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Selective monoarylation of phosphorus trichloride by the electrochemically generated organonickel σ-complex MesNiBrbpy

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The use of the electrochemically generated organonickel σ-complex MesNiBrbpy enables the selective monoarylation of phosphorus trichloride to be achieved under mild conditions.

The development of ecologically safe and resource-saving chemical and engineering processes has become an important strategic objective for science and technology. In this context, homogeneous catalysis has many attractions, notably in terms of selectivity and efficiency. For this reason, increasing attention is being given to the combination of organic electrosynthesis and catalysis with the participation of various transition metal complexes. So far, highly effective catalytic processes have been developed[1–2] involving the formation of new carbon–carbon or carbon–heteroatom bonds using organic and inorganic compounds as precursors. The selective electrosynthesis of specific organic compounds containing functional groups and chemically active centres is of particular interest.

The selective monoarylation of phosphorus trichloride is one of the key aspects in preparing new organophosphorus ligands for catalytic systems, since they are useful precursors of various organophosphorus compounds. The traditional syntheses of dichloroarylphosphines using Grignard or organolithium reagents usually do not give high yields and are associated with the need for severe conditions and flammable media, complicating the industrial synthesis of this class of compounds and requiring serious safety measures.[3] Among the dichloroarylphosphines the phosphines having bulky aromatic fragments [*e.g.*, 2,4,6-trimethylphenyl or 2,4,6-tris(*tert*-butyl)phenyl] occupy a special place. The mesitylphosphoric derivatives are useful precursors of homo- and heteropolynuclear compounds,[4] and it is known that the greater the steric capacity around the phosphorus atom in the ligand, the greater the selectivity of the catalytic processes involving the corresponding metal complexes.[5] Apart from the above drawbacks, a characteristic of all bulky dichloroarylphosphines syntheses (*e.g.*, for dichloromesitylphosphine and similar bulky derivatives) is that there are special difficulties connected, firstly, with preparing the initial Grignard reagents (the reaction of MesCl with magnesium metal does not readily proceed using the traditional procedures) and, secondly, MesMgBr undergoes slow reaction with PCl$_3$ to give a mixture of products (MesPCl$_2$, MesPClBr and MesPBr$_2$) which is difficult to separate.[6,7]

The aim of this study was to consider the possibility of selectively monoarylating phosphorus trichloride under the action of the electrochemically synthesised organonickel σ-complex MesNiBrbpy.

It is known[2] that the first and limiting stage in the electrocatalytic dehalogenation process is the oxidative addition of organic halides to an electrochemically generated complex Ni^{0}bpy:

$$\mathrm{Ni^{II}bpy + 2e \rightleftharpoons Ni^{0}bpy}$$
$$\mathrm{Ni^{0}bpy + RX \longrightarrow RNiXbpy}$$

In case of MesBr the electrochemical reduction of Ni^{II}bpy to Ni^{0}bpy in the presence of MesBr leads to the selective formation of the organonickel σ-complex MesNiBrbpy as the product of an oxidative addition of MesBr to the electrochemically generated Ni^{0}bpy.

$$\mathrm{Ni^{0}bpy + MesBr \longrightarrow MesNiBrbpy}$$

This σ-complex was extracted and characterised by different physico-chemical methods.[†] In the cyclic voltammogram of MesNiBrbpy in DMF only one reversible one-electronic wave at –1.80 V was present.

Note that the electrochemically synthesised σ-complex MesNiBrbpy is an analogue of a Grignard reagent and, consequently, the investigation of its activity in reactions pro-

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[†] *General Procedures.* All manipulations and reactions were carried out in a dry argon atmosphere. All solvents were purified and dried prior to use. Acetonitrile was purified by triple fractional distillation over phosphorus anhydride in the presence of KMnO$_4$. The concentration of residual water was 10^{-3} mol dm^{-3}. DMF was purified using a published procedure[8] to achieve a residual water content of 0.01–0.005 wt%. The supporting salts were twice recrystallised (Et$_4$NBr from MeCN and Et$_4$NBF$_4$ from ethanol) and dried in a vacuum at 70 °C for two days. Alcohols were refluxed with BaO for 5 h and then distilled. NiBr$_2$bpy was prepared according to the reported method.[9] Preparative electrolysis at a constant current density, ^{13}C and ^{1}H NMR spectroscopy, elemental analysis and ESR spectroscopy were used to establish the structure and yields of the electrosynthesis products.

Cyclic voltammograms were recorded at a glassy carbon electrode with 1.0 mm diameter in a thermostatically controlled cell in an argon atmosphere. A silver electrode Ag/AgNO$_3$ (0.01 mol dm^{-3} solution in MeCN) served as a reference electrode and a platinum wire served as an auxiliary electrode. The curve was recorded on a PI-50-1 potentiostat. The scan rate was 50 mV s^{-1}. Preparative electrolysis was performed using a B5-49 dc source in a thermostatically controlled cylindrical undivided electrolyser (a three-electrode cell) with 40 cm^3 volume. A silver electrode Ag/AgNO$_3$ (0.01 mol dm^{-3} solution in MeCN) served as a reference electrode. Platinum with a surface area of 20 cm^2 was used as a cathode. A flow of argon was bubbled through the electrolyte in the course of electrolysis. During electrolysis, the electrolyte was stirred with a magnetic stirrer. A saturated solution of Et$_4$NCl in MeCN was used as the anolyte, and the membrane was made from paper.

^{1}H NMR spectra were obtained in CDCl$_3$ on a Varian T-60 spectrometer with the working frequency 60 MHz using tetramethylsilane (TMS) as an internal standard. ^{31}P NMR spectra were recorded using a CXP-100 Bruker spectrometer (with 85% H$_3$PO$_4$ as an external standard) both with and without proton decoupling.

Electrochemical synthesis of MesNiBrbpy. The working solution (catolyte) was made by dissolving 0.1875 g (5×10^{-4} mol) of NiBr$_2$bpy, 1.05 g (5×10^{-3} mol) of Et$_4$NBr and 0.075 ml (5×10^{-4} mol) of MesBr in 30 ml of DMF. The electrolysis was carried out under potentiostatic conditions at the working electrode potential –1.52 V (reference electrode: Ag/0.01 M AgNO$_3$ in MeCN); 27 mAh of electricity were passed through the electrolyte. After the electrolysis the solvent was evaporated, and the products were extracted using diethyl ether. The ether was then evaporated and the product dried in vacuum at 30 °C to give 0.18 g of the σ-complex MesNiBrbpy (yield 87%).

Mesityl-nickel(II)-bromide-2,2′-bipyridine: mp 149 °C (decomp.). ^{1}H NMR (CDCl$_3$) δ: 8.56–8.57 (m, 2H, bpy), 8.33–8.37 (d, 2H, bpy), 7.79–7.82 (m, 2H, bpy), 7.28–7.31 (m, 2H, bpy), 6.45 (m, 2H, C$_6$H$_2$), 2.59 (s, 6H, Me), 2.17 (s, 3H, Me). Found (%): C, 55.03; H, 4.60; N, 6.03; Ni, 14.16; Br, 18.90. Calc. for C$_{19}$H$_{19}$N$_2$NiBr (%): C, 55.14; H, 4.59; N, 6.77; Ni, 14.18; Br, 19.31.

Synthesis of MesPCl$_2$. A solution of 0.2 g (0.5 mmol) of MesNiBrbpy in 40 ml of diethyl ether was added to a solution of 0.7 g (5 mmol) of phosphorus trichloride in 40 ml of diethyl ether at –70 °C (cooling bath with acetone and liquid nitrogen) with stirring for 10 min. After stirring for 2 h, the reaction mixture was slowly heated to room temperature. The ether and the excess of phosphorus trichloride were evaporated, and the residue was distilled in a vacuum to give 0.07 g of a very viscous liquid (δ^{31}P = +168.35 ppm, bp 47–49 °C/0.1 Torr). The yield of MesPCl$_2$ was 68%.

ceeding with the use of Grignard reagents is of special interest. Since one such process is the monoarylation of phosphorus trichloride, the interaction of the σ-complex MesNiBrbpy with phosphorus trichloride was investigated. By gradually adding a solution of MesNiBrbpy in Et_2O to a solution containing a tenfold excess of PCl_3 in the same solvent, at –70 °C, it was possible to carry out the selective monoarylation of phosphorus trichloride with formation of dichloromesitylphosphine as the only phosphorus-containing product.

$$\mathrm{MesNiBrbpy} + \mathrm{PCl_3} \longrightarrow \mathrm{MesPCl_2} + \mathrm{NiBrClbpy}$$

Only two signals (+221.3 and +168.3 ppm) corresponding to PCl_3 and the monoarylation product were present in the ^{31}P NMR spectrum of the reaction mixture.

Note that in this case the transhalogenation process (the halogen exchange of Cl with Br in the $MesPCl_2$ molecule) does not occur, this being a characteristic of MesMgBr usage.[6,7] This is probably associated with the stronger coordinating ability of the nickel atom with regard to Br in the organonickel σ-complex MesNiBrbpy. This feature is also one of the advantages of using this electrochemical approach for the synthesis of $MesPCl_2$ from phosphorus trichloride.

In conclusion, the use of electrochemically synthesised organonickel σ-complex MesNiBrbpy allows the selective monoarylation of phosphorus trichloride with bulky aryl groups to be carried out under mild conditions.

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