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Nickel Catalyzed Electrosynthesis of Triorganyl Phosphines from Organic Halides and Chlorophospines

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Nickel Catalyzed Electrosynthesis of Triorganyl Phosphines from Organic Halides and Chlorophosphines

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One of the important problem in preparative organic chemistry of organophosphorus compounds is the development of new synthetic approaches to compounds with P-C bonds under mild conditions. Particular attention has been given in this area to the synthesis of triorganyl phosphines much used primarily as ligands in metal complexes. Triorganylphosphines can be easily obtained by electroreduction of an organic halide in the presence of mono- or dichlorophenyl phosphine added gradually using a Ni-2,2'-bipyridine catalytic system in DMF in an undivided cell fitted with an magnesium or zinc sacrificial anode. The overall reaction is

$$RX + Ph_n PCl_{3-n} \xrightarrow{\text{NiBr}_2 \text{bipy(cat), e}} R_{3-n}Ph_nP, \quad n=1,2$$
 (1)

The first stage of the catalytic circle consists in a reduction of Ni(II) complex to activate Ni(0) form of the catalyst capable of reacting with aryl halide in oxidative addition process (eq. 3):

$$Nibipy^{2+} + 2e \rightarrow Ni^0bipy$$
 (2)

$$Ni^0bipy + ArX \longrightarrow ArNiXBipy$$
 (3)

Thus, the product with P-C bond is formed by following substitution reaction:

$$ArNiBrbipy + Ph_nPCl_{3-n} \longrightarrow Ar_{3-n}Ph_nP + NiBrClbipy$$
 (4)

The method of triorganyl phosphine electrosynthesis proved to be efficient both for aromatic halides with acceptor and donor substituents in the ring and for heteroaromatic ones (pyridine, thiophene, pyrimidine and pyrazole halides).