Electrosynthesis of mixed tertiary phosphines catalysed by nickel complexes

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A versatile method for the synthesis of tertiary phosphines with aromatic and heteroaromatic substituents by cross-coupling of chlorophosphines and organic halides catalysed by Ni^0 complexes of 2,2′-bipyridine was proposed.

The development of new approaches to the synthesis of compounds with P–C bonds under mild conditions starting from white phosphorus and its derivatives is one of the most important subjects in organophosphorus chemistry. A particular attention has been given to the methods of preparation of tertiary phosphines including compounds with heteroatoms or functional groups in the molecule.[1–3] These phosphines are of particular interest as potential ligands in water-soluble complexes of transition metals. Currently available chemical methods for the synthesis are based on the use of organometallic compounds, *e.g.*, Grignard reagents or alkali metal phosphides.[1–3] These methods are multistage and have some significant restrictions (low temperature and a considerable volume of a solvent), and the yields of desired products are not always high. It has been possible to synthesise only triaryl phosphines containing acceptor substituents (CN, COOMe *etc.*) in the aromatic ring only by reduction of appropriate phosphine oxides.[3]

An electrochemical approach can be used to design a versatile technique for the preparation of various types of tertiary phosphines. A procedure for the electrosynthesis of trialkyl and tribenzyl phosphines using soluble anodes was previously proposed.[4] Unfortunately, this procedure is unsuitable for the synthesis of tertiary phosphines with aryl and, especially, heteroaromatic substituents attached to the phosphorus atom.

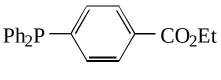
The aim of this study was to develop a versatible method for the preparation of mixed tertiary phosphines on the basis of cross-coupling reactions of diphenylchloro- and phenyldichlorophosphines with aryl halides or *C*-halogen derivatives of sulfur- or nitrogen-containing heterocycles catalysed by electrochemically generated Ni^0 complexes. We decided on $NiBr_2bipy$ as the starting complex of Ni^{II} because of its greater reactivity as compared with coordinatively unsaturated nickel complexes we used previously.[5,6] The reactions were carried out in an undivided cell equipped with a magnesium or zinc anode in the absence of a specially added supporting electrolyte. The use of soluble anodes, in some instances, makes it possible not only to simplify the electrochemical process significantly but also to control the direction of the reaction.[7] The electrolysis was performed at a constant current density and room temperature until the concentration of the desired product in solution became constant.

Mixed diphenylaryl phosphines **3** were isolated as a result of a cross-coupling reaction between diphenylchlorophosphine **1** with aryl bromides **2** under conditions of metallocomplex catalysis. The yields varied from 45 to 70% (Scheme 1) and were influenced by the nature of substituents in the aromatic ring and by the anode material.

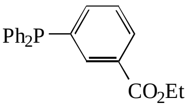
Note that a magnesium anode should be used for the synthesis of tertiary phosphines with donor substituents, and a zinc anode is recommended for the preparation of phosphines with acceptor substituents. Mixing of all reagents before the electrolysis also lowers the yield of desired product to 15–20%.

$$\underset{\mathbf{1}}{Ph_2PCl} + \underset{\mathbf{2}}{ArBr} \xrightarrow[DMF]{NiBr_2bipy/e^-} \underset{\mathbf{3}}{Ph_2PAr}$$

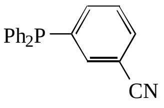
Scheme 1



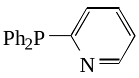
3a



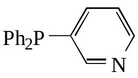
3b



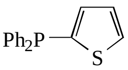
3c



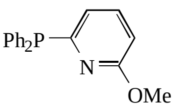
6a



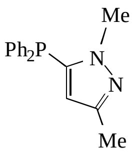
6b



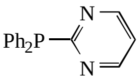
6c



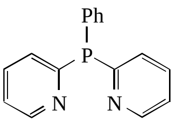
6d



6e



6f



6g

Compounds **3** were purified by column chromatography. The structures were proved by NMR spectroscopy, and the composition was found by mass spectrometry.†

We suppose that the first stage of a catalytic cycle is the electrochemical reduction of a Ni^{II} complex to a Ni^0 complex. The latter is a catalyst of the reaction and can react with aryl bromide according to Scheme 2 with the formation of organonickel compound **4**, which reacts with chlorophosphine **1** to form product **3** with the regeneration of the Ni^{II} complex.

$$Ni^{2+}bipy \xrightarrow{2e} Ni^0bipy \xrightarrow{\mathbf{2}} \underset{\mathbf{4}}{ArNiBrbipy} \xrightarrow[-\,NiBrClbipy]{\mathbf{1}} \mathbf{3}$$

Scheme 2

Model compound **5** was obtained to support the proposed scheme. This compound is the stable σ-complex *o*-MeC_6H_4-NiBrbipy prepared by the electrochemical reduction of $NiBr_2bipy$ in the presence of the corresponding tolyl bromide at a potential of –1.2 V with reference to an SCE. The addition of chlorophosphine **1** to compound **5** leads to an instantaneous disappearance of the red colour and the development of a green colour of the solution, which is characteristic of Ni^{II} complexes. Diphenyl-*o*-tolylphosphine and a minor amount of its oxide were isolated from the reaction mixture.

Nickel diphenylphosphide obtained by an analogous procedure does not react with aryl halides. Thus, this route can be excluded from the discussion of the cross-coupling reaction. Moreover, the experimental data can explain the fact that it is necessary to perform the process with continuous addition of chlorophosphine **1** to the reaction mixture in order to obtain tertiary phosphines **3** in high yields.

The proposed method for the electrosynthesis of tertiary phosphines under conditions of metallocomplex catalysis is versatile and makes it possible to introduce a phosphine group into heterocyclic compounds like pyridine, thiophene, pyrimidine, pyrazole and their derivatives under mild conditions. As a result of the cross-coupling reaction of corresponding *C*-halides with mono- and dichlorophosphines, a wide variety of mixed phosphines **6**, which were not easily accessible, were obtained in high yields.

$$R_nPCl_{3-n} + R'\text{–}X \xrightarrow[\text{DMF}]{\text{NiBr}_2\text{bipy/e}^-} R_nPR'_{3-n}$$

6

Scheme 3

Thus, we proposed a new versatile method for the one-step preparation of mixed tertiary phosphines containing both aryls with acceptor or donor groups in the aromatic rings and some heterocycles as substituents at the phosphorus atom under mild conditions.

[†] Yields were calculated on a chlorophosphine basis. Zn and Mg anodes were used for preparation of compounds **3** and **6**, respectively. NMR spectra were recorded for solutions in $CDCl_3$.

3a: yield 63%. Mp 99–100 °C. ^{1}H NMR, δ: 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). ^{13}C NMR, δ: 166.17 (s, COO), 143.70 (d, C–P, *J* 14.9 Hz), 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. ^{31}P NMR, δ: –6.7. Found (%): C, 75.34; H, 5.93; P, 9.28. Calc. for $C_{21}H_{19}PO_2$ (%): C, 75.45; H, 5.69; P, 9.28.

3b: yield 66%. Mp 100–101 °C. ^{1}H NMR, δ: 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). ^{13}C NMR, δ: 161.21 (s, COO), 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. ^{31}P NMR, δ: –7.0. Found (%): C, 75.60; H, 5.80; P, 9.31. Calc. for $C_{21}H_{19}PO_2$ (%): C, 75.45; H, 5.69; P, 9.28.

3c: yield 45%. Mp 97–98 °C (lit.,[3] mp 96–98 °C). ^{1}H NMR, δ: 7.10–7.80 (m). ^{13}C NMR, δ: 140.79 (d, *J* 17.1 Hz), 136.79, 136.09, 133.98, 133.14, 132.71, 132.15, 131.90, 130.77, 129.72, 129.49, 118.79 (s, CN), 112.98 (d, C–CN, *J* 6.0 Hz). ^{31}P NMR, δ: –6.0.

6a: yield 80%. Mp 81–83 °C (lit.,[2] mp 82–84 °C). ^{1}H NMR, δ: 8.54–8.57 (m, 1H), 7.15–7.34 (m, 10H), 6.90–6.98 (m, 2H). ^{13}C NMR, δ: 163.91 (d, *J* 4.1 Hz), 150.25 (d, *J* 12.5 Hz), 136.17 (*J* 10.5 Hz), 135.70, 134.32, 133.93, 129.03, 128.66, 128.52, 127.92, 127.62, 122.15. ^{31}P NMR, δ: –5.5.

6b: yield 63%. Mp 83–84 °C. ^{1}H NMR, δ: 8.53 (dd, 2H, *J* 4.40 Hz), 7.16–7.57 (m, 14H). ^{13}C NMR, δ: 154.28 (d, *J* 23.6 Hz), 149.72, 141.19, 104.87, 135.95, 135.75, 133.79 (d, *J* 19.7 Hz), 128.91, 128.76, 123.65, 123.57. ^{31}P NMR, δ: –13.5.

6c: yield 65%. Mp 42–43 °C (lit.,[8] mp 44–46 °C). ^{1}H NMR, δ: 7.49 (d, 1H, *J* 4.5 Hz), 7.24–7.39 (m, 12H), 7.07 (t, 1H, *J* 4.5 Hz). ^{13}C NMR, δ: 137.96 (d, *J* 8.5 Hz), 136.33 (d, *J* 25.5 Hz), 133.93, 133.08 (d, *J* 19.6 Hz), 132.03, 128.68 (d, *J* 16.4 Hz), 128.38, 128.04 (d, *J* 7.9 Hz), 127.96. ^{31}P NMR, δ: –21.2.

6d: yield 66%. Mp 83 °C. ^{1}H NMR, δ: 7.24–7.36 (m, 6H), 7.18–7.22 (m, 7H), 3.63 (s, 3H). ^{13}C NMR, δ: 163.49, 153.52, 139.25, 138.12 (d, *J* 4.2 Hz), 136.78 (d, *J* 10.0 Hz), 134.29 (d, *J* 19.5 Hz), 128.94, 128.52, 128.37, 122.04, 121.62, 113.71, 53.20. ^{31}P NMR, δ: –4.98.

6e: yield 25%. Mp 74–75 °C (lit.,[8] mp 75 °C). ^{1}H NMR, δ: 7.18–7.31 (m, 10H), 6.63 (s, 1H), 3.71 (s, 3H), 2.13 (s, 3H). ^{13}C NMR, δ: 152.41 (d, *J* 22.0 Hz), 135.50 (d, *J* 9.8 Hz), 133.20 (d, *J* 20.0 Hz), 136.92, 128.11, 128.31, 111.20 (d, *J* 6.1 Hz), 38.67, 37.23. ^{31}P NMR, δ: –33.1.

6f: yield 50%. Mp 118–119 °C. ^{1}H NMR, δ: 8.59 (d, 2H, *J* 4.87 Hz), 7.26–7.48 (m, 10H), 6.98–7.03 (m, 1H). ^{13}C NMR, δ: 156.49 (d, *J* 7.0 Hz), 134.58 (d, *J* 20.0 Hz), 129.24, 128.52, 128.37, 118.81. ^{31}P NMR, δ: –0.2. Found (%): C, 72.65; H, 4.98; P, 11.61; N, 10.21. Calc. for $C_{16}H_{13}N_2P$: C, 72.73; H, 4.92; P, 11.74; N, 10.61.

6g: yield 68%. Mp 96–98 °C (lit.,[8] mp 96 °C). ^{1}H NMR, δ: 7.06–7.18 (m, 4H), 7.29–7.31 (m, 3H), 7.39–7.54 (m, 4H), 8.63–8.70 (dd, 2H, *J* 4.7 Hz). ^{13}C NMR, δ: 150.34 (d, *J* 13.0 Hz), 135.45 (d, *J* 23 Hz), 134.80, 129.59, 128.85, 128.70, 128.55, 129.19, 122.46. ^{31}P NMR, δ: –4.0.

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