Journal of Organometallic Chemistry, 267 (1984) 213–219
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

OXIDATIVE ADDITION REACTIONS OF ARYL HALIDES ON $[NiBr(PPh_3)_3]$

M. ANTON, N. CLOS and G. MULLER

Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona (Spain)

(Received December 14th, 1983)

Summary

The oxidative addition of aryl halides RX, (R = 2,3-, 2,6-, or 3,5-$C_6H_3Cl_2$, Ph, 2-MeC_6H_4; X = I, Br) to $[NiBr(PPh_3)_3]$ has been studied. The reaction of the iododichlorobenzenes give the organometallics $[NiXR(PPh_3)_2]$. The reactivity of the aryl halides decreases from RI to RBr; with RCl no reaction is observed. An aromatic nucleophilic substitution process may be involved in the reaction between nickel and the polychloroaryl halide.

The presence of RH may be due to a mechanism involving the formation of RX^- species. The greater lability of PPh_3 with respect to PMe_2Ph or PEt_3 may explain the fact that no RH is observed in the reaction of halopolychlorobenzenes with complexes of nickel(0) or nickel(I) containing PPh_3.

Introduction

The reactions of aryl halides with nickel(0) complexes have received much attention, both from the point of view of the mechanism [1,2], and with respect to the organometallic synthesis [3–5]. The standard reaction of the organic halide with nickel(0) complexes gives the organometal $[NiXRL_2]$ but often also nickel(I) species [2,6]. The proposed mechanism involves displacement of the halide by a metallic nucleophile (eq. 1) [5,7] and a non-chain free radical mechanism (eq. 2) [2,8] that may be initiated by electron transfer to the aryl halide

$$ML_n + RX \rightarrow [L_nMR]^+X^- \rightarrow [MXRL_n] \qquad (1)$$

$$ML_n + RX \rightarrow [L_nM]^+[RX\cdot]^- \rightarrow [MXRL_n] \qquad (2)$$

The mechanism clearly depends on the metal substrate, the organic halide and the reaction conditions, but the role of the intermediate oxidation state of nickel in the reaction is not clear, nor is there much information on the behaviour of organic halides towards the compounds $[NiXL_3]$. Morvillo and Turco [9] have observed that in the addition of methyl and ethyl halides to $[NiX(PEt_3)_3]$ complexes, the reaction is 10–20 slower than that to nickel(0) complexes but the product distribution is

0022-328X/84/$03.00 © 1984 Elsevier Sequoia S.A.

analogous. Tsou and Kochi [2] indicate that the reaction of the aryl halides with $[NiX(PEt_3)_3]$ gives $[NiX_2(PEt_3)_2]$ and the R• radical which by abstraction of the hydrogen of the solvent produces RH. We have previously studied the oxidative addition of halopolychlorobenzenes on $[Ni(PPh_3)_n]$ [5], which can be interpreted in terms of a nucleophilic displacement on the aryl halide. Following this line, we now report a study of the reaction of the same aryl halides with the complexes $[NiX(PPh_3)_3]$. The organometallic complexes $[NiXR(PPh_3)_2]$ are obtained, with only minor amounts of RH or R–R. The reaction is considerably slower than the oxidative addition to nickel(0) complexes, but the bonding of the aryl radical to the metal may be the same in the both cases.

Experimental

General

The solvents used were purified by standard methods and distilled before use. All reactions were carried out under carefully deoxygenated nitrogen. The polychlorohalobenzenes were purchased and used as received, or prepared by diazotization of the appropriate polychloroanilines, and were monitored by GLC. The GLC analyses were performed on a Hewlett-Packard 5710A instrument using a 2 m 5% SE-30 on Chromosorb Q column coupled to a Hewlett-Packard 3390 integrator.

Preparation of $[NiBr(PPh_3)_3]$

$[NiCl_2(PPh_3)_2]$ (0.64 g, 1 mmol) and PPh_3 (0.52 g, 2 mmol) were suspended in THF (10 ml) at room temperature and the mixture was treated with 8 ml of a solution of ethylmagnesium bromide prepared from 1 ml of ethyl bromide and 0.5 g of Mg in 20 ml of THF. The solution, which turned red, was stirred for 15 min and treated with 5 ml of absolute ethanol to destroy any excess of ethylmagnesium bromide. To this solution, $[NiCl_2(PPh_3)_2]$ (0.64 g, 1 mmol) and 15 ml of absolute ethanol were added, and the mixture stirred for 1 h. The yellow precipitate which formed was filtered off under a N_2 atmosphere, dried in vacuo, and stored under N_2. Yield about 70%. Anal. Found (calcd.) C 68.0 (70.08); H 4.9 (4.90)%.

General oxidative addition reaction (example)

$C_6H_3Cl_2I$ (0.205 g, 0.75 mmol) dissolved in 15 ml of a 1 : 1 deoxygenated benzene-alkanes mixture was heated in an inert atmosphere to reflux. Then $[NiBr(PPh_3)_3]$ (0.235 g, 0.25 mmol) was added and the reflux maintained for 1 h. After cooling to room temperature, the mixture was washed with 1 *M* HCl (10 ml) and three times with water. The remaining solution was dried, concentrated by evaporation to 3–5 ml and then diluted with 10 ml of methanol. The yellow precipitate of $[NiBr(C_6H_3Cl_2)(PPh_3)_2]$ was collected (yield in Table 1). The solution and the evaporated solvent were tested by GLC for the aryl derivatives remaining in the solution.

Oxidative addition reaction on $[NiX(PMe_2Ph)_3]$

A solution (8 ml) of ethylmagnesium bromide (prepared from 1 ml of ethyl bromide and 0.5 g of Mg in 20 ml of THF) was added to a mixture of $[NiCl_2(PMe_2Ph)_2]$ (0.405 g, 1 mmol) and PMe_2Ph (0.280 g, 2 mmol) in 10 ml of THF. The solution turned yellow, and after 10 min, first 20 ml of absolute ethanol and then [$NiCl_2(PMe_2Ph)_2$] (0.405 g, 1 mmol) were added. The yellow-green solution was treated with 2,3-$C_6H_3Cl_2I$ (0.6 g, 1 mmol) whereupon, in a period of 30 min, the solution turned dark green. Then it was concentrated under reduced pressure to half of the original volume and left at −20°C overnight. A dark green residue was filtered off, the solution was concentrated under reduced pressure, and 15 ml of CH_2Cl_2 were added. The solution was washed with 1 *M* HCl and with water, concentrated almost to dryness and treated with methanol. A yellow precipitate was collected in very low yield after 2 h at −30°C (see Table 2).

Results and discussion

The yellow compound [$NiBr(PPh_3)_3$] has been prepared by reaction of the equivalent amounts of solutions of [$Ni(PPh_3)_4$] and [$NiCl_2(PPh_3)_2$] with a great excess of bromide ion. This compounds can also be prepared by reduction of [$NiX_2(PPh_3)_2$] with $NaBH_4$ [10]. [$NiBr(PPh_3)_3$] is extremely sensitive to oxygen, especially in solution, and must be used inmediately after its preparation, otherwise, as observed experimentally, the nickel(I) content of the starting material gradually decreases.

The oxidative addition reactions of aryl halides on [$NiBr(PPh_3)_3$] have been carried out in mixtures of benzene and alkanes in order to reach a compromise between the required solubility for a fast reaction and the greatest possible stabilization. The presence of free phosphine increases the stability of the nickel(I) solutions but its effect on the rate of the addition reaction has not been examined. The product distribution was monitored by gas chromatography. The solvents were separated by vacuum distillation, recovered in cold traps and tested by GLC. Sometimes the product distribution control was supplemented with DMG gravimetries to confirm the amount of Ni remaining as free nickel(II) in the different washing solutions.

The results obtained in the reaction between [$NiBr(PPh_3)_3$] and iodopolychloro-

TABLE 1

REACTION OF RX WITH [$NiBr(PPh_3)_3$] IN BENZENE/HEXANE SOLUTION [a]

RX	[RX]/[Ni^I]	[$NiBrR(PPh_3)_2$] [b] (%)	Observations
2,3-$C_6H_3Cl_2I$	1	20	
	2	40	
	2	47	With free PPh_3 : (PPh_3/Ni^I) = 1/1)
	3	46 [c]	
	3	20	5% Duroquinone with respect to RX [d]
	3	8	10% Duroquinone with respect to RX [d]
2,3-$C_6H_3Cl_2Br$	3	12 [c]	1% R–R [e]
1,2,3-$C_6H_3Cl_3$	3	–	
2,6-$C_6H_3Cl_2I$	3	34 [c]	
	3	32	Reaction in the dark
	3	–	Reaction at room temperature
3,5-$C_6H_3Cl_2I$	3	5 [c]	5% R–R and 1% R–H [e]

[a] At 60°C unless otherwise stated. [b] Yield based on starting Ni^I. [c] Mean value of four or more reactions. [d] Less than 1% in R–R and RH based on starting RX. [e] Weight% based on starting RX observed in the solution after separation of [$NiXRL_2$].

benzenes are given in Table 1. This reaction gives organometallic derivatives of nickel(II) (analogously to the addition reaction of the nickel(0) species) with almost total conversion.

$$[NiBr(PPh_3)_3] + C_6H_3Cl_2I \rightarrow [NiX(C_6H_3Cl_2)(PPh_3)_2] + [NiX_2(PPh_3)_2]$$

The formation of the organometallic complexes $[NiX(C_6H_3Cl_2)(PPh_3)_2]$, previously reported [5], was monitored by IR spectroscopy. For most of them X = Br but in some cases X = I and, if the washing with HCl is repeated several times or if the concentration of this acid is high, the compound with X = Cl can be detected. The only stable compound of the type $[NiX_2(PPh_3)_2]$ under the reaction conditions used is $[NiI_2(PPh_3)_2]$, which is the cause of the brown colour observed during and after the end of the reaction. The addition of HCl decomposes the compound giving nickel(II) salts. The visible spectra of the solutions before being washed show (among others) a maximum at 465 nm, confirming $[NiI_2(PPh_3)_2]$.

As a whole, the products of the reaction correspond to an oxidative addition with an overall one-electron change at each nickel atom. The presence of increasing amounts of duroquinone, which can act as a free radical inhibitor, leads to a gradual decrease in the yield of the organometallic. On the other hand, $[NiBr(PPh_3)_3]$ decomposes readily in the presence of duroquinone.

The resulting solutions do not contain significant amounts of R–H similarly to that observed in the oxidative addition reactions of $[Ni(PPh_3)_4]$ [5]. R–H does not form by decomposition of the $[NiXR(PPh_3)_2]$ solution since the compounds with *ortho*-substituents are stable in the reaction conditions, and in any case they would give R–R [5]. For 3,5-$C_6H_3Cl_2I$, an overall yield of about 20% is obtained. Only in this last case is some R–H detected.

The study of the addition reactions of halopolychlorobenzenes on $[Ni(PPh_3)_4]$ and $[NiBr(PPh_3)_3]$ shows the greater ease of oxidation of nickel(0) with respect to nickel(I). The reactions involving nickel(0) were carried out at room temperature but those with nickel(I) were carried out under heating.

The reaction of 1,2,3-$C_6H_3Cl_3$ with nickel(0) is fast and leads to $[NiXR(PPh_3)_2]$ with good yield, but no reaction takes place with nickel(I). This difference indicates that these addition reactions on nickel(I) do not take place with the previous disproportionation step:

$$[NiBr(PPh_3)_3] \leftrightarrows [Ni(PPh_3)_4] + [NiBr_2(PPh_3)_2]$$

It may also be pointed out that the formation of nickel(I) species in the oxidative additions at room temperature in the reaction with $[Ni(PPh_3)_4]$ would be detected since in this conditions no further addition take place.

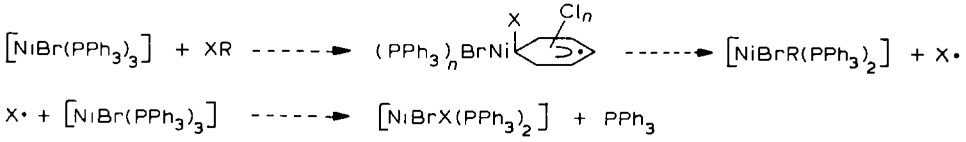
The ease of oxidation increases markedly as the nature of the aryl halide changes in the order $RCl < RBr < RI$. This is also the order of decrease of the C–X bond energy. Furthermore, one-electron reductions of the aryl halides are favoured for the iodo derivatives, as indicated by the values of the half-wave potentials ($E_{1/2}$) obtained by polarography [2,4].

As a rule, the ease of aromatic nucleophilic substitution in the RX compounds increases in the order $F > Cl > Br > I$. This order is not related to the C–X bond energy and the rate determining step of the process is considered to occur previous to the breaking of the bond. The oxidative addition reaction of aryl halides activated by electron-withdrawing substituents, on $[Ni(PPh_3)_4]$ [5] or $[NiBr(PPh_3)_3]$ may be considered as an aromatic nucleophilic substitution, but the main step must be related to the electron transfer from nickel to the aryl halide as well as to the dissociation of the C–X bond.

The small differences between the amounts transformed of 2,3-$C_6H_3Cl_2I$ and 2,6-$C_6H_3Cl_2I$ may be related to the greater steric difficulty for the approach of a group with *ortho* chlorine atoms. The slightly lower conversion of 3,5-$C_6H_3Cl_2I$ could be due to a lower ability of the group, which does not posses *ortho*-chlorine atoms, to stabilize an intermediate with negative charge on the ring. In any case the sterical effects for this reaction are not important.

The occurrence of RX^- cannot be accepted given the non-existence of RH in the resulting solutions. Furthermore, the lower mean life of those species is that of the iodo-derivative [2] and therefore the aryl iodide should give the highest proportion of RH. Another factor which may favour the immediate formation of the Ni–R bond, even when it is not possible to propose in which step it occurs, is the greater ease of displacement of PPh_3 with respect to other less bulky phosphines.

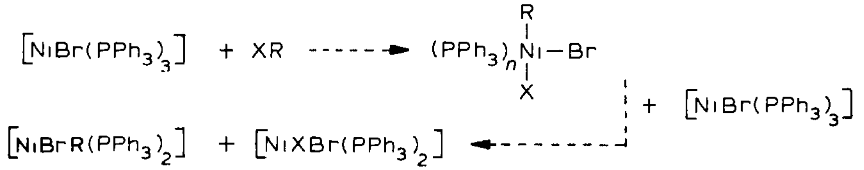
Thus, the oxidative addition reaction of polychloroaryl halides on $[NiBr(PPh_3)_3]$ may be interpreted as a nucleophilic attack of nickel(I) on the aryl halide:



$$[NiBr(PPh_3)_3] + XR \dashrightarrow [NiBrR(PPh_3)_2] + X\cdot$$

$$X\cdot + [NiBr(PPh_3)_3] \dashrightarrow [NiBrX(PPh_3)_2] + PPh_3$$

However, it is also compatible with a two electron addition reaction:



$$[NiBr(PPh_3)_3] + XR \dashrightarrow (PPh_3)_n Ni(R)(X)-Br$$

$$(PPh_3)_n Ni(R)(X)-Br + [NiBr(PPh_3)_3] \dashrightarrow [NiBrR(PPh_3)_2] + [NiXBr(PPh_3)_2]$$

To distinguish between the two possible pathways is difficult since it has not been possible to show the existence of radicals X•; besides, in the reaction with an excess of RX the argument reduces to considering the possibility of formation of nickel(III) species. Compounds of this class, $[NiBr_2R(P)_2]$, have been reported for $P = PMe_2Ph$ and when R is a highly electronegative group, such as $-CCl{=}CCl_2$ or $-C_6Cl_5$ [11]. Red products may also be obtained on treating $[NiXR(PPh_3)_2]$ with *N*-bromosuccinimide when $R = C_2Cl_3$ or 2,6-$C_6H_3Cl_2$ [12]. These products decompose rapidly giving the starting organometallic compound.

The nickel(I)–nickel(III) mechanism has been proposed in some other cases [13]. The formation of organometallic compounds such as the bromo-derivative cannot be considered as conclusive evidence for the nucleophilic substitution. The similarity with the addition reactions of $[Ni(PPh_3)_n]$ and $[NiBr(PPh_3)_3]$ suggests that the process may probably occurs via nucleophilic substitution.

Several oxidative addition reactions with halobenzenes and *o*-tolyl halides were examined in order to assess the effect of the decrease of electronegativity of R (Table 2). The reaction with nickel(I) shows the same behaviour and only the iodo-derivative reacts in significant amounts. When R = Ph the organometallic compound

TABLE 2

REACTION OF RX WITH [$NiBrL_3$] IN BENZENE-HEXANE SOLUTION [a]

RX	[RX]/[Ni^I]	L	[$NiXRL_2$] [b] (%)	Observations
o-C_6H_4MeI	3	PPh_3	12	5% o-PhMeBr [c,d]
o-C_6H_4MeBr	3	PPh_3	–	0.8% R–R [c], a nickel mirror is formed
PhI	3	PPh_3		17% R–R [c e]
PhBr	3	PPh_3		5% R–R [c e]
2,3-$C_6H_3Cl_2I$	1	PMe_2Ph	5	7% R–R and 3% RH [c]

[a] At 60°C. [b] Yield based on starting Ni^I. [c] Weight% based on starting RX observed in the solution after separation of [$NiXRL_2$]. [d] Less than 0.5% of R–R. [e] The amount of Ph–Ph in the reaction mixture changes with the time, even at room temperature; therefore other processes must be involved [16].

decomposes and only biphenyl is observed. The oxidative addition proceeds to a much smaller extent with a decrease in electronegativity of R. When the reaction is carried out with *o*-iodotoluene, *o*-bromotoluene is formed. The halogen exchange between aryl halide and halide ion catalyzed by nickel(I) species has been studied previously by Tsou and Kochi [14].

The reaction of 2,3-$C_6H_3Cl_2I$ with a solution of equimolar amounts of [$Ni(PMe_2Ph)_n$] and [$NiCl_2(PMe_2Ph)_2$] was also examined. The results indicate the formation of an organometallic complex (difficult to isolate in the solid state by precipitation due to its solubility) which decomposes thermally giving R–R. Some R–H is also formed. The yield in the formation of the organometallic [$NiBr(2,3$-$C_6H_3Cl_2)(PMe_2Ph)_2$], including the amount decomposed and detected as R–R, is about 15%, which is less than that observed with PPh_3 under the same conditions.

The reducing capacity of [$NiBrL_3$] is likely to be higher when L = PMe_2Ph than when L = PPh_3, in accord with the order observed in the cyclic voltammetries of [NiL_4] (L = PPh_3, PEt_3) [15]. Therefore the lower extent of the reaction could be related to differences in the phosphine lability, which must affect in some way the formation of the intermediate or, its further evolution, since the nickel atom looses a phosphine ligand during the process of formation of the organometallic. The appearance of R–H indicates the possible existence of free $[RX\bullet]^-$, in accord with the greater difficulty of the aryl halide to coordinate to the central atom on changing the nature of the phosphine ligand.

Acknowledgements

We thank the Comisión Asesora Científica y Técnica for financial support.

References

1 M. Foa and L. Cassar, J. Chem. Soc., Dalton Trans., (1975) 2572.
2 T.T. Tsou and J.K. Kochi, J. Am. Chem. Soc., 101 (1979) 6319.
3 D.R. Fahey and J E. Mahan, J. Am. Chem. Soc., 99 (1977) 2501.
4 E. Uhlig and W. Poppitz, Z. Anorg. Allg. Chem., 477 (1981) 167.
5 M. Antón, G. Muller and J. Sales, Transition Met. Chem., 8 (1983) 79.
6 P. Stoppioni, A. Biliotti and R. Morassi, J. Organomet. Chem., 236 (1982) 119.
7 D.R. Fahey, J. Am. Chem. Soc , 92 (1970) 402.
8 J.A. Connor and P.I. Riley, J. Chem. Soc., Chem. Commun., (1976) 634.

9 A. Morvillo and A. Turco, J. Organomet. Chem., 224 (1982) 387.
10 F. Caballero, M. Gómez and P. Royo, Transition Met. Chem., 2 (1977) 130.
11 K. Ogura, M. Wada and N. Sonoda, J. Organomet. Chem., 165 (1979) C10.
12 M. Antón, unpublished results.
13 T.T. Tsou and J.K. Kochi, J. Am. Chem. Soc., 101 (1979) 7547.
14 T.T. Tsou and J.K. Kochi, J. Org. Chem., 45 (1980) 1930.
15 J.K. Kochi, Pure Appl. Chem. 52 (1980) 593.
16 A. Nakamura and S. Otsuka, Tetrahedron Lett., (1974) 463.