Fast Reactions at Planar Four-co-ordinate Complexes. Part 3.† Kinetics and Mechanism of Substitution Reactions of Sterically Hindered Aniono(mesityl)bis(triethylphosphine)nickel(II) Complexes

By **Matteo Cusumano** * and **Vittorio Ricevuto**, Istituto di Chimica Fisica and Istituto di Chimica Generale, Università di Messina, Italy

The kinetics of displacement of ligand X from the complexes *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)X]$ by a variety of nucleophiles Y^- (X = Cl, Br, I, N_3, or NO_2; Y = Cl, Br, I, NO_2, SCN, or N_3) has been studied in ethanol at 25 °C. The results suggest that the substitution proceeds by means of two competing paths, one associative and the other solvolytic. The kinetic parameters are compared with those relating to the reactions of the analogous complexes *trans*-$[Ni(PEt_3)_2(C_6H_4Me\text{-}o)X]$ and *trans*-$[Pt(PEt_3)_2R(Cl)]$ (R = mesityl or *o*-tolyl) under the same experimental conditions.

KINETIC studies of substitution reactions of square-planar nickel(II) complexes have seldom been performed[1-5] since most are unsuitable because of low stability in solution and extremely high lability. Further complications often arise from possible planar–octahedral equilibria involving the complex and the ligand or the solvent. Complexes of the type *trans*-$[Ni(PEt_3)_2R(X)]$ (R = *ortho*-substituted aryl) are however free from these limitations; here, electronic and steric effects of the *ortho* substituents[6] stabilize the complexes and prevent solvation along the axial position. In addition, these substrates are relatively inert to substitution.

In a previous paper[5] we have shown the feasibility of the replacement reactions (1) in ethanol at 25 °C and suggested a mechanism in which the process takes place

$$\textit{trans}\text{-}[Ni(PEt_3)_2(C_6H_4Me\text{-}o)X] + Y^- \longrightarrow \textit{trans}\text{-}[Ni(PEt_3)_2(C_6H_4Me\text{-}o)Y] + X^- \quad (1)$$
$$(X = Cl, Br, I, N_3, \text{ or } NO_2;\ Y = Cl, Br, I, \text{ or } SCN)$$

through two competing paths, an associative and a solvolytic path. We have now extended our investigations to reactions (2) in ethanol at 25 °C, in order to study the effect of increasing steric hindrance on the rates of reaction and to confirm the mechanism suggested for these sterically hindered nickel(II) complexes; more specifically, process (3) has been investigated in the bulky solvent Bu^tOH and in ethanol in the presence of I^- ion. Kinetic data relative to reactions (4) under the

$$\textit{trans}\text{-}[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)X] + Y^- \longrightarrow \textit{trans}\text{-}[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)Y] + X^- \quad (2)$$
$$(X = Cl, Br, I, N_3, \text{ or } NO_2;\ Y = Cl, Br, I, NO_2, SCN, \text{ or } N_3)$$

$$\textit{trans}\text{-}[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)I] + Br^- \longrightarrow \textit{trans}\text{-}[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)Br] + I^- \quad (3)$$

same experimental conditions (solvent, ethanol; 25 °C) are also presented.

$$\textit{trans}\text{-}[M(PEt_3)_2R(Cl)] + [CN]^- \longrightarrow \textit{trans}\text{-}[M(PEt_3)_2R(CN)] + Cl^- \quad (4)$$
$$(M = Pt^{II} \text{ or } Ni^{II};\ R = o\text{-tolyl or mesityl})$$

EXPERIMENTAL

Reagents.—The complex *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)Cl]$ was prepared according to the procedure of Chatt and Shaw.[6] Complexes of the type *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)X]$ (X = Br, I, SCN, NO_2, or N_3) were obtained from the chloro-complex by metathetic exchange. Ethanol was distilled from magnesium ethoxide. Other chemical products were reagent-grade commercial materials and were used without further purification.

Kinetics.—The reactions were followed spectrophotometrically. A Beckman DU spectrophotometer, equipped

---

† Part 2, L. Cattalini, M. Cusumano, V. Ricevuto, and M. Trozzi, *J.C.S. Dalton*, 1975, 771.

[1] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.

[2] R. K. Murmann, *Inorg. Chem.*, 1963, **2**, 116.

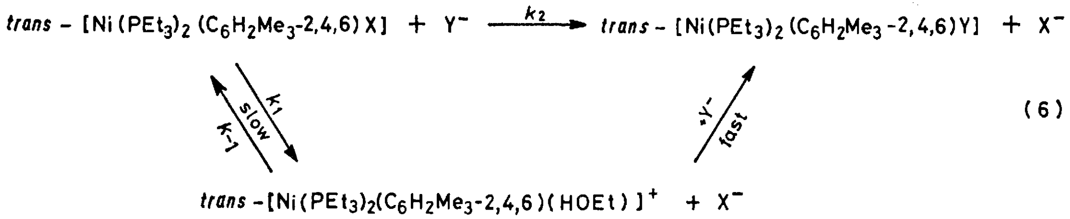
[3] L. Cattalini, M. Martelli, and P. Rigo, *Inorg. Chim. Acta*, 1967, **1**, 149.

[4] E. J. Billo, *Inorg. Chem.*, 1973, **12**, 2783.

[5] M. Cusumano, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Soc. Peloritana Sci. fis. mat. nat.*, 1974, **54**, 157.

[6] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

with a Saitron 301 photometer and a Servogor 5 recording potentiometer, was used to monitor the kinetic course of the slower reactions. Fast reactions were followed using a Durrum–Gibson model D 110 stopped-flow spectrophotometer equipped with a Kel-F flow system. All the kinetic runs were performed under pseudo-first-order conditions with respect to the complex; the procedure used to obtain the observed rate constants [deposited as Supplementary Publication No. SUP 22296 (7 pp.) *] has already been described.[7] The effect of ionic strength on the rate of these reactions was negligible.



(6)

RESULTS AND DISCUSSION

The experimental results are in agreement with a two term-rate law under pseudo-first-order conditions.

$$k_{\text{obs.}} = k_1 + k_2[\text{Y}^-] \qquad (5)$$

Values of k_1 and k_2, obtained by least-squares analysis, are listed in Table 1 together with those referring to reactions of the analogous complexes *trans*-[Ni(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)X]. The fact that for some nucleophiles the rates of reactions are independent of the reagent concentration suggests that the process takes place *via* the two paths in mechanism (6) where the rate constant k_2 refers to bimolecular attack on the complex by the entering nucleophile and k_1 may be related to an interchange dissociative path[8] involving the solvent. Experimental evidence to support this scheme, which is formally identical to that proposed by Faraone *et al.*[9,10] for the analogous platinum(II) complexes, is presented herein. Reaction (3) was studied in Bu^{t}OH at 29 °C (see Table 1). The value of rate constant k_1 for the solvolytic path is some seven times lower than that obtained in ethanol at 25 °C, in accord with the poor co-ordinating properties of the bulky molecule Bu^{t}OH, while that of the second-order rate constant k_2 is affected only to a minor extent by the change of solvent. Further evidence of the validity of scheme (6) comes from the kinetic data relative to reaction (3) performed in the presence of a large excess of I$^-$ (0.1 mol dm^{-3}); the presence of the leaving anion, which suppresses the solvolysis, affects the term k_1, which decreases to zero, within experimental error, without altering the values of the second-order rate constant k_2 (see Table 1).

TABLE 1

Rate constants k_1 and k_2 for the reactions *trans*-[Ni(PEt$_3$)$_2$-R(X)] + Y$^-$ in ethanol at 25 °C

		R = mesityl		R = *o*-tolyl [a]	
X	Y	10^2k_1 [b]/s^{-1}	k_2/ dm^3 mol^{-1} s^{-1}	10^2k_1 [b]/ s^{-1}	k_2/ dm^3 mol^{-1} s^{-1}
Cl	NO$_2$		0.0		
	Br		0.0		0.0
	I	5.62 ± 0.29	0.0	160	0.0
	SCN		9.07 ± 0.29		307
	CN				15 500 ± 400
Br	NO$_2$		0.0		
	Cl		0.0		5.0
	I	12.86 ± 0.81	1.09 ± 0.04	350	17.5
	SCN		15.87 ± 0.34		584
	N$_3$		21.6 ± 0.94		
I	NO$_2$		0.0		
	Cl		0.55 ± 0.12		31.2
	Br	17.12 ± 0.53	1.83 ± 0.05	560	34.1
	Br [c]	2.3 ± 0.13	2.39 ± 0.04		
	SCN [d]	0.0	57.84 ± 3.40		
	SCN		58.68 ± 1.14		1 280
	N$_3$		145.0 ± 7.38		
N$_3$	Cl		0.0		0.0
	SCN	6.6 ± 1.4	18.49 ± 0.29	160	
NO$_2$	SCN	0.88 ± 0.14	2.02 ± 0.03	26	16.2

[a] Values from ref. 5. [b] Average value. [c] In Bu^{t}OH at 29 °C. [d] In the presence of I$^-$ (0.25 mol dm^{-3}).

A second-order contribution for all the complexes *trans*-[Ni(PEt$_3$)$_2$(C$_6$H$_2$Me$_3$-2,4,6)X] is present only with the reagents [SCN]$^-$ and [N$_3$]$^-$; nevertheless, nucleophiles such as Cl$^-$ and Br$^-$ can exhibit definite values of k_2 depending on the leaving group X (see Figure). The possibility of a direct bimolecular attack of a given nucleophile on the complexes considered is therefore dependent on the nature of the leaving group; in particular, the availability of the nickel(II) centre to interact directly with the entering group decreases in the order I > Br > Cl. This order parallels that of the lability of the leaving group, which is I > Br > Cl ~ N$_3$ > NO$_2$. In this respect it does not seem likely that the solvation of the leaving anion plays any important role in determining the rate of solvolysis or that of the direct attack by the nucleophile. In fact, ethanol should be more effective in easing the Ni–Cl bond breaking than that of Ni–I by hydrogen-bond formation with the halides.

The above findings can be interpreted in a simple physical manner; the size of the co-ordinated halogen affects the steric properties of the nickel(II) centre. This steric effect increases in the series Cl > Br > I; on moving from *trans*-[Ni(PEt$_3$)$_2$(C$_6$H$_2$Me$_3$-2,4,6)Cl] to *trans*-[Ni(PEt$_3$)$_2$(C$_6$H$_2$Me$_3$-2,4,6)Br] and *trans*-[Ni(PEt$_3$)$_2$(C$_6$H$_2$Me$_3$-2,4,6)I] the steric strain on the centre of reaction

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[7] M. Cusumano, G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1974, 490.

[8] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' W. A. Benjamin, New York, 1965, ch. 11.

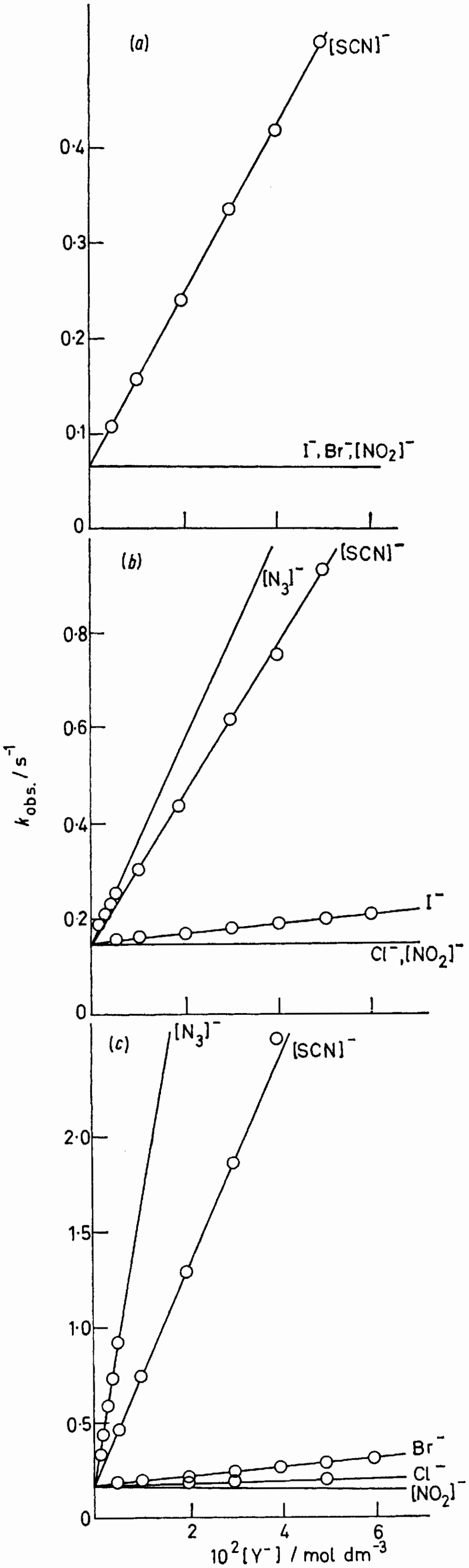
[9] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, 1969, **8**, 2207.

[10] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, 1970, **9**, 1525.

is relieved with increasing effectiveness since the bulkier I^- can spread the groups surrounding the nickel(II) atom to a larger extent than Br^- and Cl^-. As a consequence, a poor nucleophile such as Cl^- can reach the site of reaction and react *via* a direct bimolecular path with the complex *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)I]$, but it cannot interact with the more crowded nickel(II) atom in the other complexes. On the other hand, the only entering groups which always give a second-order contribution to the overall process are those such as $[SCN]^-$ and $[N_3]^-$, which are potentially biphilic; therefore the capacity of these nucleophiles to overcome the steric barrier probably stems from their ability to form a particularly strong bond with the nickel(II) atom in the transition state, by virtue of π interactions.* The lability sequence of the halides, paralleling their decreasing size, I > Br > Cl is not inconsistent with a mechanism in which the term k_1 is probably to be referred to an I_d process [8] rather than to a simple associative path in which the solvent acts as the nucleophile.

The availability of the values of the second-order rate constant k_2 for reaction of *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)I]$ with several entering groups makes it possible for the first time to list a nucleophilicity scale in nickel(II) square-planar complexes, namely $[N_3]^- > [SCN]^- > Br^- > Cl^-$. A significant feature of this sequence is the position of azide which behaves as the most effective entering group of those considered; this appears to be a marked difference between nickel(II) square-planar complexes and those of other isoelectronic ions since azide acts as a poor nucleophile toward platinum(II) and palladium(II) substrates.[11] The 'harder' character [12] of Ni^{II} with respect to Pt^{II} and Pd^{II} may account for this difference.

Turning now to the comparison between the substrates *trans*-$[Ni(PEt_3)_2(C_6H_4Me\text{-}o)X]$ and *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)X]$ we note that, apart from the relative reactivity, the kinetic behaviour is the same. In fact, the nucleophilicity order of the entering group ($[N_3]^- > [SCN]^- > Br^- > Cl^-$) is identical in the two series of complexes and so is the lability sequence of the leaving group X ($I > Br > Cl \sim N_3 > NO_2$). The decrease in reactivity on going from *trans*-$[Ni(PEt_3)_2(C_6H_4Me\text{-}o)X]$ to *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)X]$ is in line with the increasing steric hindrance caused by the presence of two methyl groups in the latter complex, shielding the nickel atom, compared with one in the former. It is noteworthy that the presence of a second methyl group



Dependence of the pseudo-first-order rate constants on the nucleophile concentration at 25 °C in ethanol for the reactions (*a*) *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)Cl] + Y^-$, (*b*) *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)Br] + Y^-$, and (*c*) *trans*-$[Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)I] + Y^-$

---

* One of the referees suggests that, alternatively, the observed large k_2 values for the entering ligands $[NCS]^-$ and $[N_3]^-$ (small atom bound to the metal and linear geometry) could be attributed to steric considerations.

[11] L. Cattalini, in 'Inorganic Reaction Mechanism,' ed. J. O. Edwards, Wiley, New York, 1970.

[12] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

does not alter the discrimination of the complexes towards the various entering groups.

Finally, it is of interest to compare the kinetic behaviour of the complexes *trans*-[Ni(PEt$_3$)$_2$R(Cl)] (R = mesityl or tolyl) with the analogous derivatives of the isoelectronic ion Pt^{II} under the same experimental conditions. According to mechanism (6) this comparison can be made by an analysis of both the rate constants k_1 and k_2. Concerning k_1, the difference in reactivity between *o*-tolyl derivatives of Ni^{II} and Pt^{II} is *ca.* 1 000 while that of the mesityl derivatives is almost 300 (Table 2). Turning to the second-order rate constant k_2, a direct comparison is possible only for reaction of the *o*-tolyl derivatives with [CN]$^-$ for which experimental data are available: the nickel substrate reacts *ca.* 10^5 times faster than the platinum analogue. Nevertheless, a rough estimation of k_2 for reaction of *trans*-[Ni(PEt$_3$)$_2$-(C$_6$H$_2$Me$_3$-2,4,6)Cl] with [CN]$^-$ can be made. Thus the difference between the values of k_2 referring to reactions (1) and (2) ranges between factors of 17—56 in the nucleophilic series with all the complexes examined. The lowest value of k_2 obtainable in this way is 276 dm^3 mol^{-1} s^{-1} which gives a ratio of k_2(Ni) : k_2(Pt) of 7 × 10^4 : 1 for the chloro(mesityl) complexes, nearly equal to that for the corresponding *o*-tolyl derivatives.

TABLE 2

Rate constants $k_{obs.}$, k_1, and k_2 for the reaction *trans*-[Pt(PEt$_3$)$_2$R(Cl)] + Y$^-$ in ethanol at 25 °C

		R = tolyl			R = mesityl		
Y$^-$	10^2[Y$^-$] mol dm^{-3}	10$^3k_{obs.}$/s^{-1}	10$^3k_1$ */s^{-1}	10$^3k_2$/ dm^3 mol^{-1} s^{-1}	10$^3k_{obs.}$/s^{-1}	10$^3k_1$ */s^{-1}	10$^3k_2$/ dm^3 mol^{-1} s^{-1}
SCN	0.1	1.46			0.18		
	1	1.42			0.18		
	2	1.40		0.0	0.16		0.0
	5	1.41					
	10	1.43			0.17		
I	1	1.49			0.18		
	2	1.41			0.18		
	5	1.45			0.17		
	10	1.42	1.43 ± 0.03	0.0	0.18	0.17 ± 0.01	0.0
N$_3$	0.1	1.42			0.16		
	0.25	1.41			0.18		
	0.5	1.44					
	0.75	1.39		0.0	0.18		0.0
	1	1.43			0.16		
CN	0.1	1.58			0.18		
	0.3	1.92					
	0.4	2.06		159.7 ± 2.44	0.19		3.74 ± 0.01
	0.5	2.24			0.20		
	0.8	2.70			0.21		

* Average value.

This result is in contrast to that previously found by other workers [1] who reported that when two methyl groups, instead of one, block the positions above and below the plane of the complex the difference in lability between nickel(II) and platinum(II) complexes is strongly reduced. It must be noted that this statement is based on an analysis of kinetic data which have been shown to be inconsistent.[13] The larger reactivity of nickel(II) complexes with respect to those of Pt^{II} can probably be related to the greater tendency of the square-planar nickel complexes to give five- and six-co-ordinate [14] species. It is very significant that the nucleophile [SCN]$^-$ gives a second-order contribution to the rate of replacement of Cl$^-$ in the substrate *trans*-[Ni(PEt$_3$)$_2$-R(Cl)] but reacts only *via* the solvolytic path with the analogous platinum(II) substrates.

We thank the Italian C.N.R. for support.

[7/2043 *Received, 21st November*, 1977]

---

[13] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1974, 1377.

[14] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, ch. 5.