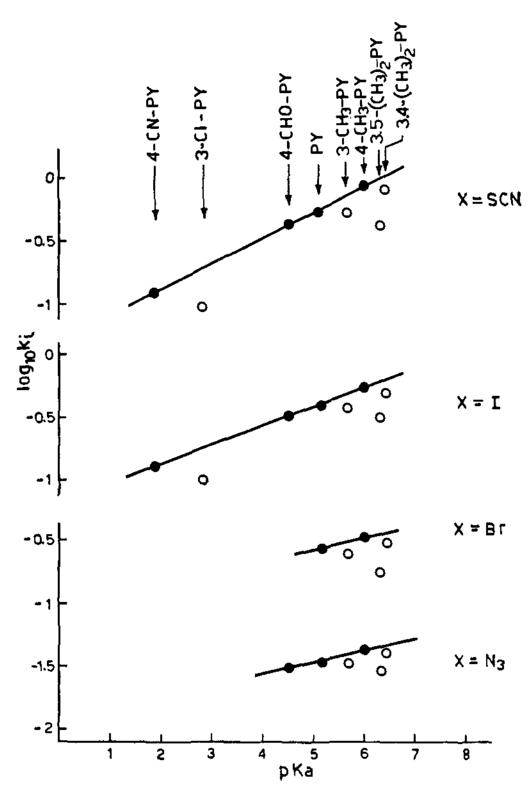

Figure 4. Plot of log k_i *vs.* the pK_a of the amine: ●, 4-substituted pyridines; ○, 3- and 3,5-substituted pyridines.

by the n_{Pt} values[16] of the *cis* anionic ligands

$$\text{CNS } (4.26) > \text{I } (4.03) > \text{Br } (2.57) > \text{N}_3 \text{ } (2.19) \quad (5)$$

which have been shown to give a relative order of micropolarizability.[18] The same sequence might be observed in this case, at least insofar as Pt^{II} and Pd^{II} complexes can be expected to behave in the same way. By plotting the values of log k_i against those relative to the reactions of the diiodo complexes, chosen as a reference system (Figure 3), straight lines are obtained. If only a leaving-group effect would be operating, these lines might be parallel to each other and have a slope 1.0. In the present case different slopes are observed, and they can be taken as a relative measure of the *cis* effect on the discrimination. The resulting sequence is

$$\text{CNS}(1.35) > \text{I}(1.00) > \text{Br}(0.7) > \text{N}_3(0.65)$$

which is much the same as sequence (5).

The Role of the Amine Molecules. Three amine molecules are involved in reaction 3, namely the entering group and the ligands which are *cis* and *trans* to the leaving group in the substrate. An increase in the basicity of the amine will enhance the nucleophilicity of the entering group, and one could therefore expect a corresponding increase of reactivity. However, the basicity of the two amine molecules already present in the substrate will likewise be increased, and this may lead to a decrease of reactivity, since the greater donation of negative charge to the reaction center might decrease the electrophilicity of the substrate. Therefore one cannot say, *a priori*, whether or not the result will be an increase of reactivity.

Researches on the reactions of amines (mainly pyridine derivatives) with planar complexes have been made in the past few years, and linear free-energy relationships between the reactivity (expressed in terms of log k) and the σ donor ability (expressed in terms of pK_a) have been always found for amines having the same form of steric hindrance.[10,19–22] At the same time, steric retardation has been observed in the reactions of pyridines having a methyl group *ortho* to the nitrogen. This is a consequence of the limited possibility of free rotation of the amine molecule in the transition state, which is due to the repulsion between the *ortho* substituents and the ligands which occupy the axial position in the trigonal-bipyramidal transition state.

In Figure 4, the values of log k_i are plotted against the pK_a of the amine, and a linear increase of reactivity with basicity can be observed, as far as 4-substituted pyridines are concerned. The 3- and 3,5-substituted pyridines are slightly less reactive than expected. It seems possible to attribute these deviations to some form of repulsion between the 3 and 3,5 substituents and the axial ligands in the transition state, as previously done for 2-substituted pyridines. In fact, the deviations are always greater with 3,5-dimethylpyridine than with 3-methylpyridine and are larger when the more bulky substituent is present in the pyridine ring (*i.e.*, in the case of 3-chloropyridine).

This type of retardation is quite uncommon, but it is not completely surprising that it has been observed in these reactions, since the available data relative to the retardation effects of 2-substituted pyridines showed that they are significantly larger for Pd^{II} than for Pt^{II} and Au^{III} substrates.[15,19–22]

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Table II. Analytical Figures and Melting Points Relative to the New Palladium(II) Complexes

Complex	% C		% H		% N		Mp, °C
	Calcd	Found	Calcd	Found	Calcd	Found	
$Pd(C_{14}H_{14}S_2)Br_2$	32.79	32.6	2.74	2.8	...		279
$Pd(C_{14}H_{14}S_2)I_2$	27.78	27.8	2.32	2.4	...		241
$Pd(C_{14}H_{14}S_2)(N_3)_2$	38.49	38.6	3.23	3.3	19.2	19.1	170
$Pd(C_{14}H_{14}S_2)(CNS)_2$	41.0	41.0	2.99	3.2	5.97	5.9	200 dec
$Pd(C_{12}H_{12}S_2)I_2$	24.80	24.7	2.07	2.0	...		>235
$Pd(C_{15}H_{16}S_2)I_2$	29.0	29.5	2.58	2.55	...		130 dec

A point to note is that in Figure 3 these deviations are not observed and all the points lie on the straight line. It means that the retardation effect of each amine changes in a proportional way on going from one type of substrate to another.

Moreover, such an unusual form of retardation seems to suggest that the bond between the metal and the entering amine is well formed in the transition state.

The Intimate Mechanism. It was pointed out[7] that these planar complexes undergo substitution through an associative mechanism. It implies that the reaction profile contain a minimum, corresponding to the presence of a labile intermediate, and two maxima. Experimental evidence has been presented in recent works.[12–15,23–25]

It is usually difficult to establish whether the first or the second maximum in the reaction profile is the transition state. In a limit description, where bond breaking and bond making are completely divorced from each other, the first maximum corresponds to a situation where the bond between the metal and the leaving group is not significantly broken and the second to a situation where the bond between the metal and the entering group is completely formed. In the first case bond formation is the driving force of the reaction, in the second bond breaking. In a comparison of the kinetic behavior of platinum(II) and gold(III) complexes,[26] the influence of the effective nuclear charge of the metal in determining the separation between bond making and bond breaking was discussed, and it was pointed out that the extent of the separation is larger for Pt^{II} than for Au^{III}. This is also in accord to what is known for the reactions of Rh^{I} substrates,[25] and, on the basis of the same argument, the sequence of asynchronicity in the mechanism might be expected to be $Rh^{I} > Pd^{II} > Pt^{II} > Au^{III}$.

The discussion reported above on the effects of the nature of the amine molecules in reaction 3 leads to the conclusion that the bond between the entering amine and the metal is well formed in the transition state. It could suggest that the driving force of all the reactions reported here is the breaking of the bond between the metal and the leaving group, X.

In this case, the increase of reactivity with the basicity of the amine observed in each of the four types of substrates (Figure 4) can be easily interpreted. It seems reasonable to assume that the effects of the σ donor ability of the two amine molecules in the substrate, acting as nonparticipating ligands, will be greater than that of the entering amine. A relative larger amount of negative charge on the reaction center will favor the concentration of the charge on the developing anion in the transition state, resulting therefore in an increase of rate. This is in accord with some preliminary observation on the effect of the solvent. On going from 1,2-dimethoxyethane to a mixture containing 5% water, the dielectric constant, ϵ, increases[27] from 6.6 to 9.1, and the rate (for the reaction where X = I and am = pyridine) also increases from 0.385 to 0.81 M^{-1} sec^{-1}. In methanol ($\epsilon = 32.6$) the isomerization is too fast to be followed by the usual techniques. These facts appear to be an indication of an assistance of the solvent to the developing anion.

Experimental Section

Materials. The complexes [Pd(S–S)X_2] (X = Br, N_3, CNS, I; S–S = C_6H_5–S–$(CH_2)_2$–S–C_6H_5) were obtained by reaction of [Pd(S–S)Cl_2][28] with an excess of NaX in acetone–methanol mixture (1:1) at 50° for 20 min. The products were precipitated by adding water to the concentrated solution and purified by recrystallization from boiling acetone. The complexes containing different sulfur ligands, S–S, were obtained by the same procedure. The corresponding analytical figures are reported in Table II. The complexes *trans*-[Pd(am)$_2X_2$] were prepared according to the methods reported in the literature.[29] The substrate *cis*-[Pd$(NH_3)_2Br_2$] was prepared as reported by Layton, *et al.*[30] The *cis* structure has been confirmed by comparison of the infrared spectra with those reported in the literature.[31] The amines were commercial products, reagent grade, purified when necessary by distillation over KOH pellets. The solvent, 1,2-dimethoxyethane, was purified before use by refluxing and distillation over metallic sodium.

Kinetics. Known volumes of thermostated solutions of the appropriate complex and amine were mixed in the spectrophotometer cell which was placed in the thermostated compartment of an Optica-CF-4R double-beam recording spectrophotometer. The spectrum changes characteristic of the reacting system were determined by scanning the near-ultraviolet region (300–400 mμ) at known intervals. In the case of the faster reactions, once the spectrum changes were characterized and suitable wavelengths were chosen to study the reaction, the kinetics were followed by looking at the wavelength at the chosen value and recording the change of optical density as a function of time.

Acknowledgments. We thank Dr. R. Ross for a sample of 1,8-bis(dimethylthio)naphthalene and Dr. M. L. Tobe for stimulating discussions. The work has been financially supported by the Italian Council for Research (C.N.R., Rome).

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