

## Mechanism of Nucleophilic Substitution in Palladium(II) Complexes of Terpyridine

M. CUSUMANO and G. GUGLIELMO

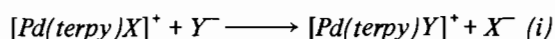
Istituto di Chimica Fisica, Università di Messina, 98100 Messina, Italy

V. RICEVUTO

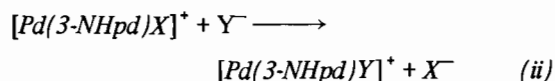
Istituto di Chimica Generale, Università di Messina, 98100 Messina, Italy

Received July 28, 1977

*Rates of nucleophilic substitution reactions (i) [terpy = terpyridine; X = Cl, Br, I, N<sub>3</sub>, NO<sub>2</sub>; Y = Cl, Br, N<sub>3</sub>, I, (NH<sub>2</sub>)<sub>2</sub>CS] have been*



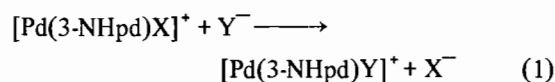
*measured in methanol at 25 °C and  $\mu = 0.1$ . The results are compared with those relating to the analogous reactions (ii) [3-NHpd = 3-azapentane-1,5-diamine] on the quantitative basis of nucleophilic discrimination factors and intrinsic reactivities:*



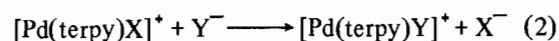
*The larger reactivity of [Pd(terpy)X]<sup>+</sup> is interpreted on the assumption that the chelating terpyridine group enhances more effectively the electrophilicity of palladium(II) through  $\pi$ -interaction than 3-azapentane-1,5-diamine does.*

### Introduction

Over the past few years we have been concerned with the kinetic behaviour of palladium(II) complexes [1-5]; in particular we have extensively investigated [2] the role of the leaving group in the kinetics of the reactions:



(3-NHpd = 3-azapentane-1,5-diamine) in methanol at 25 °C. The results have shown that, in spite of the large difference in reactivity between analogous platinum(II) and palladium(II) complexes, the lability order is very similar; in addition, there are indications that the free energy changes related to bond forming and weakening during the formation of the transition state are independent, thereby suggesting that such processes are asynchronous. We have now extended our investigations to the reactions:



(terpy = terpyridine; X = Cl, Br, I, N<sub>3</sub>, NO<sub>2</sub>; Y = Cl, Br, N<sub>3</sub>, I, thiourea) in methanol at 25 °C. Our purpose is to compare the kinetic parameters of these processes with those relating to reactions (1) and to study the role played by the unreplacable chelate group on the reactivity of the two systems.

### Experimental

#### Material

All the compounds of the type [Pd(terpy)X]X were prepared according to previously reported procedures [6, 7] and were characterized through their i.r. spectra and elemental analyses. Methanol was distilled from magnesium methoxide. All other products were reagent grade and were used without further purification.

#### Kinetics

The reactions were studied spectrophotometrically by the use of a Durrum-Gibson (model D-110) stopped-flow spectrophotometer equipped with a Kel-F flow system. The temperature was controlled to within  $\pm 0.1$  °C. In order to ensure pseudo-first-order conditions with respect to the complex and to force the reactions to completion, all the kinetic runs were performed in the presence of a large excess of nucleophile; the complex concentration was kept constant ( $5-10 \times 10^{-5}$  M) and the ligand concentration was varied through at least four (usually six) values. The ionic strength of the reaction mixtures was kept constant at 0.1 M by means of LiNO<sub>3</sub>. The observed pseudo-first-order rate constants  $k_{\text{obsd}}$  were obtained with the standard procedure from analysis of Polaroid photographs of the oscilloscope traces\*. The observed rate constants  $k_{\text{obsd}}$  were reproducible within 10%.

\*A listing of the pseudo-first-order rate constants is available on request from the editor.

TABLE I. First-order and Second-order Rate Constants for Reactions (1) and (2) in Methanol at 25 °C ( $\mu = 0.1$ ).<sup>a</sup>

Leaving group X	$k_1$ ( $s^{-1}$ ) <sup>b</sup>	Entering Group				
		$Cl^-$	$N_3^-$	$Br^-$	$I^-$	Thiourea
		$k_2$ ( $M^{-1} s^{-1}$ )				
$NO_2$	0.18 ( $10^{-3}$ )	87.4 ± 3.8 (0.06)	345 ± 7.3 (0.18)	476 ± 4.6 (0.26)	14800 ± 450 (3.7)	
$N_3$	0.52 (0.03)	284 ± 3.9 (1.06)		2120 ± 16 (2.1)	57200 ± 1000 (28.3)	
Cl	2.7 (0.6)		3960 ± 90 (40)	5790 ± 62 (80)	135000 ± 3200 (630)	127000 ± 5900 (3100)
Br	8.4 (0.5)	2050 ± 48 (22)	14200 ± 393 (37)		296000 ± 3100 (650)	191000 ± 7200 (2850)
I	13.3 (0.12)	5600 ± 24 (6.5)	22400 ± 1480 (9.7)	45000 ± 450 (17.2)		

<sup>a</sup>Values in brackets refer to reaction (1) (see reference 2). <sup>b</sup>Average values.

TABLE II. Second Order Rate Constants for the Reaction of  $[Pd(terpy)X]^+$  with  $Cl^-$  in Methanol at 25 °C at the Ionic Strength 0.1 and 0.01.

Leaving group X	$\mu = 0.1$ $k_2$ ( $M^{-1} s^{-1}$ )	$\mu = 0.01$ $k_2$ ( $M^{-1} s^{-1}$ )
$NO_2$	87.4 ± 3.8	256 ± 8.6
$N_3$	284 ± 3.9	589 ± 21
Br	2050 ± 48	4560 ± 118
I	5600 ± 24	10830 ± 277

## Results and Discussion

The identity of the final spectra of reaction with those of authentic samples of  $[Pd(terpy)Y]^+$  is an evidence that the process monitored is indeed that of reaction (2). In agreement with the usual two-term rate law (under pseudo-first-order conditions)

$$k_{obsd} = k_1 + k_2 [Y] \quad (3)$$

straight lines with non-zero intercepts were obtained by plotting the values of  $k_{obsd}$  against the nucleophile concentration.

The values of  $k_1$  and  $k_2$ , obtained by least-squares analysis, are listed in Table I. The second order rate constant,  $k_2$ , decreases with increasing ionic strength (Table II).

Two preliminary observations can be made on inspection of Table I: i) the order of reactivity of entering group Y (*i.e.* thiourea >  $I^-$  >  $Br^-$  >  $N_3^-$  >  $Cl^-$ ) is the same throughout the series of complexes examined; ii) the lability sequence of leaving group X is independent of the nature of the entering group, being  $I > Br > Cl > N_3 > NO_2$ . These observations

are in agreement with the general trend shown by substitution in square-planar complexes [8]; nevertheless, if we compare the values of  $k_1$  and  $k_2$  for these reactions with those relating to processes (1), interesting differences can be noted. The sequence of lability of leaving group in the two series of complexes differs in the relative lability of the halides; furthermore, although the order of nucleophilicity is the same for all the substrates, there is a large difference of reactivity between the two series of complexes.

The complexes of type  $[Pd(terpy)X]^+$  are both more reactive (about 1000 times) and more discriminating than their  $[Pd(3-NHpd)X]^+$  analogs. The best way of comparing quantitatively the reactivity of these substrates is to apply the L.F.E.R. followed by palladium(II) square-planar complexes [1]

$$\log k_2 = s n_{Pd}^0 + \log k_1 \quad (4)$$

where  $s$  is the nucleophilic discrimination factor and represents the sensitivity of the substrate to changes in the nature of the entering group,  $n_{Pd}^0$ 's are the nucleophilic reactivity constants toward palladium(II) complexes and  $\log k_1$  represents the intrinsic reactivity of the complex. The values of  $\log k_1$  and  $s$  for the various complexes, from least-squares analysis of the plots of  $\log k_2$  against  $n_{Pd}^0$ , are listed in Table III. Those values which deviated markedly from linearity, *i.e.*  $\log k_2$  for reaction of  $[Pd(terpy)Cl]^+$  and  $[Pd(terpy)Br]^+$  with the biphilic thiourea, have been discarded.

The constancy of the discrimination factor throughout the series of complexes  $[Pd(terpy)X]^+$  and  $[Pd(3-NHpd)X]^+$ , differing only in the leaving group, indicates that the relative lability of X is inde-

TABLE III. Intrinsic Reactivities,  $\log k_1$ , and Nucleophilic Discrimination Factors,  $s$ , for the complexes  $[\text{Pd}(3\text{-NHpd})\text{X}]^+$  and  $[\text{Pd}(\text{terpy})\text{X}]^+$ .

Complex	$L_3 = \text{terpy}$		$L_3 = 3\text{NHpd}$	
	$s$	$\log k_1$	$s$	$\log k_1$
$[\text{Pd}L_3\text{NO}_2]^+$	$0.87 \pm 0.04$	$-0.85 \pm 0.2$	$0.54 \pm 0.06$	$-2.8 \pm 0.3$
$[\text{Pd}L_3\text{N}_3]^+$	$0.90 \pm 0.02$	$-0.38 \pm 0.08$	$0.58 \pm 0.12$	$-1.6 \pm 0.7$
$[\text{Pd}L_3\text{Cl}]^+$	$0.85 \pm 0.04$	$0.26 \pm 0.18$	$0.51 \pm 0.04$	$-0.23 \pm 0.08$
$[\text{Pd}L_3\text{Br}]^+$	$0.82 \pm 0.09$	$0.85 \pm 0.4$	$0.51 \pm 0.04$	$-0.27 \pm 0.2$
$[\text{Pd}L_3\text{I}]^+$	$0.86 \pm 0.06$	$1.1 \pm 0.2$	$0.51 \pm 0.02$	$-0.88 \pm 0.1$

pendent of the nature of the entering reagent Y. On the other hand, the large variation of  $\log k_1$ , both among complexes belonging to the same group and between complexes of the two different groups, shows that the reactivity of palladium(II) substrates is an intrinsic property of the complex depending on the nature of all four atoms or groups bound to the central atom. In the present case, if we consider two complexes having the same leaving group, the difference of reactivity will obviously depend only on the nature of the tridentate amine bound to palladium(II). In the complexes with terpyridine the nitrogen atoms, which are coplanar, are capable of giving extensive  $\pi$ -interaction with the metal atom [9], thereby enhancing markedly the electrophilicity of the reaction centre over those containing 3-NH-azapentane-1,2 diamine. This will lead to an easier attack of the nucleophile and to a higher reactivity of the complexes  $[\text{Pd}(\text{terpy})\text{X}]^+$  compared with their  $[\text{Pd}(3\text{-NHpd})\text{X}]^+$  analogous. In addition, the delocalization of negative charge operated by the ligand terpyridine, which facilitates formation of the new bond, will enhance the contribution of the nucleophile to stabilization of the transition state; the rate of reaction will therefore be more affected by changes in the entering reagent. The larger delocalization of negative charge in the complexes of the type  $[\text{Pd}(\text{terpy})\text{X}]^+$  with respect to those of the type  $[\text{Pd}(3\text{-NHpd})\text{X}]^+$  is reflected in the difference of kinetic behaviour toward the nucleophile thiourea; while no deviation from the  $n_{\text{Pd}}^0$  scale is observed for the latter type of complexes, the rates of reaction of the former one with thiourea are significantly lower than expected on the basis of equation (4). This is the result of the lower extent to which thiourea can behave as a biphilic reagent [10, 11] through  $\pi$ -interaction with palladium(II) in the transition state.

Finally, it is interesting to note that while the least reactive substrate in the two series of complexes is the one having  $\text{NO}_2$  as leaving group, the most reactive is  $[\text{Pd}L_3\text{I}]^+$  when  $L_3$  is terpyridine and  $[\text{Pd}L_3\text{Cl}]^+$  when  $L_3$  is 3-NH-azapentane-1,2 diamine. This inversion in the sequence of lability indicates that for palladium(II) complexes also the role of the leaving group is largely dependent on the nature of the substrate being examined [8].

#### Acknowledgments

This work was supported by the Italian Consiglio Nazionale delle Ricerche.

#### References

- 1 M. Cusumano, G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc. Dalton*, 490 (1974).
- 2 L. Cattalini, M. Cusumano, V. Ricevuto and M. Trozzi, *J. Chem. Soc. Dalton*, 771 (1975).
- 3 M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo and M. Trozzi, *Inorg. Chim. Acta*, 16, 135 (1976).
- 4 M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo and M. Trozzi, *Inorg. Chim. Acta*, 17, 45 (1976).
- 5 L. Cattalini, M. Cusumano and S. Degetto, *J. Chem. Soc., Dalton*, in press.
- 6 G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649 (1937).
- 7 F. Basolo, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc.*, 82, 4200 (1960).
- 8 L. Cattalini in "Inorganic Reaction Mechanisms", ed. J. O. Edwards, Wiley, New York (1970).
- 9 W. R. Mc Whinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 12, 135 (1969).
- 10 H. B. Gray, *J. Am. Chem. Soc.*, 84, 1548 (1962).
- 11 L. Cattalini, A. Orio, and M. Nicolini, *J. Am. Chem. Soc.*, 88, 5734 (1966).