Substitution of Coordinate Phosphines in Planar Nickel (II) Complexes

L. Cattalini, M. Martelli, P. Rigo

The kinetics of displacement of phosphine ligands from a series of complexes of the type trans-[Ni(phosphine)$_2$(NCS)$_2$] *by bipyridyl have been investigated. The recations follow the two-term rate law which is a general feature for planar complexes of d^8 transition metal ions. A linear relationship between the reactivity and the basicity of the various phosphines is observed and its significance is discussed.*

Introduction

The few data available from the literature[1] about the kinetic behaviour of planar Ni(II) complexes indicate that they react much faster than the analogous Pd(II) and Pt(II) derivatives. The observed rate constant at comparable concentrations for the replacement of the coordinated chloride by pyridine in the series of sterically hindered substrates of the form *trans*-[M(PEt$_3$)$_2$(o-tolyl)Cl] are 1.7×10^{-5}, 5.8×10^{-3} and 1.6×10^{-2} sec^{-1} at 25, —40 and —65°C respectively for M = Pt, Pd and Ni. It is estimated that at a constant temperature the rates are in the ratio $1 : 10^{5-6} : 10^{7-8}$ and the effectiveness of steric hindrance in decreasing the reactivity is greater when M = Ni. In the reactions of [M(dien)(SCN)]$^+$ with pyridine, the rate increases by a factor of 10^6 just on going from M = Pt to M = Pd and the data for the nickel substrate are not available. There is, however, evidence that nucleophilic substitutions on planar Ni(II) derivatives follow the usual two-terms rate law:

$$\text{rate} = (k_1 + k_2[Y])[\text{complex}] \qquad (1)$$

where Y is the entering group.

During some non kinetic studies of a series of complexes of the form *trans*-[Ni(phosphine)$_2$(NCS)$_2$] one of us (P.R.) had observed a slow reaction between these substrates and amines and it was thought that these systems would merit a kinetic study. A preliminary approach to the problem indicated that a bidentate entering group such as bipyridyl enabled us to avoid the complication of a planar-octahedral equilibria between amino-thiocyanato-Ni(II) species in the reaction mixtures. The complexes are quite stable in the solvent dimethoxyethane and do not precipitate during the course of the reaction. In every case the overall reaction studied was of the form,

trans-[Ni(phosphine)$_2$(NCS)$_2$] + 2 bipy →

trans-[Ni(bipy)$_2$(NCS)$_2$] + 2 phosphine
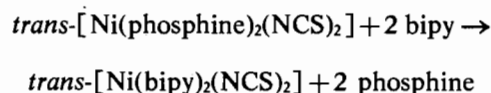
Although this represents what is obviously a multistage process which at some stage involves a permanent increase of coordination number, evidence will be produced to show that the kinetics refer to a rate determining displacement of the first phosphine in the square planar substrate.

Experimental Section

Materials. The various phosphines were obtained by following the methods reported in the literature.[2] The diethylcyclohexylphosphine, which preparation was not previously described, was obtained with a similar method.[3] All the complexes of the type *trans*-dithyocianato-bis(phosphine)nickel(II) were obtained using the general methods already described in the literature.[4] The analytical data for all the complexes examined in this work are summarized in Table I. The complex, *trans*-[Ni(bipy)$_2$(NCS)$_2$], was prepared by adding an excess of 2,2′-bipyridyl to a solution of one of the four-coordinated phosphine-complexes in 1,2-dichloroethane and its nature was confirmed by analysis and by comparison of I.R. absorption bands with those reported in the literature.[5] 2,2′-bipyridyl and dimethoxyethane were both pure commercial sample.

Kinetics. Freshly prepared solutions of the complex and of bipyridyl were brought to the reaction temperature separately and mixed in the thermostated cell of an Optica-CF4 double beam recording spectrophotometer. The solutions of the complexes in dimethoxyethane obey Beer's law and are stable, at least during the time required to follow the kinetics. The changes in optical density were followed at a wavelength within the range 350-380 mμ where there was a sufficient variation for the rate constants to be conveniently

(1) C. H. Langford and H. B. Gray, «Ligand Substitution Processes», W. A. Benjamin Inc., New York, N. Y., (1965), Chapter 2 and references therein.

(2) K. A. Jensen, P. A. Nielsen and C. T. Pedersen, *Acta Chim. Scand.*, *17*, 1115 (1963).
(3) A. Turco, P. Rigo, private communication.
(4) A. Turco, V. Scatturin, G. Giacometti, *Nature*, *183*, 604 (1959); L. Venanzi, *J. Chem. Soc.*, 719 (1958).
(5) C. M. Harris, E. D. McKenzie, *J. Inorg. Nucl. Chem.*, *19* 372 (1961).

Table I. Analytical data for the examined nickel(II) complexes *trans*-[Ni(phosphine)₂(NCS)₂]

Phosphine	Ni calc.	Ni found.	C calc.	C found.	H calc.	H found.	N calc.	N found.
triethyl-	14.2	14.1	40.9	41.1	7.3	7.2	6.8	6.7
diethylcyclohexyl-	11.3	11.4	50.9	49.9	8.1	8.05	5.4	5.4
ethyldicyclohexyl-	9.4	9.2	57.4	57.2	8.47	8.43	4.5	4.55
tricyclohexyl-	8.0	7.95	62	61.4	8.9	8.71	3.6	3.7
tri-n-propyl-	11.8	11.9	48.5	49.1	8.4	8.3	5.6	5.65
tri-n-butyl-	10.1	10.3	53.9	53.5	9.3	9.35	4.8	4.7
t-[Ni(bipy)₂(NCS)₂]	12	12.3	49.4	49.9	3.3	3.4	17.3	17.2

calculated. In all the experiments the concentration of the entering bipy was varied within the range $10^{-4} - 1 M$ and that of the examined nickel complex was always small enough to provide pseudo first order conditions and to avoid possible equilibria. The observed rate constants for each experiment were calculated from the plot of $\log_{10} (D_{\infty}-D_t)$ against time (D_{∞} and D_t being the values of optical density at the end of the reaction and at the time t respectively), and are summarized in Table II. Some reactions were repeated several times under the same conditions and the reproducibility was better than 5%.

Table II. Observed rate constants for the reactions of the complexes *trans*-[Ni(phosphine)₂(NCS)₂] with 2,2'-bipyridyl in dimethoxyethane

Phosphine	Temperature °C	$10^4 \times$ [bipy] mole/1	$10^3 \times k_{obs}$ sec^{-1}
Triethylphosphine	25	4	10.2
»	»	10	17.7
»	»	16	24.8
»	»	20	29.2
Diethylcyclohexylphosphine	»	1	7.1
»	»	10	8.6
»	»	20	9.6
»	»	100	20.5
Ethyldicyclohexylphosphine	»	1	4.7
»	»	10	4.85
»	»	50	5.4
Tricyclohexylphosphine	»	10	1.62
»	»	100	1.71
»	»	500	1.88
»	»	1,000	2.15
»	35	5	3.8
»	»	50	3.86
»	»	500	4.25
Tri-n-propyl-phosphine	25	20	11.0
»	»	100	18.8
»	»	500	45.0
»	»	1,000	79.0
Tri-b-butylphosphine	»	20	8.5
»	»	100	10
»	»	200	16
»	»	1,000	24.5

Results and Discussion

The pseudo first order rate constants, k_{obs}, varied with the concentration of the entering group, according to the expression

$$k_{obs} = k_1 + k_2[\text{bipy}]$$

The values of k_1 and k_2 for any one complex, obtained

from the intercept and the slope of the linear plot of k_{obs} against [bipy] are collected in Table III. The reactions of the complexes containing ethyldiphenylphosphine, diethylphenylphosphine and triphenylphosphine are too fast to measure with the usual tecniques, (under our experimental conditions).

Table III. First and second order rate constants for the reactions of *trans*-[Ni(phosphine)₂(NCS)₂] with 2,2'-bipyridyl in dimethoxyethane

Phosphine	T°C	$10^3 \times k_1$ sec^{-1}	$10^3 \times k_2$ $M^{-1} \times$ sec^{-1}	$-\Sigma\sigma^{*a}$
Triethylphosphine	25	5.5	12,000	0.30
Diethylcyclohexylphosphine	»	7.0	1,350	0.35
Tri-n-propylphosphine	»	10	690	0.36
Tri-n-butylphosphine	»	8.0	165	0.39
Ethyldicyclohexylphosphine	»	4.7	140	0.40
Tricyclohexylphosphine	»	1.64	5.1	0.45
»	35	3.8	9.0	
Ethyldiphenylphosphine	25			
Diethylphenylphosphine	»	Too fast to measure		
Triphenylphosphine	»			

^{a} —σ^* for ethyl = 0.10; propyl = 0.12; butyl = 0.13; cyclohexyl = 0.15; phenyl = —0.6 (from ref. 6).

The fact that the rate law for this process is the same as that observed for the reactions of all other d^8 substrates does not, in itself, prove that the usual interpretation in terms of an associative mechanism with a trigonal-bypiramidal intermediate involving the solvent as reagent in the k_1 term[1] is necessarily correct in this case. In order to clarify this point we have obtained the activation parameters for the reactions of the complex containing tricyclohexylphosphine, where the k_1 term is relatively greater in comparison to k_2 than in other cases. The values are $\Delta H_1^* \cong 15$ kcal/mole, $\Delta S_1^* \cong$ —26 e.u. and $\Delta H_2^* \cong 8$ kcal/mole, $\Delta S_2^* \cong$ —32 e.u. for k_1 and k_2 terms respectively. The activation entropies are both negative and that fact strongly suggests that the same associative mechanism is operating in both the reaction paths. Moreover it is to be noted that the better entering group, bipy, leads to a smaller value of ΔH^*.

Since the reactions always occur in one stage and the initial and final spectra closely correspond to those of the starting material and of the final octahedral product *trans*-[Ni(bipy)₂(NCS)₂] respectively, the rate determining process is clearly the first step and subsequent reactions must be considerably faster. It is apparent, from the data in Table III, that the observed rates is very dependent upon the nature of the phosphine ligand

in the complex. It seems reasonable, therefore, to assume, but difficult to prove that the first rate determining step is a bimolecular substitution at a square-planar complex (from the general kinetic form and activation parameters) and that the leaving group is the phosphine (from the sensitivity of rate to the nature of the phosphine).

A linear relationship is observed between the values of $\log_{10}k_2$ and the σ donor properties of the phosphines, expressed here as the sum of the Taft σ^*-values[6] for the three aliphatic ligands bonded to the phosphorus atom. The relationship can be expressed with the equation:

$$\log_{10}k_2 = 7.81 + 22.2\,(\Sigma\sigma^*)$$

and one can see from the data in Table III that the $\Sigma\sigma^*$ values for phosphines containing phenyl groups, owing to the value of σ^* for C_6H_5, lead to values of k_2 that would be far too large to be determined by our tecniques. The linear relationship indicates that steric factors are not significant in determining the reaction rates. Moreover, since the values of $\Sigma\sigma^*$ do not take into account the possibility of π contributions, it seems that the possible π interactions between filled d orbitals of the metal and empty d orbitals of the phosphorus atom do not influence significantly the reaction rates, or that the influence is the same in all the cases.

The decrease in reactivity, $\log_{10}k_2$, parallels the in-crease in the basicity of the phosphine. This can be due either to a smaller electrophilicity of the substrates containing the more basic phosphines, which will make attack by the nucleophile bipy more difficult, or to a greater difficulty in breaking the Ni-P bond during the formation of the transition state, or possibly to both these factors. The discussion of this point would require information extending ower a much wider range of nucleophiles.

It is of interest to note that it is the phosphine ligand that is displaced and not the thiocyanate. Such a process is not observed with planar complexes of other d^8 metals. In the case of Pt(II) even the reaction with very strong nucleophiles such as thiourea or I^- never result in the displacement of the coordinate phosphine. The only exception appears to be[7] the complex trans-$[Pt(C_5H_{11}N)_2(PPh_3)Cl]^+$ where a strong steric hindrance effect probably assists the departure of the phosphine. We cannot yet explain this point, and further investigations are now in progress in order to thraw more light upon it. However it might be of significance to bear in mind that nickel(II) lies in the borderline region between «soft» and «hard» behaviour.

(6) R. W. Taft Jr., «Steric Effects in Organic Chemistry», M. S. Newmann Ed., J. Wiley and S. Inc., New York, (1956).

(7) M. Martelli. R. Ettorre, private communication.