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Nickel-catalysed electrochemical coupling between mono- or di-chlorophenylphosphines and aryl or heteroaryl halides

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Abstract

Nickel-catalysed electrochemical cross-coupling between aryl- or heteroaryl-halides and chlorodiphenylphosphine or dichlorophenylphosphine affords tertiary phosphines in good to high yields. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Aryl and heteroaryl tertiary phosphines are useful ligands in homogeneous catalysis. The presence of phenyl groups substituted with various functionalities is of great interest to modify the electronic properties of the ligand and then modulate the reactivity of the metallic centre associated with it, or to give access to precursors of hydrosoluble complexes, or to prepare ligands which can be immobilised easily. Also mixed aryl-heteroaryl phosphines combining the complexing properties of the phosphorus atom and of the heteroatom, specially nitrogen, can display useful new properties [1].

The chemical methods involving the reaction between halophosphines and organometallic reagents are not convenient to prepare arylphosphines bearing electron-withdrawing groups. Phosphides (Ph_2PM, with M = Li, Na or K) undergo direct substitution with 2- or 4-halopyridines and also with aryl halides or sulfonates which are not reactive with strong nucleophiles. Palladium catalyses the reaction between trimethylstannyl-diphenylphosphine or trimethylsilyl-diphenylphosphine and various aromatic halides [2]. Nickel has been used also to catalyse the formation of BINAP from Ph_2PH and 1,1′-binaphtyltriflate [3]. Recently, the direct coupling between Ph_2PCl and various *ortho*-substituted aryl triflates or aryl halides has been reported to occur in good yields in the presence of nickel as catalyst and zinc as reductant, in DMF at 100–110°C [4].

We have described previously an electrochemical method of synthesis of alkyl- or benzyl-diphenylphosphines by reduction of a mixture of the alkylhalide and Ph_2PCl in DMF or NMP in the presence of a sacrificial magnesium anode [5]. This electrochemical coupling is not convenient however for the arylation of chlorophosphines because the electrogenerated phosphide does not react with aryl halides. In the course of our research on cross-coupling reactions between aryl

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or heteroaryl halides and various halo compounds [6–8] catalysed by electrogenerated Ni(0) complexes we have investigated also the reactions involving Ph_2PCl and $PhPCl_2$ reported here (Eq. (1)).

$$n\,ArX + P(C_6H_5)_{3-n}Cl_n \xrightarrow[\text{sacrificial anode}]{\text{e, Ni-cat}} Ar_nP(C_6H_5)_{3-n} \qquad (1)$$

2. Results and discussion

We have reported previously on the efficient electroreductive coupling of arylhalides [6] or of halothiophenes [7] with α-halo-esters or -ketones in the presence of Ni-2,2′-bypiridine (bpy) as a catalyst and a sacrificial anode. We have used the same procedure for the electrochemical synthesis of tertiary phosphines. The reactions were carried out in an undivided electrolysis cell flushed with argon and fitted with a magnesium rod as the anode and a nickel foam as the cathode, at room temperature under a constant current intensity of 0.2–0.5 A. The aryl or heteroaryl halide (one equivalent) and $NiBr_2bpy$ (0.1 equivalent) were added to a solution of DMF containing NBu_4BF_4 as the supporting electrolyte. Ph_2PCl or $PhPCl_2$ was added portionwise, i.e. 0.1 equivalents of Ph_2PCl, or 0.05 equivalents of $PPhCl_2$, for every 0.2 Faraday passed per mole of ArX, until the concentration of the tertiary phosphine, as determined by GC analysis, was constant, which amounted to 0.5–0.75 equivalents of Ph_2PCl and 0.2–0.3 equivalents of $PhPCl_2$. When the reaction was conducted with a stoichiometric mixture of the aryl halide and Ph_2PCl, no cross-coupling occurred; Ph_2PCl was converted into Ph_2PH and Ph_2PPPh_2 due to the faster reaction of the chlorophosphine with Ni(0) as compared with most aryl halides.

Results are reported in Table 1. In most cases moderate to good yields of tertiary phosphines were obtained and this simple method is notably very convenient to prepare various tertiary phosphines containing heteroaryl groups (Table 1, entries 9, 10, 11, 12, 14, 15), or aryl groups bearing electronwithdrawing substituents (Table 1, entries 6, 7, 8). For these last compounds the use of a zinc sacrificial anode gave better results than a magnesium one. The presence of zinc ions generated by the oxidation of the anode buffers the potential of the solution at a value higher than for the reduction of the arylhalide. The main side products are a reduction of the aryl halide and the chlorophosphine.

In our previous studies on the coupling reactions between aryl halides and activated halides [6,7] or 2-halo-pyridine [8] we have shown that the coupling occurs via a σ-arylnickel(I) complex formed by electroreduction of σ-arylnickel(II) obtained first by oxidative addition of the aryl halide to the electrogenerated zerovalent nickel. For the electrosynthesis of the tertiary phosphines the cathode potential was between −1.1 and −1.5 V/SCE; this indicates that the coupling may not require the reduction of σ-arylnickel(II) into σ-arylnickel(I). Indeed, we have shown that a σ-arylnickel(II)–bpy complex reacts rapidly with Ph_2PCl in the following experiment: a stable σ-arylnickel(II) complex can be obtained by electroreduction of $NiBr_2bpy$ in DMF in the presence of *ortho*-substituted phenyl bromides like *o*-bromotoluene; on the addition of Ph_2PCl (one equivalent) the red colour typical for σ-arylnickel(II)bpy quite rapidly turned into the green of NiX_2bpy, and the tertiary phosphine was obtained. We cannot, however, exclude the occurrence, at the high current intensity (0.2–0.5 A) used in this process, of the formation of arylNi(I)bpy and its reaction with the chlorophosphine. These two routes are shown on Scheme 1.

In the same reaction conditions, the use of PCl_3 in place of Ph_2PCl or $PhPCl_2$ and PhBr or PhI led to the formation of PPh_3 but in quite a low yield and only at the beginning of the electrolysis. We first thought of a possible side reaction of PCl_3 with DMF and we thus used acetonitrile as the solvent, but we obtained the same results. PCl_3 is probably two reactive towards the electrogenerated zerovalent nickel and the species derived do not react with the aromatic halides.

This methodology offers a simple and efficient approach to the preparation of various tertiary phosphines. It can be a useful alternative to the chemical procedure reported in Ref. [4] as it does not rely on the reactivity of zinc powder, and can be controlled more easily in large scale experiments than procedures using reactive metals.

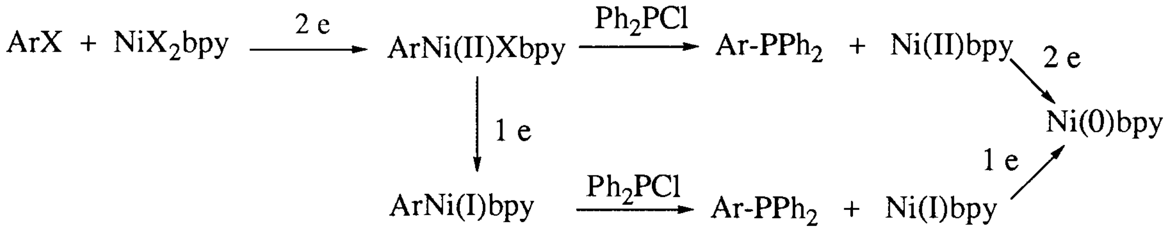
3. Experimental

The single-compartment cell was fitted with a rod of magnesium or zinc as the anode, surrounded by a cylindrical nickel grid as the cathode. To the solution of Bu_4NBF_4 (0.5 mmol), $NiBr_2bpy$ (1 mmol), the aryl or heteroarylhalide (15 mmol) in DMF (40 ml) was added dropwise the appropriate phosphine at a rate of 1 mol of Ph_2PCl per 2 F of electricity or 1 mol of $PhPCl_2$ per 4 F of electricity while a current of 0.5 A was applied until ArX was consumed. The solution was then hydrolysed using 0.1 N NH_4Cl and extracted with Et_2O. The organic layers were washed with H_2O, dried, and the solvent was evaporated. The products were purified by column chromatography on silica gel with pentane/Et_2O mixtures as the eluents. Most tertiary phosphines are known, and they were characterised on the basis of

Table 1
Nickel-catalyzed electrochemical coupling of aryl or heteroaryl halides and chlorophosphines

Entry	Ph_nPCl_{3-n}	ArX	Product	Yield %[a]
1	Ph_2PCl	PhBr	**1**	87
2		$2\text{-}BrC_6H_4CH_3$	**2**	54
3		$4\text{-}BrC_6H_4CH_3$	**3**	56
4		$4\text{-}CH_3O\text{–}C_4H_5Br$	**4**	52
5		$4\text{-}Me_2N\text{–}C_6H_4Br$	**5**	70
6		$4\text{-}CO_2Et\text{–}C_6H_4Br$	**6**	63[b]
7		$3\text{-}CO_2Et\text{–}C_6H_4Br$	**7**	66[b]
8		$2\text{-}Cl\text{–}C_5H_4N$	**8**	80
9		$3\text{-}Cl\text{–}C_5H_4N$	**9**	63
10		$2\text{-}Cl\text{–}C_4H_3S$	**10**	65
11		$2\text{-}Cl\text{-}6\text{-}CH_3O\text{–}C_5H_3N$	**11**	66
12		$2\text{-}Cl\text{–}C_4H_3N_2$	**12**	50
13		$3\text{-}CN\text{–}C_6H_4Br$	**13**	45[b]
14			**14**	25
15	$PhPCl_2$	PhBr	**1**	72
16		$2\text{-}Cl\text{–}C_5H_4N$	**15**	68

[a] Experimental conditions: see text; isolate yields % vs chlorophosphine.
[b] Anode of Zn.



Scheme 1.

spectroscopic data and melting point by comparison to literature data. Compounds **6**, **7**, and **12** are new. Product analysis: ^{1}H- and ^{13}C-NMR (ref. TMS), and ^{31}P-NMR (ref. 85% H_3PO_4) were recorded on an AC 200 Bruker spectrometer; GC-MS spectra were recorded on a Finnigan ITD 800 spectrometer.

3.1. (4-Ethoxycarbonylphenyl)diphenylphosphine **6**

Mass., *m/z* (rel. intensity): 334 (M^+, 100); 306 (9); 183 (22); 152 (6); 107 (8); 77 (5); ^{13}C NMR (50 MHz, $CDCl_3$): 166.17; 143.70 (d, $J = 14.9$ Hz, C–P); 136.05 (d, $J = 10.7$ Hz); 133.97; 133.57; 133.17; 132.77; 131.77; 130.22; 129.17; 129.03; 128.95; 128.58; 128.43; 60.84; 14.16; ^{1}H-NMR (200 MHz, $CDCl_3$): 7.19–7.34 (m, 10H); 7.43 (d, 2H), 7.77 (d, 2H), 4.25 (q, 2H, $J = 21.5$ Hz); 1.27 (t, 3H, $J = 14.3$ Hz); ^{31}P-NMR (81 MHz, $CDCl_3$): −6.7; m.p. 99–100°C. Anal. Calc. for $C_{21}H_{19}PO_2$: C, 75.45; H, 5.69; P, 9.28; Found: C, 75.34; H, 5.93; P, 9.28.

3.2. (3-Ethoxycarbonylphenyl)diphenylphosphine **7**

Mass., *m/z* (rel. intensity): 334 (M^+, 100); 306(14); 281 (11); 207(37); 183(84); 152(28); 107(18); 77(16); ^{13}C-NMR (50 MHz, $CDCl_3$): 161.21; 138.19; 137.80; 137.49; 136.56; 136.35; 135.03; 134.55; 133.65 (d, $J =$ 19.5 Hz); 130.70; 130.55; 129.74; 128.88; 128.61; 128.74; 128.40; 60.95; 14.16; ^{1}H-NMR ($CDCl_3$): 7.89–7.99 (m, 12H); 7.12–7.34 (m, 12H); 4.22 (q, 2H, $J = 20.5$ Hz); 1.23 (t, 3H, $J = 7.5$ Hz); ^{31}P-NMR (81 MHz,$CDCl_3$): −7.0; m.p. 100–101°C. Anal. Calc. for $C_{21}H_{19}PO_2$: C, 75.45; H, 5.69; P, 9.28; Found: C, 75.60; H, 5.80; P, 9.31.

3.3. 2-diphenylphosphinopyrimidine 12

Mass., *m/z* (rel. intensity): 264 (M^+, 100); 184(27), 107(28); ^{13}C-NMR (50 Mhz, $CDCl_3$): 156.49 (d, $J = 7$ Hz), 134.58 (d, $J = 20$ Hz), 129.24; 128.52; 128.37; 118.81; ^{1}H-NMR (200 Mhz, $CDCl_3$): 8.59 (d, 2H, $J =$ 4.87 Hz), 7.26–7.48 (m, 10H); 6.98–7.03 (m, 1H); ^{31}P-NMR (81 MHz, $CDCl_3$): −0.2; m.p. 118–119°C. Anal. Calc. for $C_{16}H_{13}N_2P$: C, 72.73; H, 4.92; P,11.74; N, 10.61; Found: C, 72.65; H, 4.98; P, 11.61;N, 10.21.

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