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A Study of the Electrochemical Synthesis of Tri-*n*-butylstannyldiphenylphosphine and of the Reaction between Chlorodiphenylphosphine and Alkyl Halides

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The electrochemical synthesis of tri-*n*-butylstannyldiphenylphosphine is described, and a new mechanism for the electrochemical coupling between Ph_2PCl and Bu_3SnCl and between PH_2PCl and alkyl halides is proposed.

Trialkylstannylphosphines, R_3SnPR_2, have attracted considerable attention in the last decade owing to their usefulness in organometallic synthesis,[1–4] affording compounds which would otherwise prove inaccessible. However, they are of limited use because of inherent difficulties in their preparation. This work focuses on the development of an electrochemical synthetic route using chlorodiphenylphosphine as starting material.

Perichon *et al.*[7,8] have used a mixture of Ph_2PCl and an alkyl chloride or bromide in DMF (*N,N*-dimethylformamide) with Mg as a sacrificial anode under controlled-current conditions to prepare alkyldiphenylphosphines. The following mechanism was proposed:

$$\textit{cathode:}\quad Ph_2PCl + 2e^- \rightarrow Ph_2P^- + Cl^- \tag{3}$$

$$\textit{anode:}\quad Mg \rightarrow Mg^{2+} + 2e^- \tag{4}$$

$$\textit{solution:}\quad Ph_2P^- + RX \rightarrow Ph_2PR + X^- \tag{5}$$

Here we report on our attempts to repeat these findings using Bu_3SnCl instead of an ordinary alkyl halide.

Initially, possible interactions between the components of our system were investigated, and the formation of tetraphenyldiphosphine was detected. In the presence of an electric current, only Ph_2PPPh_2 was formed when Ph_2PCl reacted with Bu^nBr, $Br[CH_2]_4Br$ or Bu_3SnCl in an undivided electrochemical cell with Mg as a sacrificial anode under controlled potential conditions (−1.6 *vs.* SCE). Other workers[11] have reported that electrolysis of Ph_2PCl solution in acetonitrile in the presence of an excess of $PhCH_2Br$ in a conventional two-compartment cell with Pt electrodes does not yield the expected benzyldiphenylphosphine. The following mechanism was proposed to account for the formation of the reaction products:

$$Ph_2P{-}PPh_2 + PhCH_2Br \rightarrow Ph_2P{-}P^+Ph_2(CH_2Ph)Br^- \tag{7}$$

$$Br^-Ph_2P{-}P^+Ph_2(CH_2Ph) \rightarrow Ph_2PBr + Ph_2PCH_2Ph \tag{8}$$

$$Ph_2PCH_2Ph + PhCH_2Br \rightarrow Ph_2P^+(CH_2Ph)_2Br^- \tag{9}$$

We propose the following interpretation of the results as an alternative to that suggested by Perichon *et al.*[7,8] It is known that under controlled-current conditions the potential of an electrochemical system is not always constant but can shift gradually to progressively more negative potentials. If the solution contains more than one electroactive species, eventually a new electrode reaction occurs.[12] In such a system the sequence of electrochemical reactions is determined by the relative values of the reduction potentials for each compound. A sequence leading to the tertiary phosphines is proposed as follows:

$$Ph_2PCl + 2e^- \rightarrow Ph_2P^- + Cl^- \qquad E^1_{1/2} \tag{10}$$

$$Ph_2P^- + Ph_2PCl \rightarrow Ph_2P{-}PPh_2 + Cl$$

$$Ph_2P{-}PPh_2 + 2e^- \leftrightarrows 2Ph_2P^- \qquad E^2_{1/2} \tag{11}$$

$$Ph_2P^+RX \rightarrow Ph_2PR + X^-$$

or

$$Ph_2P^{\bullet} + RX \rightarrow Ph_2PR + X^{\bullet}$$

However, if alkyl halide reduction occurs before the $Ph_2P{-}PPh_2$ reduction, the formation of the tetraphenyldiphosphine is primarily observed.

$$R^{\bullet} \text{ or } R^- + Ph_2P{-}PPh_2 \rightarrow \text{no reaction} \tag{12}$$

Consequently, an alkyl halide with a reduction potential more negative than that of tetraphenyldiphosphine should give the alkyldiphenylphosphine as the major product under constant-current conditions.

Comparison of the reduction potentials ($E_{1/2}$) for Ph_2PCl and Bu_3SnCl in DMF at the Pt electrode showed that the first reduction wave of Bu_3SnCl had a slightly less negative value than that of $Ph_2P{-}PPh_2$, while the second wave had approximately the same value. From these data it might be expected that the reduction of Bu_3SnCl would be slightly more favourable in comparison with $Ph_2P{-}PPh_2$. However, the similarity of the $E_{1/2}$ values suggests that at some potential both reactions occur simultaneously. This is possible because the reduction waves overlap to some extent. Both electrogenerated species will react with the constituents of the solution:

$$Bu_3SnCl + e^- \rightarrow [Bu_3Sn^{\bullet}] + Cl^-$$

$$[Bu_3Sn^{\bullet}] + Bu_3SnCl \rightarrow Bu_3SnSnBu_3 + Cl^{\bullet\,17}$$

$$[Bu_3Sn^{\bullet}] + Ph_2P{-}PPh_2 \rightarrow \text{no reaction} \tag{13}$$

$$Ph_2P{-}PPh_2 + 2e^- \rightarrow 2[Ph_2P^-]$$

$$[Ph_2P^-] + Bu_3SnCl \rightarrow Bu_3SnPPh_2 + Cl^- \tag{14}$$

It is clear that the first reaction depletes the supply of Bu_3SnCl necessary to provide for the second reaction. The second reaction gives tributylstannyldiphenylphosphine, the required product.

This work clearly shows that: (1) Bu_3SnPPh_2 is synthesised in the course of the electrolysis as a result of cleavage of the P—P bond in Ph_2PPPh_2; (2) reduction of Bu_3SnCl occurs more easily than that of Ph_2PPPh_2; and (3) the yield of Bu_3SnPPh_2 can be increased by increasing the concentration of Bu_3SnCl in the mixture.

Techniques used: CV, ^{31}P NMR, MS

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Table 1: Half-wave potentials for the electrochemical reduction of Ph_2PCl

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Fig. 1(*a*): Cathodic reduction of Ph_2PCl in DMF at Pt working electrode

Fig. 1(*b*): CV of Ph_2PCl in DMF at Pt working electrode

Fig. 2: Cathodic reduction of Bu_3SnCl in DMF at Pt wire electrode

Fig. 3: CV of Bu_3SnCl in DMF at glassy carbon rotating disc electrode

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