Substitution Reactions on Sterically Hindered Square-planar *trans*-[NiBr(R)-$(PR'_3)_2$] (R = aryl) Complexes. Effects of the Substituents of the Aryl Ligand *

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Substitution reactions of sterically hindered *trans*-[NiBr(R)$(PPh_3)_2$] complexes (R = C_6Cl_5, C_6F_5, $C_6H_2Me_3$-2,4,6, C_6HCl_4-2,3,5,6, C_6HCl_4-2,3,4,6, C_6HCl_4-2,3,4,5, $C_6H_2Cl_3$-2,3,4, $C_6H_3Cl_2$-2,4, or C_6H_4Cl-2) and of *trans*-[NiBr(R)$(PR'_3)_2$] (PR'_3 = $PEtPh_2$ or $PMePh_2$; R = C_6Cl_5, C_6F_5, $C_6H_2Me_3$-2,4,6, or $C_6H_2Cl_3$-2,3,4) have been studied in acetone solution. The reaction rates obey the well established two-term rate law $k_{obs} = k_S + k_{an}$[anion] and seem to be solely controlled by steric factors; namely, the existence of one or two substituents on the R ligand, in an *ortho* position with respect to the Ni–C bond. The different donor ability of the ligand might be considered only for R = $C_6H_2Me_3$-2,4,6. The effects of the *para* and *meta* chloro substituents of the R ligand on the reaction rates are negligible. Steric strain in the molecule, as a whole, is also considered by studying the effect of a decrease in the phosphine size on the reaction rate.

Substitution reactions of square-planar metal complexes have been thoroughly studied from a kinetic point of view for inert platinum(II) compounds. These studies have resulted in a well documented proposal for a reaction mechanism that could be easily and generally applied to all square-planar complexes of transition metals.[1]

Studies on anionic ligand-subtitution reactions of square-planar nickel(II) organometallic complexes have seldom been studied kinetically. The main difficulties in such studies arise from the high lability of the complexes, as well as their low stability in solution. This low stability affects the complexes both through decomposition, either *via* direct attack of the solvent on the nickel centre or *via* air oxidation, and by unwanted side substitution reactions of the in-coming ligand.

However, by making the right choice of stabilizing ligands, most of these problems can be partially avoided. Compounds of the type *trans*-[NiX(R)L_2] (L = phosphine, X = halide, R = aryl) are reasonably stable in solution when the organic ligand, R, is an *ortho*-substituted aryl group. Although some electronic influence is present, both in the strength of the Ni–R bond and in the lability of the other ligands attached to the nickel(II) centre, the stabilization effect of these *ortho* substituents on the complexes is mainly steric in character. These substituents seem to act by blocking possible solvent attack along the axial direction.[2–8] So, in spite of the high lability of organonickel complexes, these *ortho*-substituted aryl compounds show substitution rates slow enough to allow a reasonable kinetic study.

The importance of the steric blocking effect of the *ortho*-substituted aryl ligands should increase dramatically with decreasing size of the complex central ion, $Ni^{2+} < Pd^{2+} < Pt^{2+}$. In order to quantify kinetically this effect in the nickel compounds, we have studied a group of substitution reactions of sterically hindered *trans*-[NiBr(R)L_2] (L = phosphine, R = *ortho*-substituted aryl ligand) by $[NH_4][NCS]$ in acetone solution.

Experimental

Reagents.—All the organometallic complexes were prepared according to well known procedures: *trans*-[NiBr(C_6Cl_5)$(PPh_3)_2$],[9] *trans*-[NiBr(C_6F_5)$(PPh_3)_2$],[10] *trans*-[NiBr(C_6F_5)$(PMePh_2)_2$],[11] *trans*-[NiBr($C_6H_2Me_3$-2,4,6)$(PMePh_2)_2$],[11] and *trans*-[NiX($C_6H_nCl_{(5-n)}$)$(PPh_3)_2$].[12] The bromo derivatives were obtained from mixtures of chloro and bromo complexes by metathetic exchange with LiBr in acetone, in the presence of small quantities of free phosphine to prevent decomposition. The compounds containing $PEtPh_2$ and $PMePh_2$ were obtained by phosphine exchange on *trans*-[NiBr(R)$(PPh_3)_2$] in toluene solution. The acetone used was reagent grade and dried with anhydrous Na_2SO_4, distilled, and stored over 4 Å Linde molecular sieves. All other chemicals were reagent grade and commercially available, and were used, after drying, without further purification.

Table 1. Phosphorus-31 n.m.r. chemical shifts of the complexes studied, in dichloromethane solution.

trans Complex	δ^a/p.p.m.
[NiBr(C_6Cl_5)$(PPh_3)_2$]	20.37
[NiBr(C_6HCl_4-2,3,4,6)$(PPh_3)_2$]	20.34
[NiBr(C_6HCl_4-2,3,5,6)$(PPh_3)_2$]	20.70
[NiBr(C_6HCl_4-2,3,4,5)$(PPh_3)_2$]	22.09
[NiBr($C_6H_2Cl_3$-2,4,6)$(PPh_3)_2$]	20.85
[NiBr($C_6H_2Cl_3$-2,3,4)$(PPh_3)_2$]	21.90
[NiBr($C_6H_3Cl_2$-2,4)$(PPh_3)_2$]	22.09
[NiBr(C_6F_5)$(PPh_3)_2$]	22.91
[NiBr($C_6H_2Me_3$-2,4,6)$(PPh_3)_2$]^b	18.97
[NiBr(C_6Cl_5)$(PEtPh_2)_2$]	18.32
[NiBr(C_6F_5)$(PEtPh_2)_2$]	19.51
[NiBr($C_6H_2Me_3$-2,4,6)$(PEtPh_2)_2$]^b	15.06
[NiBr($C_6H_2Cl_3$-2,3,4)$(PEtPh_2)_2$]^b	18.05
[NiBr(C_6Cl_5)$(PMePh_2)_2$]^b	8.00
[NiBr(C_6F_5)$(PMePh_2)_2$]	8.72
[NiBr($C_6H_2Me_3$-2,4,6)$(PMePh_2)_2$]^b	4.67
[NiBr($C_6H_2Cl_3$-2,3,4)$(PMePh_2)_2$]	8.12

^{a} Low field, +ve, from H_3PO_4. ^{b} In toluene.

Characterization.—The complexes were characterized by their i.r., ^1H and ^{31}P n.m.r. spectra, and elemental analyses. The ^{31}P n.m.r. spectra were used to check for the absence of chloro

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* *Supplementary data available* (No. SUP 56753, 5 pp.): observed rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 2. Electronic spectral data for all the *trans*-$[NiX(R)L_2]$ complexes studied, in acetone solution

		X = Br		X = NCS[a]	
R	L	λ/nm	ε/dm³ mol⁻¹ cm⁻¹	λ/nm	ε/dm³ mol⁻¹ cm⁻¹
C_6Cl_5	PPh_3	452	477	425	878
C_6HCl_4-2,3,4,6		443	460	433	770
C_6HCl_4-2,3,5,6		442	480	433	730
$C_6H_2Cl_3$-2,4,6		447	315	432	623
C_6HCl_4-2,3,4,5		437	592	423	*b*
$C_6H_2Me_3$-2,4,6		442	416	419	600
C_6F_5		442	510	435	*b*
$C_6H_2Cl_3$-2,3,4		435	491	385	*b*
$C_6H_3Cl_2$-2,4		435	362	*b*	*b*
C_6H_4Cl-2		426	398	*b*	*b*
C_6Cl_5	$PEtPh_2$	444	379	424	647
$C_6H_2Me_3$-2,4,6		435	509	407	755
C_6F_5		437	499	425	852
$C_6H_2Cl_3$-2,3,4		428	755	408	*b*
C_6Cl_5	$PMePh_2$	435	425	420	780
$C_6H_2Me_3$-2,4,6		425	529	399	793
C_6F_5		427	603	418	*b*
$C_6H_2Cl_3$-2,3,4		417	653	395	*b*

[a] Approximate values. Obtained on addition of solid $[NH_4][NCS]$ to solutions of the corresponding bromo complexes of known concentration. [b] Decomposition of the final product occurs.

complexes in the final products. Table 1 shows the ^{31}P chemical shifts of all the bromo complexes in dichloromethane. Substitution of bromide by chloride was observed when ^{31}P n.m.r. spectra were run in $CDCl_3$.

Electronic Spectra.—Electronic spectra of the bromo complexes were recorded on a UV5230 Beckmann instrument in the range 550—350 nm, immediately after solution. After addition of an excess of dry solid ammonium thiocyanate to the bromo complexes, spectra of the new thiocyanato complexes were recorded. Table 2 shows spectrophotometric data for all the complexes studied.

Kinetics.—Reactions were followed spectrophotometrically at the wavelength where the thiocyanato complexes showed a maximum, or an inflection point whenever decomposition took place. Slow reactions {substrates being *trans*-$[NiR(Br)(PPh_3)_2]$ with R = C_6Cl_5, C_6HCl_4-2,3,4,6, C_6HCl_4-2,3,5,6, or $C_6H_2Cl_3$-2,4,6} were monitored *in situ* in the thermostatted cell compartment (±0.1 °C) of an UV5230 Beckman instrument by mixing the right amounts of $[NH_4][NCS]$ and nickel bromo complex solutions in acetone. Fast reactions were monitored using a thermostatted Durrum-110 stopped-flow spectrophotometer interfaced to an Apple II computer.

All runs were performed under pseudo-first-order conditions. Observed rate constants were derived using linear and exponential unweighted least-squares methods.[13] No ionic strength effect was observed for the anation second-order rate constants as had been found previously.[2] When decomposition of the final complex was observed, the time-scale was set so as to obtain only the initial reaction step. Standard unknown final reading methods[14] were also used. In all other cases a good linear or exponential fit was observed. Least-square errors for the rate constants were always within 5—20% of the calculated values, depending on the stability of the final product.

Isosbestic points were observed for reactions with half-lives long enough to record consecutive spectra.

Results and Discussion

The reactions selected to study the effect of the substituents of the R ligands on the rates of substitution of severely hindered *trans*-$[NiX(R)L_2]$ complexes were *trans*-$[NiBr(R)L_2]$ + $[NH_4][NCS] \longrightarrow$ *trans*-$[Ni(NCS)RL_2]$ + $[NH_4]Br$ where L = PPh_3, $PMePh_2$, or $PEtPh_2$. Thiocyanate was chosen as the incoming ligand since it allows us to obtain information on both the solvolitic and anionic paths of the well established mechanism (1) for these substitution reactions.[1] The solvent used was acetone, since it offers a reasonable equilibrium between solubility and stability of the organometallic complexes in solution. However, complexes with R = $C_6H_2Me_3$-2,4,6 or C_6H_4Cl-2 partially decompose in a few hours. Addition of a large excess of thiocyanate to solutions of the bromo complexes, containing polyhalogenoaryl ligands with only one *ortho*-chloro group blocking the nickel centre, leads to decomposition (Table 2). This behaviour can be interpreted as a result of the substitution of the phosphine by thiocyanate, and further decomposition of the anionic complex formed. Anionic complexes of this type have been prepared[15] or proposed[16] for palladium and platinum centres.

Experimental kinetic results are in perfect agreement with the well known two-term rate law[1] derived from mechanism (1).

$$\begin{tikzcd}
trans\text{-}[NiBr(R)L_2] + NCS^- \arrow[r, "k_{an}"] \arrow[d, "k_s"'] & trans\text{-}[Ni(NCS)RL_2] + Br^- \\
trans\text{-}[Ni(Me_2CO)RL_2]^+ \arrow[ur, "+\,NCS^-", "\text{fast}"'] &
\end{tikzcd} \qquad (1)$$

Observed rate constants for all substitution reactions studied in acetone are given in SUP 56753.

Plots of $k_{obs.}$ *versus* $[NCS^-]$ are linear (Figures 1—3) according to the derivation of the rate law for mechanism (1) under pseudo first order conditions (2). Since the ligand NCS^- was used, $k_{obs.}$ is always dependent on thiocyanate concentration and no solvent-only substitution processes were observed, as for other entering ligands (such as Cl^- or NO_2^-) in other systems with L = PEt_3 and R = $C_6H_2Me_3$-2,4,6 in ethanol solutions.[2]

$$k_{obs.} = k_S + k_{an.}[NCS^-] \qquad (2)$$

From a linear least-squares analysis of the plots of $k_{obs.}$ *versus*

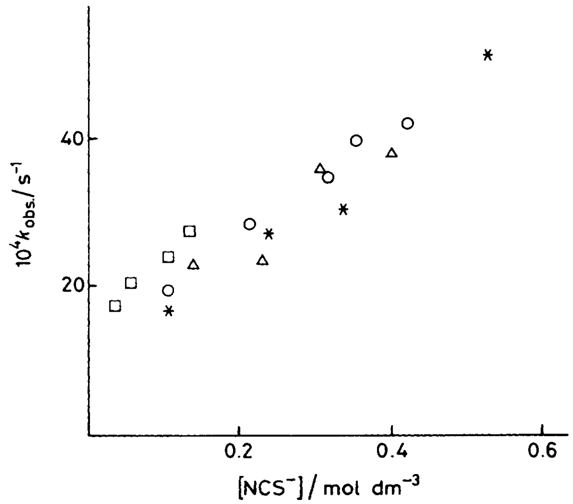

Figure 1. Dependence of the observed rate constants, $k_{obs.}$, on [NCS⁻] for the substitution of Br⁻ by NCS⁻ in *trans*-[NiBr(R)(PPh$_3$)$_2$]. R = C_6Cl_5 (○), C_6HCl_4-2,3,5,6 (*), C_6HCl_4-2,3,4,6 (△), or $C_6H_2Cl_3$-2,4,6 (□). In acetone at 25 °C

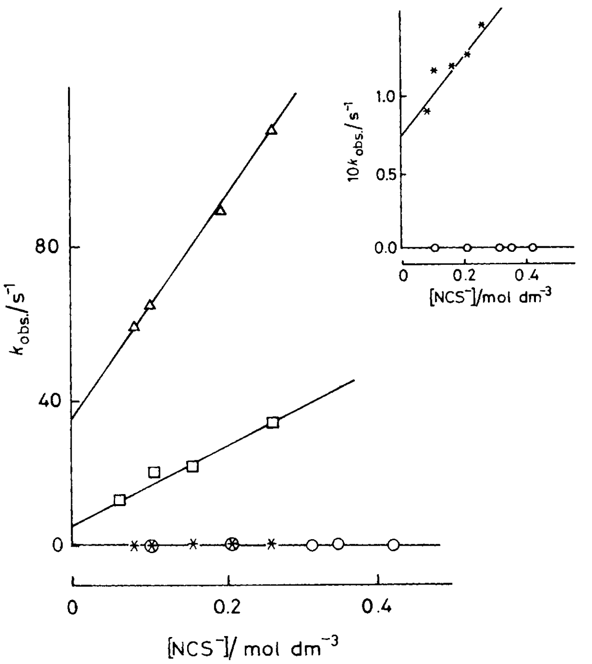

Figure 2. Dependence of the observed rate constants, $k_{obs.}$, on [NCS⁻] for the substitution of Br⁻ by NCS⁻ in *trans*-[NiBr(R)(PPh$_3$)$_2$]. R = C_6Cl_5 (○), $C_6H_2Me_3$-2,4,6 (*), C_6F_5 (△), or C_6HCl_4-2,3,4,5 (□). In acetone at 25 °C

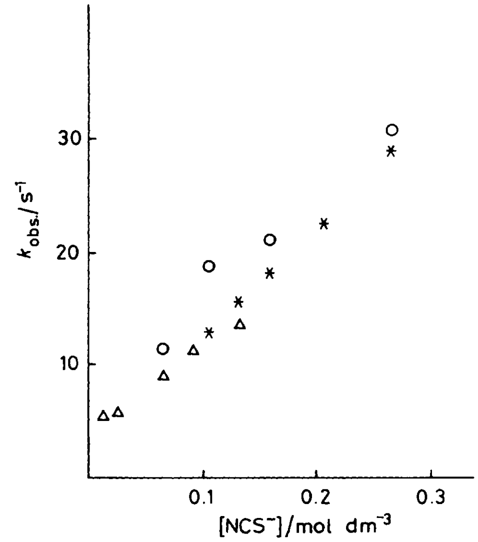

Figure 3. Dependence of the observed rate constants, $k_{obs.}$, on [NCS⁻] for the substitution of Br⁻ by NCS⁻ in *trans*-[NiBr(R)(PPh$_3$)$_2$], R = C_6HCl_4-2,3,4,5 (○), $C_6H_2Cl_3$-2,3,4 (*), or $C_6H_3Cl_2$-2,4 (△). In acetone at 25 °C

Table 3. Rate constants k_S and $k_{an.}$ for the reactions of *trans*-[NiBr(R)(PPh$_3$)$_3$] with NCS⁻ at 25 °C in acetone solution

R	k_S/s^{-1}	$k_{an.}/dm^3\ mol^{-1}\ s^{-1}$
C_6Cl_5	$(1.3 \pm 0.3) \times 10^{-4}$	$(6.6 \pm 1.0) \times 10^{-4}$
C_6HCl_4-2,3,5,6	$(0.7 \pm 0.2) \times 10^{-4}$	$(8.1 \pm 0.9) \times 10^{-4}$
C_6HCl_4-2,3,4,6	$(1.0 \pm 0.5) \times 10^{-4}$	$(7.9 \pm 1.2) \times 10^{-4}$
$C_6H_2Cl_3$-2,4,6	$(1.4 \pm 0.1) \times 10^{-4}$	$(9.4 \pm 1.1) \times 10^{-4}$
$C_6H_2Me_3$-2,4,6	$(5.2 \pm 0.6) \times 10^{-2}$	$(3.0 \pm 0.4) \times 10^{-1}$
C_6F_5	$(3.4 \pm 0.1) \times 10$	$(2.9 \pm 0.6) \times 10^2$
C_6HCl_4-2,3,4,5	6.0 ± 2.5	$(10 \pm 1.5) \times 10$
$C_6H_2Cl_3$-2,3,4	2.0 ± 0.8	$(10 \pm 0.5) \times 10$
$C_6H_3Cl_2$-2,4	3.3 ± 0.5	$(8.3 \pm 0.6) \times 10$
C_6H_4Cl-2	3.7 ± 0.4	$(4.3 \pm 0.2) \times 10$

Table 4. Steric factors of R *ortho* substituents and Ni–C bond distances for related *trans*-[NiX(R)L$_2$] compounds

X	R	L	Steric factor (ESV)[a] for *ortho* substituents	Ni–C distance (Å)
C_6F_5	C_6Cl_5	$PMePh_2$	0.55[b] 0.27[d]	1.905[c] 1.978
C_2Cl_3	$C_6H_2Me_3$-2,4,6	PMe_2Ph	0.52	1.936[e]
Br	C_6F_5	$PMePh_2$	0.27	1.880[f]
C_6F_5	C_6F_5	$PMePh_2$	0.27	1.939[g]

[a] Ref. 23. [b] For the chloro substituent. [c] M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 1971, 3463. [d] For the fluoro substituent. [e] J. M. Coronas, G. Muller, M. Rocamora, C. Miravilles, and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1985, 2333. [f] M. R. Churchill, L. K. Kolra, and M. V. Veidis, *Inorg. Chem.*, 1973, **12**, 1656. [g] M. R. Churchill and M. V. Veidis, *J. Chem. Soc., Dalton Trans.*, 1972, 670.

[NCS⁻], k_S (s⁻¹) and $k_{an.}$ (dm⁻³ mol s⁻¹) were derived. Table 3 shows the values at 25 °C in acetone solution for reactions of the complexes studied. It is clear that the steric effect of the R groups *trans* to the leaving group of the nickel(II) centre is a determining factor. In particular *ortho*-substituent effects seem to be dominant, both for the solvent and for direct substitution paths (Figures 1 and 3). Table 4 gives a steric factor for the three *ortho* substituents of the aryl group as well as Ni–C bond lengths for related compounds. Since the C_6Cl_5 and C_6F_5 ligands are considered as having equivalent electronegativity {their phenol derivatives have similar values of pK_a,[17] and also the C_6Cl_5 ligand shows even shorter Ni–C distances than C_6F_5 in the compound *trans*-[Ni(C_6Cl_5)(C_6F_5)(PMePh$_2$)$_2$)] (Table 4)}, the different substitution rate constants obtained could be easily associated with the different steric hindrances of the fluoro and chloro *ortho* substituents.

The intermediate behaviour of the complexes with R = $C_6H_2Me_3$-2,4,6 is far from being clearly associated with thermodynamic or kinetic factors.[18,19] The van der Waals radii of the methyl (2.00 Å)[20] and chlorine (1.70—1.90 Å)[21] groups are similar. Furthermore, in esterification and hydrolysis

Table 5. Rate constants k_S and $k_{an.}$ at 15 and 5 °C, and activation parameters, for the reactions of *trans*-[NiBr(R)(PPh$_3$)$_2$] with NCS$^-$ in acetone

R	T/°C	k_S/s^{-1}	$k_{an.}$/dm^3 mol^{-1} s^{-1}
C_6Cl_5	15	$(6.1 \pm 0.6) \times 10^{-5}$	$(3.1 \pm 0.2) \times 10^{-4}$
	5	$(1.7 \pm 0.5) \times 10^{-5}$	$(8.6 \pm 1.5) \times 10^{-5}$
$C_6H_2Me_3$-2,4,6	15	$(2.3 \pm 0.5) \times 10^{-2}$	$(3.5 \pm 0.1) \times 10^{-1}$
	5	$(1.7 \pm 0.3) \times 10^{-2}$	$(1.8 \pm 0.1) \times 10^{-1}$
$\Delta H^\ddagger$ (C_6Cl_5)/kJ mol^{-1}		66.1	68.2
$\Delta S^\ddagger$ (C_6Cl_5)/J K^{-1} mol^{-1}		−98.7	−77.8
$\Delta H^\ddagger$ ($C_6H_2Me_3$-2,4,6)/kJ mol^{-1}		48.1	37.1
$\Delta S^\ddagger$ ($C_6H_2Me_3$-2,4,6)/J K^{-1} mol^{-1}		−108	−148

Table 6. Rate constants k_S and $k_{an.}$ for the reactions of *trans*-[NiBr(R)L$_2$] with NCS$^-$ (L = PEtPh$_2$ or PMePh$_2$) at 25 °C in acetone solution

R	L	k_S/s^{-1}	$k_{an.}$/dm^3 mol^{-1} s^{-1}
C_6Cl_5	PEtPh$_2$	$(2.3 \pm 0.2) \times 10^{-1}$	3.3 ± 0.2
	PMePh$_2$	$(2.3 \pm 0.2) \times 10^{-1}$	1.3 ± 0.2
$C_6H_2Me_3$-2,4,6	PEtPh$_2$	$(5.5 \pm 0.3) \times 10$	$(4.0 \pm 0.1) \times 10^2$
	PMePh$_2$	3.2 ± 0.2	$(3.2 \pm 0.1) \times 10^2$
C_6F_5	PEtPh$_2$	$(2.2 \pm 0.5) \times 10^2$	$(2.7 \pm 0.3) \times 10^3$
	PMePh$_2$	*	$(4.2 \pm 0.4) \times 10^4$
$C_6H_2Cl_3$-2,3,4	PEtPh$_2$	$(5.7 \pm 0.5) \times 10$	$(1.8 \pm 0.1) \times 10^3$
	PMePh$_2$	*	$(1.2 \pm 0.2) \times 10^4$

* No meaningful k_S value can be calculated due to the error involved in having a very small intercept with a large slope.

reactions of *ortho*-benzoate groups, the steric factors associated with halogen substituents were of the order Cl (0.18), Br (0.01), methyl (0.0), and I (−0.20).[22] However with organometallic compounds as substrates, and anionic in-coming ligands, we have to assume that the greater electronic density of the chlorine may lead to a practical reaction size, this being slightly larger for the Cl than for the Me substituents. This is in good agreement with values for the steric factor given by Charton.[23] Some influence due to the different basicity of the ligand can also be expected. The basicity of the $C_6H_2Me_3$-2,4,6 ligand may be responsible for the decomposition of the complexes in acetone solution, probably due to increase in the electronic density at the nickel centre. This favours dissociation of the phosphine whenever nucleophilic attack by the solvent takes place. In the substitution processes, formation of the five-co-ordinate intermediate is mainly controlled sterically, but bond breaking of the leaving group may be affected favourably by the increase in electron density at the nickel centre, when compared with high-electronegativity ligands such as C_6F_5 and C_6Cl_5.

Thus, the increase in the rate constants k_S and $k_{an.}$ in parallel to the decrease in the size of the *ortho* substituents, points to an I_a mechanism for the substitution reactions, both *via* the direct or solvolytic path. All complexes with R having two *ortho* chloro groups showed approximately the same k_S and $k_{an.}$ values, as well as the complexes having only one chloro group in an *ortho* position.

The effect of aryl substituents in other than *ortho* positions to the Ni–C bond seems to be negligible. Electronic effects, both inductive, related to the successive elimination of the *meta* chloro groups ($C_6Cl_5 \longrightarrow C_6HCl_4$-2,3,4,6 $\longrightarrow C_6H_2Cl_3$-2,4,6, and C_6HCl_4-2,3,4,5 $\longrightarrow C_6H_2Cl_3$-2,3,4 $\longrightarrow C_6H_3Cl_2$-2,4), and resonant, related to the elimination of the *para* chloro group ($C_6Cl_5 \longrightarrow C_6HCl_4$-2,3,5,6, and $C_6H_3Cl_2$-2,4 $\longrightarrow C_6H_4Cl$-2), are clearly non-dominant in the rates of substitution of these complexes. So, long-distance electronic effects must be small when compared with *ortho* electronic and steric effects,[24,25] as has already been observed.[22]

For compounds with R = C_6Cl_5 and $C_6H_2Me_3$-2,4,6 with triphenylphosphine, values of $k_{obs.}$ were determined at 25, 15, and 5 °C, and activation parameters were then evaluated by Eyring plots. Table 5 shows the values of the activation entropies and enthalpies for the corresponding substitution reactions. The activation entropies are clearly negative, suggesting, again, an associatively activated mechanism. The activation enthalpies are less informative since the nickel(II) centre changes from one reaction to another.

Changes in the phosphine stabilizing ligand dramatically affect the values of k_S and $k_{an.}$ increasing the rates from PPh$_3$ to PEtPh$_2$ or PMePh$_2$ (Table 6). This effect of the *cis* non-labile ligands may be related to the size of the phosphine (cone angles: PPh$_3$, 145; PEtPh$_2$, 140; and PMePh$_2$, 136°[26]), or the basicity [pK_a = 2.73 (PPh$_3$), 4.91 (PEtPh$_2$), and 4.65 (PMePh$_2$).[27]] The sequence of increasing reaction rate, $C_6Cl_5 < C_6H_2Me_3$-2,4,6 $< C_6H_2Cl_3$-2,3,4 $< C_6F_5$, remains the same as for the PPh$_3$ series, but the span of the rate constants is quite different. That is, $k_{an.}$ ratios for the C_6Cl_5:$C_6H_2Me_3$-2,4,6:$C_6H_2Cl_3$-2,4,6:C_6F_5 (L = PPh$_3$) systems are 1:500:150 000:440 000, but when triphenylphosphine is substituted by ethyldiphenyl- or methyldiphenyl-phosphine (Table 6) this ratio changes to 1:120:550:820 and 1:250:9 200:32 000 respectively. The gradual decrease in the differences between $k_{an.}$ values from C_6Cl_5 to C_6F_5 on going from PPh$_3$ to the other phosphines may be related to a decrease of the overall steric strain in the whole molecule, thus favouring the substitution reaction. Therefore, the increase in the reaction rate on changing the phosphine may be related to the gradual decrease of the size of the phosphine. This effect has already been found for the reactions of *cis*- and *trans*-[PtCl(R)(PEt$_3$)$_2$] with CN$^-$. The $k_{an.}$ ratio obtained for R = $C_6H_2Me_3$-2,4,6:C_6H_4Me-2:C_6H_5 was 1:20:800 for the *trans* complexes, and 1:7 900:69 000 for the *cis* complexes, associated with increase in the steric strain on going from *trans* to *cis* complexes. In our case there is no change in the distribution of the leaving, in-coming, and *trans* ligands. So the difference is significant.

Quantification of this *cis* effect is currently under further study.

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