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THE ADDITION OF ARYL HALIDES TO TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)

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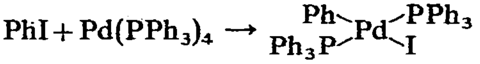
SUMMARY

The order of reactivity of halobenzenes towards oxidative addition to $Pd(PPh_3)_4$ has been found to be $PhI > PhBr > PhCl$. Iodobenzene will react with $Pd(PPh_3)_4$ in benzene at room temperature, and bromobenzene will react at 80°. Chlorobenzene, however, is unreactive even at 135°. Aryl chlorides substituted with electron-donating groups similarly are unreactive, but aryl chlorides substituted with electron-withdrawing groups are reactive. This increased reactivity, and order of reactivity $4\text{-}NO_2C_6H_4Cl > 4\text{-}CN\text{-}C_6H_4Cl > 4\text{-}PhCOC_6H_4Cl > PhCl$ suggests that the mechanism of the oxidative addition is similar to that of a bimolecular nucleophilic aromatic displacement reaction in which breaking of the bond to the leaving group is involved in the rate determining step.

RESULTS AND DISCUSSION

In a previous study[1] it was found that iodobenzene reacted rapidly at room temperature with tetrakis(triphenylphosphine)palladium(0) in benzene solution to give iodo(phenyl)bis(triphenylphosphine)palladium(II) in high yield:



$$PhI + Pd(PPh_3)_4 \rightarrow \begin{matrix} Ph \\ Ph_3P \end{matrix}\!\!>\!Pd\!<\!\!\begin{matrix} PPh_3 \\ I \end{matrix}$$

More recently, we have investigated this reaction using bromobenzene and chlorobenzene instead of iodobenzene. No reaction could be observed with bromobenzene at room temperature, but at 80° the reaction proceeded smoothly to give the desired bromo(phenyl)bis(triphenylphosphine)palladium(II) in good yield. In benzene solvent, the reaction with chlorobenzene did not proceed even at 135°, and the use of still higher temperatures to force this reaction was ruled out for even at 135° the thermal decomposition of tetrakis(triphenylphosphine)palladium(0) had become a serious problem[*].

Thus it was established that the relative reactivities of halobenzenes with

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[*] In contrast it has recently been reported[2] that $Pd(PPh_3)_4$ reacts readily in refluxing chlorobenzene to give chloro(phenyl)bis(triphenylphosphine)palladium(II). Apparently in the absence of solvent the rate of oxidative addition at this temperature is greater than the rate of thermal decomposition of the $Pd(PPh_3)_4$.

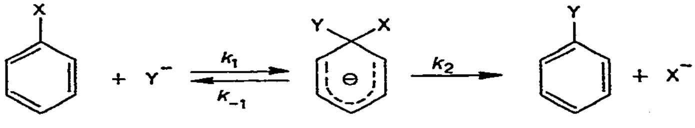
$Pd(PPh_3)_4$ were in the order iodobenzene > bromobenzene > chlorobenzene, a sequence that strongly suggests that carbon–halogen bond breaking has occurred to an appreciable extent in the rate-determining transition state of the reaction.

The reaction was next studied with a variety of substituted halobenzenes in order to determine what effects these substituents might have on the reactivity of the halobenzenes in this reaction. Chlorobenzenes substituted with electron-donating groups were found to be inactive. Thus *p*-chloroanisole gave no product with $Pd(PPh_3)_4$ even after heating at 135° for 16 h. On the other hand, chlorobenzenes substituted with electron withdrawing groups were found to be considerably more reactive than chlorobenzene itself. No attempt was made to measure the rates of reaction of these substituted chlorobenzenes with $Pd(PPh_3)_4$, but determination of the minimum temperature at which they formed appreciable amounts of adducts gave some indication of their relative reactivities. While chlorobenzene was unreactive at 135°, *p*-chlorobenzophenone gave an 89% yield of adduct at 135°, *p*-chlorobenzonitrile gave a 97% yield of adduct at 100°, and *p*-nitrochlorobenzene gave an 86% yield of adduct at 80°. Thus it is seen that the reactivities of these substituted chlorobenzenes roughly parallel the electron-withdrawing power of the substituents.

Since electron-withdrawing substituents increased the reactivity of chlorobenzenes so dramatically, their effect on the reactivity of fluorobenzenes was also examined. However, neither hexafluorobenzene nor *p*-nitrofluorobenzene could be added to $Pd(PPh_3)_4$ even at 135°.

In each of the addition reactions only one isomer of the palladium product was isolated and the values of ν(Pd–Cl) suggests that this was the *trans*-form[3]. The isolation of the *trans*-forms from reaction mixtures containing triphenylphosphine, conditions under which the isomerization of the less stable *cis*-form would be extremely facile, would be expected, however, and is, therefore, no indication of the stereochemistry of the oxidative addition reaction.

It is interesting to compare our observations on the oxidative addition reaction with the results generally obtained in second order, aromatic nucleophilic substitution reactions*. In many aromatic nucleophilic substitutions (*e.g.* replacement of halide by ethoxide) the ease of halide displacement is observed to be $F \gg Cl \sim Br \sim I$. In these instances it has been concluded that formation of the intermediate complex (A) is rate determining (*i.e.* $k_2 \gg k_{-1}$) and that the C–X bond is not broken in the rate-determining step. In contrast, in reactions of 2,4-dinitrohalobenzenes with potassium iodide in acetone[5] and with *N*-methylamine in ethanol or in nitrobenzene[6], the ease of halide displacement is observed to be $Br > Cl > F$. In these instances it has been argued that breaking of the C–Y bond in the intermediate (A) is much faster than breaking of the C–X bond (*i.e.* $k_{-1} \gg k_2$). Under these conditions the rate of the overall reaction is dependent on the equilibrium concentration of the intermediate (A) and on k_2.



(A)

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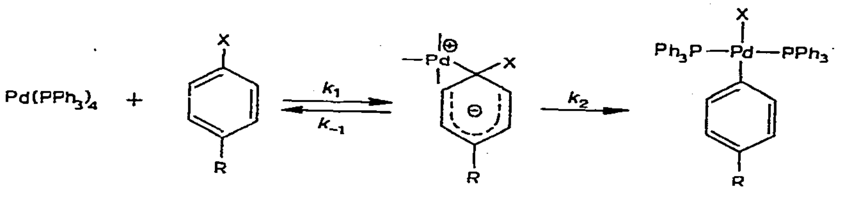
* For a review of this reaction see ref. 4.

The order of reactivity of the aryl halides towards addition to $Pd(PPh_3)_4$ suggests that this may be another example of aromatic nucleophilic substitution in which breaking of the bond to the leaving group is rate determining. In this scheme,



(B)

assuming that C–X bond breaking is important in the rate-determining step, one would predict that k_2 (and hence the overall rate coefficient, $k_2 \cdot k_1/k_{-1}$) would increase as one went from C–Cl to C–Br to C–I. We observe that chlorobenzene is less reactive than bromobenzene which in turn is less reactive than iodobenzene. One would also predict that as the electron-withdrawing ability of R increased, the equilibrium constant k_1/k_{-1} and thus the overall rate coefficient should increase. In agreement with this we observe the following order of reactivity: *p*-nitrochlorobenzene > *p*-chlorobenzonitrile

TABLE 1

$ArX + Pd(PPh_3)_4 \rightarrow ArPdX(PPh_3)_2$

No.	Ar	X	M.p. (dec.) (°C)	Isolated yield (%)[a]	Reaction temp. (°C)	ν(Pd–Cl) (cm^{-1})
(I)	$2\text{-}NO_2C_6H_4$	Cl	215–217	94	80	291, 305
(II)	$3\text{-}NO_2C_6H_4$	Cl	208–210	0	100	304
				86	135	
(III)	$4\text{-}NO_2C_6H_4$	Cl	193–196	86	80	291
(IV)	$2\text{-}CNC_6H_4$	Cl	180–183	15	100	301, 305
				85	135	
(V)	$4\text{-}CNC_6H_4$	Cl	224–226	0	80	285, 290
				97	100	
(VI)	$4\text{-}PhCOC_6H_4$	Cl	195–198	0	100	284
				89	135	
(VII)	$4\text{-}CH_3O_2CC_6H_4$	Cl	172–178	7	100	292
				83	135	
(VIII)	$4\text{-}CF_3C_6H_4$	Cl	208–210	89	135	
(IX)	$4\text{-}ClC_6H_4$	Cl	215–220	0	100	290, 294
				92	135	
(X)	$2,4\text{-}(NO_2)_2C_6H_3$	Cl	172–175	90	80	307, 309
(XI)	$3\text{-}CH_3O\text{-}4\text{-}NO_2C_6H_3$	Cl	172–175	94	135	
(XII)	C_6H_5	Br	216–220	95	80	
(XIII)	$4\text{-}CH_3COC_6H_4$	Br	180–183	93	135[b]	
(XIV)	$4\text{-}ClC_6H_4$	Br	195–196	78	135[b]	
(XV)	$4\text{-}NO_2C_6H_4$	I	192–196	90	RT	
(XVI)	C_6H_5	F		0	135	
(XVII)	$4\text{-}NO_2C_6H_4$	F		0	135	
(XVIII)	C_6H_5	Cl		0	135	
(XIX)	$4\text{-}CH_3OC_6H_4$	Cl		0	135	

[a] Based on $Pd(PPh_3)_4$. [b] The minimum temperature at which these reactions would occur was not determined.

TABLE 2

ANALYTICAL DATA

No.	Ar	X	Analysis (%)					
			Found			Calculated		
			C	H	N	C	H	N
(I)	2-$NO_2C_6H_4$	Cl	62.71	4.10	1.82	63.96	4.34	1.77
(II)	3-$NO_2C_6H_4$	Cl	63.36	4.35	1.81	63.96	4.34	1.77
(III)	4-$NO_2C_6H_4$	Cl	64.11	4.34	1.98	63.96	4.34	1.77
(IV)	2-CNC_6H_4	Cl	66.88	4.33	1.90	67.18	4.46	1.83
(V)	4-CNC_6H_4	Cl	67.17	4.39	1.82	67.18	4.46	1.83
(VI)	4-$PhCOC_6H_4$	Cl	69.90	4.77		69.43	4.64	
(VII)	4-$CH_3O_2CC_6H_4$	Cl	65.83	4.55		65.91	4.65	
(VIII)	4-$CF_3C_6H_4$	Cl	64.22	4.36		63.62	4.22	
(IX)	4-ClC_6H_4	Cl	65.90	4.64		64.81	4.40	
(X)	2,4-$(NO_2)_2C_6H_3$	Cl	60.57	4.33	3.34	60.30	4.34	3.35
(XI)	3-CH_3O-4-$NO_2C_6H_3$	Cl	62.99	4.59	1.66	63.07	4.43	1.71
(XII)	C_6H_5	Br	63.82	4.40		64.00	4.47	
(XIII)	4-$CH_3COC_6H_4$	Br	65.88	4.83		66.10	4.77	
(XIV)	4-ClC_6H_4	Br	61.43	4.06		61.40	4.17	
(XV)	4-$NO_2C_6H_4$	I	57.30	3.89	1.59	57.12	3.89	1.58

> *p*-chlorobenzophenone > chlorobenzene.

While the above mechanism would appear to adequately describe the oxidative addition reaction, it must be pointed out that we cannot exclude the possibility that the reaction occurs by an electron transfer process wherein electron(s) are transferred from the metal to the ring to give a radical anion, or possibly a dianion. Such a mechanism would also explain the observed order of reactivities, since the reduction potentials of the halobenzenes[7] are in the order $C_6H_5Cl > C_6H_5Br > C_6H_5I$. Electron-withdrawing substituents lower the antibonding orbitals of the ring and, therefore, make reduction more facile.

EXPERIMENTAL

Preparation of complexes from aryl chlorides and bromides

A mixture of tetrakis(triphenylphosphine)palladium(0) (2.2 g) and the aryl halide (1 g) in degassed benzene (15 ml) was heated overnight in a "capped" thick-wall polymer tube. (A list of the reaction temperatures is given in Table 1).

After cooling to room temperature, the benzene was removed *in vacuo* and the resulting solid was triturated with ether. These products were further purified by recrystallization from benzene, methylene chloride/hexane or chloroform/hexane. The analysis for these complexes are shown in Table 2.

Iodo(4-nitrophenyl)bis(triphenylphosphine)palladium(II)

A solution of *p*-nitroiodobenzene (1.1 g) in benzene (5 ml) was added to a suspension of $Pd(PPh_3)_4$ (2.2 g) in benzene (50 ml). The solution was stirred at room temperature for 1 h and worked up in the usual manner.

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