Oxidative Addition of Aryl Halides to Tris(triphenylphosphine)nickel(0)

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The oxidative addition of aryl halides, RC_6H_4X, to tris(triphenylphosphine)nickel(0) has been studied (R = H, *m*- or *p*-Me, -Cl, -CN, and -OPh, *p*-OMe, -COMe, and -COPh, and *m*-CO_2Me; X = Cl, Br, or I). The effects of substituents on the aryl halides and of the halide as leaving group have been investigated by competitive measurements. The reactions of *p*-chloroanisole and *p*- and *m*-dichlorobenzene display first-order kinetics with respect to the aryl halides and the nickel complex. Triphenylphosphine decreases the reaction rate. The mechanistic implications of these results are discussed.

OXIDATIVE-ADDITION reactions of organic halides with transition-metal complexes have received much attention both from the point of view of the mechanism [1-5] and the properties of the adducts.[5-8] The reactions afford a ready method of preparation of complexes containing carbon–metal σ bonds, which are intermediates in several catalytic processes. Aryl and vinyl halides are particularly reactive towards d^{10} transition-metal(0) complexes, *e.g.* phosphine complexes of nickel(0),[5,8-11] palladium(0),[12] and platinum(0).[10] Among these complexes the nickel ones are by far the most reactive, and straightforward reactions between chlorobenzene and nickel triaryl- or trialkyl-phosphines take place at room temperature. Based on these reactions, some catalytic processes for the synthesis of aromatic nitriles [13,14] and phosphonium salts [15] were described.

In this paper we report an extensive study of the oxidative addition of aryl halides to nickel(0) triphenylphosphine complexes. The influences of the substituent on the aryl group, of the halogen as leaving group, and of the PPh_3 concentration on reaction rate afford further information on oxidative-addition reactions.

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[13] L. Cassar, *J. Organometallic Chem.*, 1973, **54**, C57.

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EXPERIMENTAL

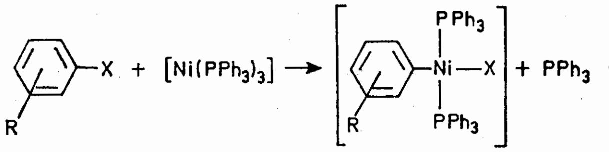
Materials.—All reagents were commercially available and used without further purification. The complex [Ni-$(PPh_3)_3$] was prepared by treating $[Ni(PPh_3)_2(C_2H_4)]$ with excess of phosphine[16] and crystallized from benzene–hexane. All the reactions were carried out under argon, and benzene was deoxygenated. Samples were analyzed by gas chromatography on a 2 m Chromosorb column of 10% silicone UCCW-982.

Determination of the Relative Rates of Oxidative Addition.—The complex $[Ni(PPh_3)_3]$ (250 mg, 0.3 mmol) and PPh_3 (131 mg, 0.5 mmol) were dissolved in benzene (20 cm^3) in a round-bottomed flask (50 cm^3) containing a magnetic stirring bar. A solution of two aromatic halides (3.3 mmol each) in benzene (5 cm^3) was then added. The mixture was stirred at 20 °C for 2—3 h. After the benzene had been evaporated *in vacuo* at room temperature, diethyl ether saturated with hydrogen chloride (20—30 cm^3) was added to the residue and the resulting mixture stirred for *ca.* 1 h. Water was then added and the organic layer analyzed by gas chromatography. The following pairs of halides were examined: *p*-dichlorobenzene–*p*-chloroanisole (1.1), –*m*-chlorotoluene (0.8), –*p*-chlorotoluene (2.0), –*p*-bromoanisole (0.33), —chlorobenzene * (1.0), and –*m*-chlorodiphenyl ether (2.3); *m*-dichlorobenzene–*p*-chloroanisole (14); *p*-chloroanisole–*p*-chlorodiphenyl ether (1.1); chlorobenzene–bromobenzene * (1.7); *p*-chlorotoluene–*p*-bromoanisole (0.17) and –*p*-chloroanisole (0.5); *m*-dichlorobenzene–*m*-chlorodiphenyl ether (3.0), –*m*-chlorobenzoate (0.17), –*p*-chlorobenzophenone (0.0072), and –*p*-chloroacetophenone (0.0077); *m*-chlorobenzonitrile–*p*-chlorobenzophenone (0.36) and –*m*-chlorobenzoate (8.3); *p*-chlorobenzophenone–*m*-chlorobenzoate (23); –*p*-chlorobenzonitrile (0.28), and –*p*-bromobenzophenone * ($\leqslant$0.01); and *p*-bromoanisole–*p*-iodotoluene (0.015 : 1).

Determination of the Absolute Rates of Oxidative Addition.—The complex $[Ni(PPh_3)_3]$ (700 mg), the internal standard (*e.g.* biphenyl), and PPh_3 were dissolved at 15 °C in benzene (20 cm^3) in a flask (50 cm^3) containing a magnetic stirring bar and a serum cap. The temperature was controlled to ± 0.1 °C by means of a constant-temperature bath. The mixture was stirred for 1 h and the aromatic halide dissolved in benzene (6 cm^3) was then added. At appropriate intervals of time, samples (1 cm^3) of the reaction mixture were removed and placed in diethyl ether (10 cm^3) saturated with hydrogen chloride. After *ca.* 0.5 h, water was added and the organic layer analyzed by gas chromatography.

RESULTS

We first examined the effect of the substituent on the aryl group in the oxidative-addition reaction of stoicheiometry (1). Relative rates in benzene were measured by carrying out competitive reactions of pairs of aryl halides under the conditions described in the Experimental section. Equimolecular quantities of the reference halide (*e.g. p*-dichlorobenzene) and the halide whose reactivity was to be established were mixed and treated with a small quantity of $[Ni(PPh_3)_3]$ to avoid a change in concentration of the two halides especially when their reactivity is quite different.



(1)

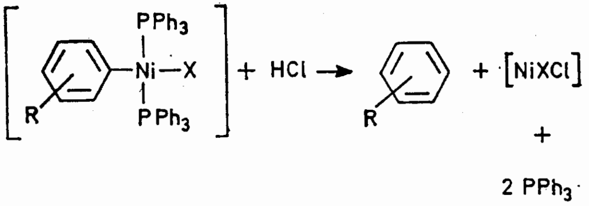
TABLE 1

Relative rates of oxidative addition at 20 °C and 0.02M-PPh_3 [reaction (1)] *

R	X	Relative rate V_{ArX}/V_{PhCl}
p-CN	Cl	6.5×10^3
p-COPh	Cl	1.8×10^3
p-COMe	Cl	1.7×10^3
m-CN	Cl	6.5×10^2
m-CO_2Me	Cl	78
m-Cl	Cl	13
m-OPh	Cl	4.3
p-Cl	Cl	1.0
H	Cl	1.0
m-Me	Cl	1.2
p-Me	Cl	0.5
p-OMe	Cl	0.9
p-OPh	Cl	0.8
p-OMe	Br	3.0
H	Br	1.7
p-COPh	Br	$\geqslant 1.8 \times 10^5$
p-Me	I	2.0×10^2

* Conditions as in the Experimental section.

The reaction mixture was then treated with hydrochloric acid in diethyl ether [equation (2)] and the aromatic hydrocarbons formed were quantitatively determined by gas chromatography.



(2)

The stoicheiometry (2) was confirmed in the case of the *m*-chloro- and *p*-methoxy-phenyl complexes. The reactions were first order in concentration of aromatic halide for the pairs of halides in Table 2. A plot of the relative rates for several *p*- and *m*-substituted aryl halides against Hammett's σ is shown in Figure 1. For oxidative addition

TABLE 2

Influence of the concentration of the aryl halide on the relative rates of oxidative addition *

ArX		[ArX, I]/ [ArX, II]	Relative rate $V_{ArX,I}/V_{ArX,II}$
p-Chloroanisole	*p*-Chlorobenzene	0.5	0.45
		2	1.9
		4	4
p-Chlorobenzonitrile	*p*-Chlorobenzophenone	1	3.4
		0.25	1
		0.125	0.45

* Conditions as in the Experimental section. Initial concentrations: $[Ni(PPh_3)_3] = 5 \times 10^{-3}$—$1.5 \times 10^{-2}$M; $[PPh_3] = 2 \times 10^{-2}$M; and $[ArX] = 5 \times 10^{-2}$—6×10^{-1}M.

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* Examined by measuring the decrease in aryl halide concentration at 15—20% conversion.

[16] P. Heimbach, *Angew. Chem.*, 1964, **76**, 586.

of a single halide, using an excess of halide at several concentrations of PPh_3, pseudo-first-order kinetics were observed in the case of *p*-methoxychlorobenzene, and *p*-dichloro- and *m*-dichloro-benzene (Table 3). Reaction rates of the more activated aryl halides were too fast for the sample-withdrawing technique.

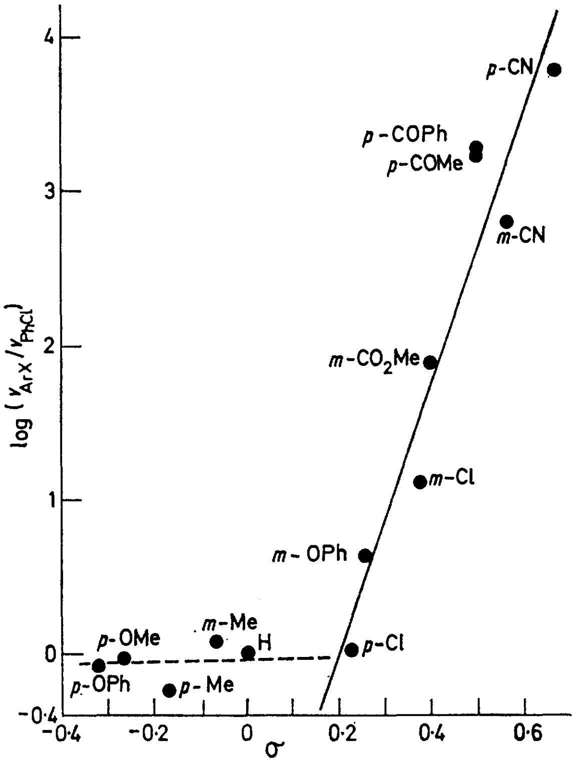

FIGURE 1 Correlation of relative rates of oxidative addition of substituted aryl halides with σ (D. M. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420) at 0.02M-PPh_3

Table 3 shows the variations in $k_{obs.}$ with the concentrations of the aryl halide and PPh_3. In all cases $k_{obs.}$ values are averages of three measurements. Values obtained at low [PPh_3] (0.025—0.040M) are based on one half-life.* In all other cases pseudo-first-order rate plots were invariably linear for at least two half-lives. Values of $k_{obs.}$ derived from the gradients of such plots were generally reproducible to ± 5%.

Even at high [PPh_3], no phosphonium salt formation was observed (15—20 °C, in benzene).

DISCUSSION

The relative-rate measurements (Table 1) show a pattern analogous to that qualitatively observed for the oxidative addition of aromatic halides to [$Pd(PPh_3)_4$].[12b] As to the plot against Hammett's σ (Figure 1), there is a good linear correlation for electron-withdrawing substituents with $\sigma > 0.23$. For this series of halides the ρ value is very high (8.8, $r = 0.96$), indicating a large sensitivity to substituent effects. The ρ value is larger than that observed in the nickel-carbonyl catalyzed carbonylation of aryl halides.[17] For substituents with $\sigma < 0.23$ there is a dramatic change in the gradient and there seems to be no difference in reactivity from *p*-dichlorobenzene ($\sigma_{p\text{-Cl}}$ 0.23) to *p*-chlorodiphenyl ether ($\sigma_{p\text{-OPh}}$ −0.32). This surprising substituent effect is accompanied by that due to the change in halogen leaving group. In fact when electron-withdrawing substituents are present on the aromatic nucleus bromide derivatives are *ca.* 100 times more reactive than chloride, and when electron-releasing groups are present the difference in reactivity is between two and three. Qualitatively similar effects have been observed in nickel-catalyzed cyanation of aryl halides.[14]

TABLE 3

Influence of the concentrations of triphenylphosphine and aryl halide on $k_{obs.}$ for reaction (1)

ArX	[ArX] N†	[PPh_3] * M	$10^4k_{obs.}$ s^{-1}	$10^4k'$ $l\ mol^{-1}\ s^{-1}$
m-Dichlorobenzene	0.22	0.45	17	77
	0.44	0.45	37	84
	0.84	0.45	730	87
	1.06	0.45	94	89
	1.26	0.45	104	83
	0.47	0.02	76	161
	0.47	0.14	53	112
	0.47	0.26	46	97
	0.47	0.36	45	95
	0.87	0.36	84	96
	0.87	0.46	82	94
p-Dichlorobenzene	0.47	0.025	3.3	7.0
	0.95	0.025	6.1	6.4
	1.80	0.025	11.1	6.2
	2.56	0.025	15.5	6.1
	0.46	0.25	1.0	2.2
	0.91	0.25	2.0	2.2
	2.44	0.25	5.9	2.4
	0.95	0.040	3.7	3.9
	0.95	0.055	3.3	3.5
	0.95	0.085	2.3	2.4
	0.95	0.14	2.3	2.4
	1.95	0.20	4.2	2.2
	0.88	0.35	1.8	2.0
	0.82	0.62	1.6	1.9
p-Chloroanisole	0.25	0.025	1.5	6.0
	0.48	0.025	2.8	5.8
	0.94	0.025	5.5	5.9
	1.27	0.025	6.9	5.4
	0.94	0.050	3.0	3.2
	0.94	0.078	1.8	1.9
	0.94	0.13	1.6	1.7
	0.90	0.24	1.6	1.8
	0.90	0.34	1.4	1.6
	0.90	0.58	1.1	1.2

* ±0.005M. † 1N = 1 equivalent of X per dm^3.

Mechanistic changes[18] can account for the observed Hammett plot and the halogen effect. The kinetic data reported in Table 3 show that reaction rates are first order in the concentration of aryl halides for *p*-chloroanisole, *p*-dichlorobenzene, and *m*-dichlorobenzene. This behaviour can be accommodated by the mechanism in equations (3)—(5) where Ar = aryl. It is assumed that [$Ni(PPh_3)_3$] + [$Ni(PPh_3)_2$] = $(a - x)$, where a is the initial concentration of Ni^0 complexes. The con-

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* 1M = 1 mol dm^{-3}.

[17] L. Cassar and M. Foà, *J. Organometallic Chem.*, 1973, **51**, 381.

[18] P. R. Wells, *Chem. Rev.*, 1963, **63**, 171; H. H. Jaffé, *ibid.*, 1953, **53**, 191.

centration of $[Ni(PPh_3)_4]$ has been neglected since the equilibrium constant for the dissociation of this species

$$[Ni(PPh_3)_3] \overset{K}{\rightleftharpoons} [Ni(PPh_3)_2] + PPh_3 \tag{3}$$

$$[Ni(PPh_3)_3] + ArX \xrightarrow{k_1} [Ni(PPh_3)_2(Ar)X] + PPh_3 \tag{4}$$

$$[Ni(PPh_3)_2] + ArX \xrightarrow{k_2} [Ni(PPh_3)_2(Ar)X] \tag{5}$$

is greater than 10 mol l^{-1}.[19] Reactions (3)—(5) give rise to the rate law (6) which on normalizing to a constant

$$\frac{dx}{dt} = \frac{(k_1[PPh_3] + k_2K)[ArX](a - x)}{K + [PPh_3]} = k_{obs.}(a - x) \tag{6}$$

[ArX] gives (7). Rearranging equation (7) we obtain

$$k' = \frac{k_{obs.}}{[ArX]} = \frac{k_1[PPh_3] + k_2K}{K + [PPh_3]} \tag{7}$$

(8). Since K is probably[19] less than 10^{-6} mol l^{-1},

$$k'(K + [PPh_3]) = k_1[PPh_3] + k_2K \tag{8}$$

equation (8) can itself be rearranged to (9). Good

$$k'[PPh_3] = k_1[PPh_3] + k_2K \tag{9}$$

linear plots were obtained when $k'[PPh_3]$ was plotted against $[PPh_3]$ (Figure 2). A similar mechanism has been proposed by Pearson for the oxidative addition of methyl iodide to $[Pt(PPh_3)_3]$.[20] From the plots in Figure 2, values of k_1 and k_2K were computed (Table 4).

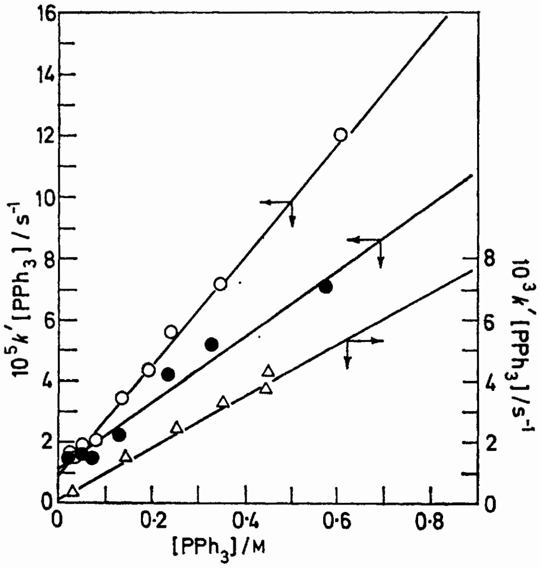

FIGURE 2 Plot of k' against $[PPh_3]$ in benzene at 15 °C for *p*-dichlorobenzene (○), *p*-chloroanisole (●), and *m*-dichlorobenzene (△)

In the light of the proposed mechanism we now make some comments on the relative-rate measurements. The relative rates measure the ratio of the $k_{obs.}$ values. From equation (6) one can derive (10). Thus the ratio

$$\text{Relative rate} = \frac{k_{obs.(ArX,I)}}{k_{obs.(ArX,II)}} = \frac{k_{1(I)}[PPh_3] + k_{2(I)}K}{k_{1(II)}[PPh_3] + k_{2(II)}K}$$

$$= \frac{k_{1(I)}}{k_{1(II)}} \text{ as } [PPh_3] \rightarrow \infty$$

$$= \frac{k_{2(I)}}{k_{2(II)}} \text{ as } [PPh_3] \rightarrow 0 \tag{10}$$

of $k_{obs.}$ values depends on $[PPh_3]$, and the relative rates in Table 1 and Figure 1 yield the ratio of $k_{obs.}$ at 0.02M-PPh_3. We also determined the relative rates for three halides (*p*- and *m*-dichlorobenzene and *p*-chloroanisole) at different $[PPh_3]$ (Table 5). A comparison (Table 5) between these data and $k_{obs.}$ ratios calculated from k_1 and k_2K [Table 4 and equation (10)] further supports the proposed mechanism. There is good agreement except in the case of *m*-dichlorobenzene at low $[PPh_3]$ where the data differed by a factor of 2. This is probably due to uncertainty in the determination of the intercepts of the plots.

TABLE 4

k Values for oxidative addition [equations (3)—(5), Figure 2] at 15 °C

	10^4k_1/l mol^{-1} s^{-1}	$10^5k_2K/s^{-1}$
p-Chloroanisole	1.0	1.1
p-Dichlorobenzene	1.8	0.9
m-Dichlorobenzene	85	20

TABLE 5

Influence of the concentration of triphenylphosphine on relative rates of oxidative addition at 20 °C *

ArX	$V_{ArX}/V_{C_6H_4Cl_2\text{-}p}$	$[PPh_3]$/M
p-Chloroanisole	0.9 (1.0) †	0.020
	0.7 (0.64) †	0.340
	0.7 (0.61) †	0.550
m-Dichlorobenzene	13 (29) †	0.020
	40 (44) †	0.340
	42 (45) †	0.550

* Conditions as described in the Experimental section.
† Calculated from data in Table 4.

Further conclusions can be drawn from the data in Table 4. If K is less than 10^{-6} mol l^{-1},[19] k_2 values are greater than 10 l mol^{-1} s^{-1}; thus there is a very large difference in reactivity between the bis and the tris phosphine complex. However, in both cases there is a qualitatively similar pattern of reactivity towards the three halides which we have studied. In fact k_1 and k_2 are very similar for *p*-chloroanisole and *p*-dichlorobenzene while *m*-dichlorobenzene has values of k_1 and k_2 larger than the other two halides. The sensitivity to substituents for the three halides seems to be similar to that obtained by competitive measurements (Table 1, Figure 1) and it is probably characteristic of oxidative addition of aryl halides to nickel(0) triphenylphosphine complexes.

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[19] C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2269.

[20] R. G. Pearson and J. Rajaram, *Inorg. Chem.*, 1974, **13**, 246.

This behaviour, in some way analogous to that observed in the reaction of aryl halides with sodium atoms,[18] suggests a halogen-abstraction mechanism. However, the observed halogen effect for substituents with $\sigma < 0.23$ and the retention of configuration for oxidative addition of vinyl halides to nickel phosphine complexes [8] make this mechanism unlikely. We prefer to consider the reaction as occurring *via* an unsymmetrical three-centre transition-state mechanism which, for electron-withdrawing substituents, can approach an aromatic nucleophilic substitution.

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