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A kinetic study of the coordination template effect in the nickel-catalysed formation of arylphosphonium salts

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Abstract

A kinetic study is reported of the nickel(II) halide-catalysed reactions of *o*-halogenoarylimine- and *o*-halogenoarylazo-template systems with tertiary phosphines in refluxing ethanol, which result in the replacement of the halogen *ortho* to the imino or azo function with formation of the related arylphosphonium salt. At a fixed concentration of catalyst, a second-order rate law is observed. The reaction rate also shows a first-order dependence on the concentration of the catalyst. Significant variations in rate have been observed which can be attributed to (a) the nature of halogen replaced by phosphorus (I > Br > Cl), (b) the donor/acceptor character of the phosphine, (c) the effects of "remote" substituents in the template substrate, and (d) the nature of the halogen of the nickel(II) halide catalyst. It is suggested that the rate data can be accommodated in terms of a mechanism involving initial reduction of nickel(II) to nickel(I), followed by oxidative insertion of the latter into the carbon–halogen bond to form an intermediate arylnickel(III) complex. Reductive elimination from the latter results in the arylphosphonium salt and regeneration of the nickel(I) species.

Introduction

In recent papers [1–3], we have shown that when aryl halides bearing appropriate donor substituents in the *ortho* position are heated in ethanol with a tertiary phosphine in the presence of nickel(II) or copper(II) catalysts, the halogen is replaced by the phosphine to form the related arylphosphonium salt. Thus, for example, the nickel(II) bromide-catalysed reactions of the *o*-haloarylimines (I; $R^1 = H$ or Me; $R^2 =$ benzyl or Ar; X = Cl, Br, I; Y = H or halogen) and the nickel(II) bromide- or copper(II) acetate-catalysed reactions of the *o*-haloarylazo

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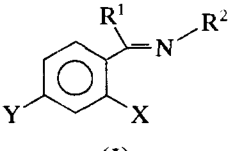
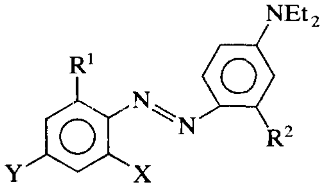
dyestuffs (II; $R^1 = H$ or Me; $R^2 = H$ or NHCOMe; X = Cl, Br, I; Y = H or halogen) yield the related phosphonium salts (III) and (IV) (R^3 = alkyl or aryl).



(I)



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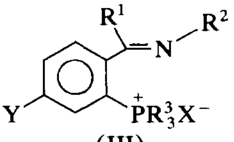

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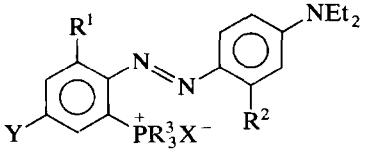


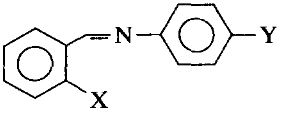
(IV)

In the absence of the transition metal catalyst these reactions do not occur. Similar substitution reactions have been achieved with *o*-haloaryl systems in which the key sp^2 hybridized nitrogen atom is part of a heterocyclic ring system [4,5]. These reactions appear to be examples of a kinetic template effect in which the sp^2 nitrogen donor aids the catalytic role of the metal ion in promoting the substitution reaction under relatively mild conditions, namely in refluxing ethanol. Normally the metal-catalysed reactions of aryl halides with tertiary phosphines proceed only at 150–200°C, usually in the absence of a solvent, although benzonitrile (b.p. 188°C) has been used for this purpose [6–9].

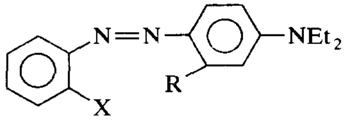
We have now carried out a kinetic study of the above nickel-catalysed reactions in order to gain some understanding of the mechanism.

A study of parameters influencing the overall yields of arylphosphonium salts in the above reactions established that the optimum molar ratio of reactants is aryl halide (1 mol): tertiary phosphine (3 mol): nickel(II) bromide (0.2 mol). When a solution of the reactants in ethanol was heated under nitrogen for up to 24 h, the related arylphosphonium salts could be isolated in virtually quantitative yield.

Initial kinetic studies of these systems have centred on a comparison of the rates of formation of the arylphosphonium salts from the imines (V) and dyestuffs (VI) by a conductivity method under the above "second-order unequal" conditions, at a fixed concentration of the nickel halide catalyst. Significant variations in rate have been observed that can be attributed to (a) the nature of the halogen replaced by phosphorus, (b) the nature of the phosphine, (c) the effect of "remote" substituents in the template, and (d) the nature of the nickel halide catalyst.



(V)



(VI)

Experimental

^1H NMR spectra were recorded on a Bruker WP80 SY spectrometer at 80 MHz. Chemical shifts are reported on the δ scale with respect to tetramethylsilane as an internal standard in deuteriochloroform. ^{31}P NMR spectra were recorded on the same instrument, and chemical shifts are reported with respect to 85% orthophosphoric acid as an external standard; shifts to high frequency are positive in sign.

The imine and dyestuff template molecules, and the related phosphonium salts, were prepared as previously described [1,2]. All of the butylphosphonium salts became hygroscopic on contact with the atmosphere and hence microanalytical data have not been obtained for these compounds, which have been characterized by NMR spectroscopy. During the kinetic study, the following new salts were characterized as the phosphonium iodides, following addition of excess potassium iodide prior to the solvent extraction salt isolation step.

*4-Methyl-*N*-(2 triphenylphosphoniobenzylidene) aniline iodide.* This was isolated as yellow crystals (42%), m.p. > 300°C (from $CHCl_3$/EtOAc). Anal. Found: C, 65.35; H, 4.65; N, 2.25. $C_{32}H_{27}INP$ calc.: C, 65.85; H, 4.65; N, 2.40%. $^{31}P(CDCl_3)$: δ 25.94 ppm. $^1H(CDCl_3)$: δ 8.5 (s, 1H), 7.65 (m, 19ArH), 6.85–5.95 ($[AX]_2$ system, 4ArH), 2.15 (s, 3H) ppm.

*4-(2-Triphenylphosphoniophenylazo)-*N,N*-diethylaniline iodide.* This was obtained as red crystals (83%), m.p. 220°C (from $CHCl_3$/EtOAc). Anal. Found: C, 62.78; H, 5.13; N, 6.18. $C_{34}H_{33}IN_3P \cdot H_2O$ calc.: C, 61.90; H, 5.35; N, 6.37%. $^{31}P(CDCl_3)$: δ 23.74 ppm. $^1H(CDCl_3)$: δ 8.2–7.4 (m, 19ArH), 6.95–6.4 ($[AX]_2$ system, 4H), 3.4 (q, 4H), 1.2 (t, 6H) ppm.

*4-(2-Tributylphosphoniophenylazo)-*N,N*-diethylaniline iodide.* This was obtained as a hygroscopic red solid (43%). ^{31}P $(CDCl_3)$: δ 31.63 ppm. ^1H $(CDCl_3)$: δ 8.5 (s, 4ArH), 7.1-6.6 ($[AX]_2$ system, 4ArH), 3.4 (q, 4H), 2.85 (m, 6H), 1.5–0.8 (m, 27H) ppm.

*2-Acetylamino-4-(2-triphenylphosphoniophenylazo)-*N,N*-diethylaniline iodide.* This was isolated as purple crystals (87%), m.p. 235°C (from $CHCl_3$/EtOAc). Anal. Found: C, 61.93; H, 5.29; N, 7.44. $C_{36}H_{36}IN_4OP$ calc.: C, 61.89; H, 5.19; N, 8.02%. $^{31}P(CDCl_3)$: δ 23.43 ppm. $^1H(CDCl_3)$: δ 8.3–7.4 (m, 23ArH), 6.1 (d, 1H), 3.4 (q, 4H), 2.3 (s, 3H), 1.2 (t, 6H) ppm.

*2-Acetylamino-4-(2-tributylphosphoniophenylazo)-*N,N*-diethylaniline iodide.* This was isolated as a hygroscopic purple solid (42%). $^{31}P(CDCl_3)$: δ 31.05 ppm. $^1H(CDCl_3)$: δ 8.1–7.5 (m, 7ArH), 6.0 (d, 1H), 3.4 (q, 4H), 2.9 (m, 6H), 2.35 (s, 3H), 1.4–0.8 (m, 27H) ppm.

N*-(2-Triphenylphosphoniobenzylidene) aniline iodide.* This was obtained as yellow crystals (35%), m.p. > 300°C (from $CHCl_3$/ether). Anal. Found: C, 63.63; H, 4.35; N, 2.18; $C_{31}H_{25}NIP \cdot H_2O$ calc.: C, 63.35; H, 4.60; N, 2.39%. $^{31}P(CDCl_3)$: δ 26.05 ppm. $^1H(CDCl_3)$: δ 8.6 (s, 1H), 8.1–7.1 (m, 24ArH) ppm.

*4-Bromo-*N*-(2-triphenylphosphoniobenzylidene) aniline iodide.* This was collected as light brown coloured crystals (56%), m.p. 200–202°C decomp. (from $CHCl_3$/ether). Anal. Found: C, 57.23; H, 3.85; N, 2.21. $C_{31}H_{24}BrINP$ calc.: C, 57.43; H, 3.73; N, 2.16%. ^{31}P $(CDCl_3)$: δ 26.17 ppm. $^1H(CDCl_3)$: δ 8.8 (s, 1H), 8.2–7.3 (m, 19ArH), 7.15–6.00 ($[AX]_2$ system, 4ArH) ppm.

*4-Phenylamino-*N*-(2-triphenylphosphoniobenzylidene) aniline iodide.* This was isolated as bright orange crystals (78%), m.p. 106°C decomp. (from $CHCl_3$/ether). Anal. Found: C, 67.63; H, 4.82; N, 4.12. $C_{37}H_{30}IN_2P$ calc.: C, 67.27; H, 4.57; N, 4.24%. $^{31}P(CDCl_3)$: δ 25.72 ppm. $^1H(CDCl_3)$: δ 8.5 (s, 1H), 8.2–7.3 (m, 24ArH), 6.85–6.00 ($[AX]_2$ system, 4ArH), 5.7 (s, 1H) ppm.

*4-Hydroxy-*N*-(2-triphenylphosphoniobenzylidene) aniline iodide.* This was isolated as a yellow solid (21%), m.p. > 300°C (from $CHCl_3$/ether). Anal. Found: C, 61.29; H, 4.13; N, 2.32. $C_{31}H_{25}INOP \cdot H_2O$ calc.: C, 61.69; H, 4.50; N, 2.32%. $^{31}P(TFA/D_2O)$: δ 26.56 ppm. $^1H(TFA, D_2O)$: δ 8.7 (s, 1H), 8.1–7.2 (m, 19ArH), 7.0–6.1 ($[AX]_2$ system, 4ArH), 5.2 (s, 1H) ppm.

*4-Diethylamino-*N*-(2-triphenylphosphoniobenzylidene) aniline iodide.* This was obtained as orange crystals (65%), m.p. 255°C (from $CHCl_3$/EtOAc). Anal. Found: C, 64.52; H, 5.31; N, 4.21. $C_{35}H_{34}IN_2P \cdot H_2O$ calc.: C, 63.90; H, 5.52; N, 4.26%. $^{31}P(CDCl_3)$: δ 25.68 ppm. $^1H(CDCl_3)$: δ 8.5 (s, 1H), 8.1–7.1 (m, 19ArH), 7.3–6.2 (m$[AX]_2$ system, 4ArH), 3.3 (q, 4H), 1.2 (t, 6H) ppm.

*4-Methoxy-*N*-(2-tris-*p*-methoxyphenylphosphoniobenzylidene) aniline iodide.* These are yellow crystals, m.p. > 256°C decomposition (from $CHCl_3$/ether). Anal. Found: C, 60.05; H, 4.80; N, 2.05. $C_{35}H_{33}INO_4P \cdot H_2O$ calc.: C, 59.40; H, 4.95; N, 2.0%. $^{31}P(CDCl_3)$: δ 25.9 ppm. $^1H(CDCl_3)$: δ 8.6 (s, 1H), 8.5–7.1 (m, 16H), 6.7–6.0 ($[AX]_2$ system, 4H), 3.8 (s, 9H), and 3.6 (s, 3H) ppm.

*4-Methoxy-*N*-(2-tris-*p*-tolylphosphoniobenzylidene) aniline iodide.* These are yellow crystals, m.p. 253°C (from $CHCl_3$/ether). Anal. Found: C, 65.80; H, 5.00; N, 2.20. $C_{35}H_{33}INOP$ calc.: C, 65.5; H, 5.15; N, 2.2%. ^{31}P $(CDCl_3)$: δ 25.9 ppm. $^1H(CDCl_3)$: δ 8.6 (s, 1H), 8.5–7.0 (m, 16H), 6.7–5.9 ($[AX]_2$ system, 4H), 3.7 (s, 1H), and 1.1 (s, 9H) ppm.

Rate studies

In preliminary experiments a solution of the template (10^{-3} mol), the phosphine (3×10^{-3} mol), and the nickel(II) halide (0.2×10^{-3} mol) in ethanol (20 cm^3) was heated under reflux under nitrogen. At appropriate intervals, 1 cm^3 aliquots were removed, and the reaction quenched by dilution to 10 cm^3 of ethanol. The resulting solution was thermostated at 25°C prior to measurement of the conductivity, using a Wayne–Kerr bridge. In most cases the reactions had reached completion after 24 h, as indicated by a limiting conductivity value. The rate data were evaluated from the conductivity data (a minimum of ten samples per run) by means of a "second-order unequal" plot of the form

$$\ln \frac{[\text{template}]_{t=0}[\text{phosphine}]_t}{[\text{template}]_t[\text{phosphine}]_{t=0}}$$

versus time, which in most cases gave a good straight line of slope k_{obs} up to 70% of completion, with correlation coefficients usually > 0.99.

In subsequent experiments at fixed concentrations of phosphine and nickel halide catalyst, the observed rate constants were shown to be largely independent of the concentration of the imine template (V; X = Br; Y = OMe) over a fourfold concentration range from 0.025 to 0.1 mol dm^{-3}. However, at fixed concentrations of imine and nickel halide catalyst, an increase in the observed rate constant was noted on increasing the concentration of the phosphine to a five- or ten-fold excess compared with the imine. This may indicate that the rate law is more complex than indicated above, perhaps involving a contribution from a term higher than first order in phosphine. Similar behaviour was noted in the related reactions of the *o*-haloarylazo templates when the phosphine concentration was varied. In addition, the latter systems revealed a decrease in rate constant on increasing the template concentration, probably indicating the diversion of the catalyst by other modes of coordination involving the template.

In order to simplify the data, and to enable rate comparisons to be made that would throw some light on key steps in the mechanism, rate data were recorded for the various systems under identical conditions as stated above, i.e. template (0.05 mol l^{-1}), phosphine (0.15 mol l^{-1}), and nickel halide (0.01 mol l^{-1}). Under these fixed concentrations of template and phosphine, an increase in the concentration of the nickel halide catalyst caused an increase in k_{obs}. Plots of $\ln(A_\infty - A_t)$ *versus* time for various catalyst concentrations were linear, with correlation coefficients > 0.997, indicating pseudo-first-order behaviour, as expected [10]. A plot of the resulting pseudo-first-order rate constants against catalyst concentration was also found to be linear. Confirmation of a second-order rate law for the reactions of the *o*-haloarylazo templates was also obtained by following the progress of the reactions by visible spectrophotometry.

Rate data are tabulated in the text. The following aspects have been examined in terms of their effect on the observed rate: (a) the nature of the halogen replaced by phosphine; (b) the nature of the phosphine; (c) the presence of remote substituents in the template; and (d) the nature of the nickel(II) halide catalyst.

Results and discussion

At a fixed concentration of the nickel(II) halide catalyst, both *o*-haloarylimine (V) and *o*-haloarylazo (VI) templates underwent reaction with tertiary phosphines in ethanol at 80°C in accordance with a second-order rate law, irrespective of the nature of the *o*-halogeno substituent X, the remote substituents Y (in V) and R (in VI), and the nature of the tertiary phosphine. The rates increase, as expected, as the concentration of the nickel(II) halide catalyst increases, and a first-order dependence on the catalyst was established. In our studies to date, the reactions of the imines (V) have received the greatest attention and will be discussed separately from the related reactions of the dyestuffs.

In the imine series (V; X = Cl, Br, I; Y = OMe) (Table 1), the nature of the *o*-halogen replaced by phosphorus had a significant effect on the rate of the reaction, the order of reactivity being I > Br > Cl (35 : 7 : 1) *. Clearly, the weaker the carbon–halogen bond, the faster the reaction, suggesting the involvement of a mechanism in which an insertion into the C–X bond is likely in the rate-determining step or which involves the formation of an intermediate whose decomposition is rate determining. The observed order of reactivity of the various halogens clearly indicates that these reactions cannot be proceeding *via* the S_NAr2 addition–elimination pathway observed for unmediated aromatic nucleophilic substitution processes, for which the order of reactivity is Cl > Br > I [11]. Our observed order of reactivity is also the inverse of the order of Ar–X bond energies [12]. Variation in the donor properties of the phosphine also had a noticeable effect on the rate of

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* In an earlier paper [2], an uncorrected typographical error led to this order being incorrectly stated.

Table 1

Rate data for the reactions of *o*-haloarylimines (V) with tertiary phosphines in refluxing ethanol containing nickel(II) halides

Imine (Initial concentration of 0.05 mol l^{-1})	R_3P (Initial concentration of 0.15 mol l^{-1})	NiX_2 (Initial concentration of 0.01 mol l^{-1})	k_{obs} (l mol^{-1} min^{-1})
X = Cl; Y = OMe	R = Ph	$NiCl_2$	0.39×10^{-3}
X = Br; Y = OMe	R = Ph	$NiBr_2$	1.91×10^{-3}
X = I; Y = OMe	R = Ph	NiI_2	13.6×10^{-3}
X = Br; Y = OMe	R = Ph	$NiBr_2$	1.91×10^{-3}
X = Br; Y = OMe	R = *p*-tolyl	$NiBr_2$	3.99×10^{-3}
X = Br; Y = OMe	R = *p*-$MeOC_6H_4$	$NiBr_2$	22.7×10^{-3}
X = Br; Y = OMe	R = Bu	$NiBr_2$	7.24×10^{-3}
X = Br; Y = OMe	R = Ph	$NiCl_2$	1.22×10^{-3}
X = Br; Y = OMe	R = Ph	$NiBr_2$	1.91×10^{-3}
X = Br; Y = OMe	R = Ph	NiI_2	2.36×10^{-3}
X = Br; Y = H	R = Ph	$NiBr_2$	1.18×10^{-3}
X = Br; Y = Me	R = Ph	$NiBr_2$	1.52×10^{-3}
X = Br; Y = Br	R = Ph	$NiBr_2$	1.55×10^{-3}
X = Br; Y = OMe	R = Ph	$NiBr_2$	1.91×10^{-3}
X = Br; Y = NHPh	R = Ph	$NiBr_2$	3.19×10^{-3}
X = Br; Y = OH	R = Ph	$NiBr_2$	3.49×10^{-3}
X = Br; Y = NEt_2	R = Ph	$NiBr_2$	3.92×10^{-3}

the reactions. For the three triarylphosphines studied, the order of reactivity was found to be tris-*p*-methoxyphenylphosphine > tris-*p*-tolylphosphine > triphenylphosphine (12:2:1). Tributylphosphine, a significantly better σ-donor than triarylphosphines [13], reacted four times faster than triphenylphosphine but three times slower than tris-*p*-methoxyphenylphosphine, perhaps indicating that the greater π-acceptor character of the triarylphosphine is of some significance in stabilizing a crucial intermediate or transition state. The influence of the remote substituent Y in the imines (V) was of interest, although relatively small, and indicates that the donor properties of the imino nitrogen are also significant. In general, the greater the electron-releasing nature of the remote substituent Y, the faster is the rate of the reaction, the greatest effect being observed for Y = NEt_2, which underwent the reaction at a rate three times faster than for Y = H. The presence of an electron-withdrawing group in the *p*-position to the imino nitrogen, *e.g.* Y = CN or NO_2, completely inhibited the reaction. The nature of the halogen present in the nickel(II) halide catalyst was also found to exert a small but measurable influence on the rate of the reaction between the imine (V; X = Br; Y = OMe) and triphenylphosphine, the order of reactivity being $NiI_2 > NiBr_2 > NiCl_2$ (2:1.5:1).

The corresponding rate studies of the *o*-haloarylazo systems (VI; X = Cl, Br, and I; R = H or NHCOMe) (Table 2) followed a similar pattern. As with the imines, the nature of the *o*-halogen had the most significant effect on rate, the order of reactivity I > Br > Cl being again observed for both series of dyestuffs. The "remote" substituent R in VI is also seen to have a significant influence.

Table 2

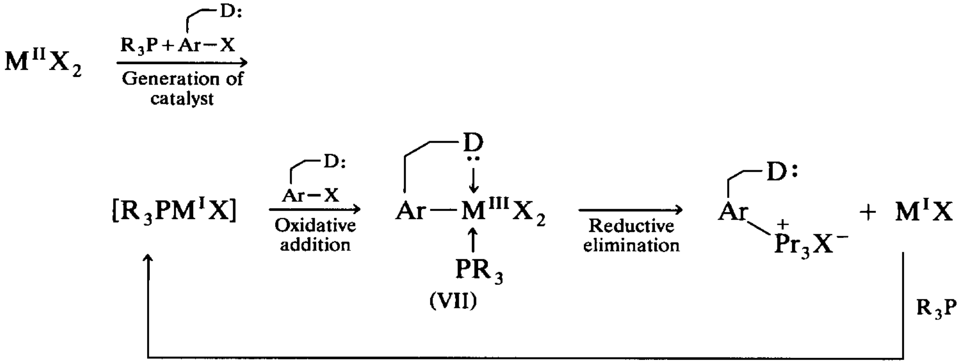
Rate data for the reaction of *o*-haloarylazo compounds (VI) with tertiary phosphines in refluxing ethanol containing nickel(II) halides

Substrate (Initial concentration of 0.05 mol l^{-1})	R_3P (Initial concentration of 0.15 mol l^{-1})	NiX_2 (Initial concentration of 0.01 mol l^{-1})	k_{obs} (l mol^{-1} min^{-1})
X = Cl; R = H	R = Ph	$NiBr_2$	1.71×10^{-3}
X = Br; R = H	R = Ph	$NiBr_2$	11.1×10^{-3}
X = I; R = H	R = Ph	$NiBr_2$	39.5×10^{-3}
X = Cl; R = NHCOMe	R = Ph	$NiBr_2$	0.74×10^{-3}
X = Br; R = NHCOMe	R = Ph	$NiBr_2$	1.29×10^{-3}
X = I; R = NHCOMe	R = Ph	$NiBr_2$	9.66×10^{-3}
X = Br; R = H	R = Ph	$NiBr_2$	11.1×10^{-3}
X = Br; R = H	R = Bu	$NiBr_2$	22.1×10^{-3}
X = Br; R = NHCOMe	R = Ph	$NiBr_2$	1.29×10^{-3}
X = Br; R = NHCOMe	R = Bu	$NiBr_2$	10.0×10^{-3}
X = Br; R = H	R = Ph	$NiCl_2$	2.78×10^{-3}
X = Br; R = H	R = Ph	$NiBr_2$	11.1×10^{-3}
X = Br; R = H	R = Ph	NiI_2	20.9×10^{-3}
X = Br; R = NHCOMe	R = Ph	$NiCl_2$	0.52×10^{-3}
X = Br; R = NHCOMe	R = Ph	$NiBr_2$	1.29×10^{-3}
X = Br; R = NHCOMe	R = Ph	NiI_2	4.32×10^{-3}

Thus, for example, the unsubstituted system (VI; X = Br; R = H) undergoes the reaction with triphenylphosphine some eight times faster than the acetylamino-substituted system (VI; X = Br; R = NHCOMe), indicating the involvement of *either* steric inhibition *or* competitive coordination for the catalyst. The superior σ-donor properties of tributylphosphine are evident in both series of *o*-haloarylazo templates (VI; R = H or NHCOMe), the trialkylphosphine reacting faster than triphenylphosphine, although the effect is more noticeable in the more crowded template (VI; R = NHCOMe). Variation in the nature of the halogen in the nickel(II) catalyst had a slightly greater influence on the rate than in the imine series.

Finally, comparison of the rates of the related reactions of the imine (V; X = Br; Y = NEt_2) and the dyestuff (VI; X = Br; R = H) reveals that the reaction of the dyestuff is some three times faster than that of the imine, perhaps indicating a small electron withdrawing influence of the additional azo-nitrogen in facilitating *either* cleavage of *or* insertion into the carbon–bromine bond.

The above kinetic data can all be accommodated in terms of the mechanism depicted in Scheme 1. The observed kinetic order in the respective reactions of the imines and dyestuffs suggests that involvement of an intermediate of the type VII involving one mole of each of the phosphine, *o*-halogenoaryl system, and the metal. It is likely that the nickel(II) halide is reduced in the presence of the phosphine and *o*-halogenoaryl template to the nickel(I) oxidation state, and that a phosphine nickel(I) species is the active catalyst which undergoes a coordination template-assisted oxidative insertion into the carbon–halogen bond to form the intermediate VII. Reductive elimination then follows, with the formation of the



Scheme 1.

carbon–phosphorus bond, and the regeneration of the nickel(I) catalyst. There are precedents in the literature for each of the above stages suggested in Scheme 1.

Although the reduction of copper(II) to copper(I) by phosphorus(III) compounds is well known [14], the related reduction of nickel(II) to nickel(I) in the absence of an additional reducing agent is less well documented. However, it is known that nickel(I) complexes can arise spontaneously in the reactions of certain nickel(II) halides with polydentate tertiary phosphines [15,16] and also that the nickel(0) complex $[Ni\{(EtO)_3P\}_4]$ is formed when nickel(II) chloride is heated in triethylphosphite [17]. An electroanalytical study of the influence of trivalent phosphorus donor ligands on the relative stability of nickel(II), nickel(I), and nickel(0) has revealed that various tertiary phosphine ligands stabilize the nickel(I) state relative to nickel(0) and nickel(II), whereas the reverse is true of trialkyl and triarylphosphite ligands [18]. The influence of the nature of the ligands on the stability of nickel(I) and palladium(I) complexes has also been the subject of some very recent papers [19,20]. The small influence of the halogen present in the nickel(II) halide catalyst in the present study can perhaps be accommodated in terms of the recent observation that for a series of nickel halide complexes of a given phosphine ligand, the redox potential $E^{\ominus}(Ni^{II}Ni^{I})$ becomes less negative in going from chloride to bromide to iodide, implying increasing stability of the nickel(I) state [20].

Oxidative insertion of palladium(0) phosphine complexes into the carbon–halogen bond of *o*-halogenoarylimines closely related to V has been described recently [21]. Evidence of the oxidative addition of aryl halides to nickel(I) halide–phosphine complexes to give arylnickel(III) complexes has been presented by Tsou and Kochi in their studies of the coupling of aryl halides to form biaryls in the presence of nickel phosphine complexes [22]. In these reactions, arylphosphonium salt formation accompanies biaryl formation, arising from the rapid collapse of a common intermediate, an arylnickel(III)–phosphine complex, with regeneration of the catalytically active nickel(I) species, much as in the present scheme. Further support for the intermediacy of arylnickel(III)–phosphine complexes was obtained from studies of the oxidation of arylnickel(II)–phosphine complexes, which resulted in high yields of the related arylphosphonium salts, in a rapid reductive elimination step [23]. In the above reactions of the imines (V), we have observed [2] that the rate of phosphonium salt formation increases rapidly when the imine is treated with the nickel(I) complex [Ni(Ph_3P)$_3$Br]. This observation lends support to the above suggestion of an *in-situ* reduction of the metal from the +2 state, followed by a coordination-assisted oxidative insertion process.

Hence in the reactions in the present study, it is likely that the oxidative addition step is rate determining. As has been pointed out [24], the formation of a five-coordinate intermediate of the type proposed in Scheme 1 would facilitate reductive elimination, since the aryl–metal bond and the metal–phosphorus bond are likely to occupy adjacent positions in the coordination sphere of the metal.

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