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Electroreduction of triphenylphosphine dichloride and the efficient one-pot reductive conversion of phosphine oxide to triphenylphosphine

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ABSTRACT

Electroreduction of triphenylphosphine dichloride in acetonitrile was performed successfully in an undivided cell fitted with an aluminium sacrificial anode and a platinum cathode. Further, the one-pot transformation of triphenylphosphine oxide to triphenylphosphine was achieved successfully by the treatment of triphenylphosphine oxide in acetonitrile with oxalyl chloride and subsequent electrochemical reduction.

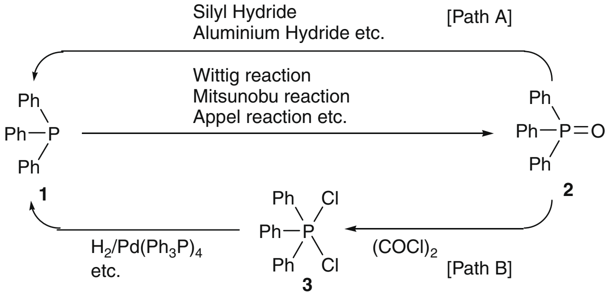
In modern organic synthesis, triphenylphosphine **1** is an important reagent for various reactions, for example, Wittig reaction,[1] Mitsunobu reaction[2] and Appel reaction.[3] In these reactions, **1** is converted to triphenylphosphine oxide **2**, which is a stable and flame-resistant chemical; as a result, a significant amount of **2** tends to be stored as troublesome waste. Facile methods involving reduction of **2** to **1** have been in great demand from the viewpoints of treatment of the troublesome waste and the use of recycled phosphine resources (Scheme 1). Indeed, many procedures for the reduction of **2** to **1** have been reported thus far. Reduction of **2** with silyl hydrides (e.g., trichlorosilane,[4] triethoxysilane/titanium tetra-*iso*-propoxide,[5] and phenylsilane[6]) and aluminium hydrides (e.g., lithium aluminium hydride,[7] lithium aluminium hydride/cerium chloride,[8] alane,[9] sodium aluminium hydride/sodium aluminium tetrachloride[10] and di-*iso*-butylaluminium hydride[11]) provides the desired product **1** with good to excellent yields (Scheme 1, Path A). Hexachlorodisilane,[12] samarium iodide/hexamethylphosphoric triamide[13] and titanocene dichloride/magnesium[14] have also been used for the reduction of **2**. However, the procedures reported thus far are not practical since they always require stoichiometric amounts of reducing agents that are expensive and/or difficult to handle.

As an alternative procedure, chlorination of **2** to form triphenylphosphine dichloride **3**[15] followed by the reduction of **3** to **1** has been intensively investigated (Scheme 1, Path B). Reduction of **3** to **1** was performed by hydrogenation under high temperature and/or high pressure in the presence of transition metal catalysts (Pt, Rh, and Pd).[16,17] Reduction of **3** with several metals such as sodium,[18] aluminium,[19] silicon[20] and iron[21] has also been reported. However, the reported procedures are not necessarily satisfactory in terms of operational simplicity and/or economic efficiency.

Electrochemical reduction, which does not require any reductant and can be carried out under mild conditions, is a highly promising procedure.[22] Indeed, electroreduction of **2** provides reagents-free, cheap, environmentally benign and straightforward access to **1**. Although there have been a few reports on the electroreduction of **2**, the reductive cleavage of the P–C bond mainly occurred to produce a complex mixture of diphenylphosphine oxide, phenylphosphine, benzene, 1,3-cyclohexadiene, etc.[23] However, the bond dissociation energy of the P–Cl bond ($H_2P–Cl$, 315.1 kJ/mol) is less than that of the P–O bond ($H_2P–OH$, 359.7 kJ/mol),[24] suggesting that upon electrochemical reduction, the P–Cl bond is cleaved more easily than the P–O bond to afford **1** efficiently.

In this Letter, we report the electroreduction of **3** as well as the 'one-pot' conversion of **2** to **1** through the chlorination of **2** to **3** and subsequent electrochemical reduction of **3** to yield **1**.

Electroreduction of triphenylphosphine dihalides **3**, **4** and **5** was carried out in a divided cell fitted with two Pt plate electrodes (1.5×1.0 cm^2 each). A typical procedure is as follows. A solution of **3** (0.5 mmol) in acetonitrile (10 mL)[25] containing tetrabutylam-



Scheme 1. System for recycling of triphenylphosphine **1** from triphenylphosphine oxide **2**.

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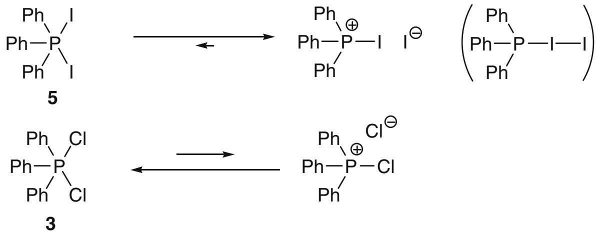
monium tetrafluoroborate (0.05 M) and an acetonitrile (10 mL) solution of tetrabutylammonium tetrafluoroborate (0.05 M) were placed in the cathode and the anode chambers, respectively, and a constant current (50 mA) was supplied. After passage of 2 F/mol of electricity, the reaction mixture was poured into a mixture of ice and 5% hydrochloric acid (5 mL), and extracted with ethyl acetate (10 mL × 3). The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed (silica gel, hexane/ethyl acetate = 3/1) to afford triphenylphosphine **1** (0.01 mmol, 2%) and **2** (0.49 mmol, 98%) which would be derived from the hydrolysis of **3** during electrolysis and/or work-up process (Table 1, entry 1). On the other hand, the electroreduction of triphenylphosphine dibromide **4** and diiodide **5** was carried out in a similar manner to provide **1** with a yield of 38% and 40%, respectively (entries 2 and 3). In all cases, no other by-products were detected.

The significant difference between the product yield in the electroreduction of **3** and the corresponding yields in the electroreduction of **4** and **5** can be explained as follows: Triphenylphosphine dihalides exist in five-coordinate and four-coordinate forms (Scheme 2). A ^{31}P NMR study of triphenylphosphine dihalides revealed that **5** ionizes completely to form iodotriphenylphosphonium iodide in a polar organic solvent, while **3** partially ionizes to form an equilibrium mixture of **3** and chlorotriphenylphosphonium chloride.[26]

In this regard, Godfrey and co-workers reported the X-ray crystal structure of triphenylphosphine dihalides.[27] **4** and **5** are ionic four-coordinate phosphonium salts, and **3** is a five-coordinate phosphorus compound, which has a trigonal bipyramidal structure. The electron density of the central phosphorus atom is lower in the four-coordinate ionic structure than that in the five-coordinate structure. Therefore, it is reasonable to assume that the ionic forms of **5** and probably **4** are reduced more easily than the non-ionic form of **3**.

We assumed that the addition of a Lewis acid would facilitate the ionization of **3** to form an ionic four-coordinate phosphonium salt. Indeed, as shown in the ^{31}P NMR spectrum of **3**, a low-field shift was observed by the addition of aluminium chloride to the solution of **3** in acetonitrile (Fig. 1). Without aluminium chloride, **3** showed a single peak at 50.1 ppm downfield from the phosphoric acid external standard. The peak shifted to 58.2 and 64.6 ppm when 0.5 and 1 equivalents of aluminium chloride were added, respectively, and further addition of aluminium chloride did not result in a more appreciable low-field shift. These results suggest that the electron density on the central phosphorus atom of **3** decreased significantly because of the formation of a 1-to-1 four-coordinate complex such as $[Ph_3PCl]^+[AlCl_4]^-$ **6**, which is expected to be reduced more easily than the five-coordinate form of **3** (Scheme 3).

The above-mentioned observation prompted us to investigate the electroreduction of **3** in the presence of aluminium chloride (Scheme 3). A mixture of **3** and aluminium chloride (1 mol equiv) in acetonitrile containing tetrabutylammonium tetrafluoroborate (0.05 M) was placed in the cathode compartment of a divided cell and a constant current (50 mA, 2 F/mol) was supplied. As expected, the yield of **1** significantly increased up to 37%.



Scheme 2. Dissociation equilibrium of triphenylphosphine dihalide.

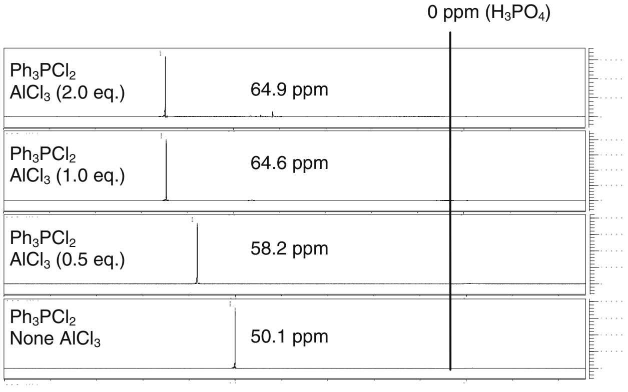
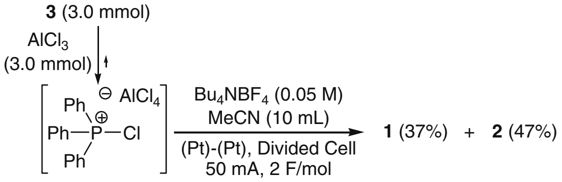


Figure 1. ^{31}P NMR spectra of $Ph_3PCl_2/AlCl_3$.



Scheme 3. Electroreduction of Ph_3PCl_2 in the presence of $AlCl_3$.

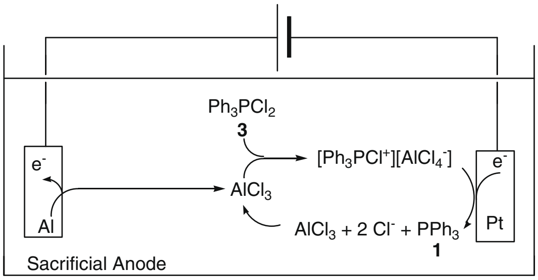


Figure 2. Sacrificial anode: a source of Lewis acid.

As aluminium chloride was generated during in situ electrolysis from the aluminium sacrificial anode, we next examined the electroreduction of **3** to **1** in an undivided cell without the addition of aluminium chloride (Fig. 2).

In fact, the electroreduction of **3** in an undivided cell fitted with a sacrificial anode was more efficiently and conveniently performed. The electrolysis was carried out in a beaker-type undivided cell fitted with an aluminium plate anode (1.5 × 1.0 cm^2) and a platinum plate cathode (1.5 × 1.0 cm^2). A solution of **3** (0.5 mmol) in acetonitrile (10 mL) containing tetrabutylammonium tetrafluoroborate (0.05 M) was placed in an undivided cell, and a constant current (50 mA) was supplied. After the passage of 2 F/mol of electricity and work-up procedure, **1** was obtained with a 34% yield and **2** with a 46% yield (Table 2, entry 1).

When 3 F/mol of electricity was passed, the yield of **1** increased to 46% (entry 2). Notably, when electrolysis was carried out by a similar procedure using a magnesium rod or a zinc plate (1.5 × 1.0 cm^2) as a sacrificial anode, the yields of **1** decreased to 7–10% (entries 3 and 4). The Mg^{2+} and Zn^{2+} salts, generated in situ from the sacrificial anodes, were rather weak Lewis acids and did not efficiently form the four-coordinate phosphonium salts ($[Ph_3PCl]^+[MgCl_3]^-$ and $[Ph_3PCl]^+[ZnCl_3]^-$). In a similar manner, the electroreduction of **4** and **5** proceeded smoothly to provide **1** with a yield of 45% and 61%, respectively.

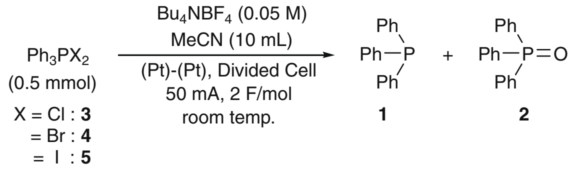
The yield of **1** was significantly improved by the increase in the concentration of **3** (Table 3, entry 2). When the concentration of **3** increased to 1 M (a 20-fold increase over that in previous entries in Tables 1 and 2), **1** was obtained with a yield of 68%. The effect of the supporting electrolyte was not significant. Tetrabutylammonium triflate and bromide could be used without appreciable change in the yield of the product (entries 3 and 4).

Finally, we examined the one-pot conversion of **2** to **1** through the chlorination of **2** with oxalyl chloride and the subsequent electrochemical reduction. A typical procedure is as follows. To a solution of **2** (5.0 mmol) and tetrabutylammonium triflate (200 mg, 0.5 mmol) in acetonitrile (5 mL) was added oxalyl chloride (0.43 mL, 1 equiv) at room temperature, and the mixture was stirred for a few minutes. An aluminium anode and a platinum cathode were immersed in the mixture, and a constant current (50 mA) was supplied. After the passage of 3 F/mol of electricity and usual work-up, triphenylphosphine **1** (3.7 mmol, 74%) and **2** (0.3 mmol, 6%) were obtained, respectively (Table 4, entry 1). In place of tetrabutylammonium triflate, aluminium chloride and bromide were used efficiently as a supporting electrolyte to produce **1** with a yield of 74% and 84%, respectively (entries 2 and 3). It is interesting to note that even without the addition of the supporting electrolytes, electroreduction proceeded smoothly to give **1** with an overall yield of 73% (entry 4).

It is likely that in the initial stage of electrolysis, chloride contaminants, for example, hydrogen chloride and aluminium chloride, derived from oxalyl chloride and/or a small amount of the ionic form of **3**, acted as a supporting electrolyte, and aluminium salts generated in situ from the sacrificial anode then worked as the supporting electrolyte. These results demonstrate the feasibility of the one-pot procedure for the conversion of **1** to **2**; thereby, offering a practical recycling system for **1**.

In conclusion, the electrochemical reduction of **3** was performed efficiently in an undivided cell fitted with an aluminium sacrificial anode and a platinum cathode, wherein aluminium chloride generated in situ from the sacrificial anode reacted with **3** and the thus formed four-coordinate ionic species ($[Ph_3PCl]^+[AlCl_4]^-$) underwent two-electron reduction at the cathode to provide **1** in moderate yields. The one-pot conversion of **2** to **1** through **3** was achieved successfully by the treatment of **2** with oxalyl chloride in acetonitrile and the subsequent electrochemical reduction of the mixture with an aluminium anode and a platinum cathode.

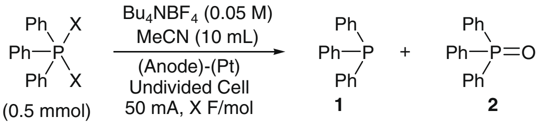
Table 1
Electroreduction of triphenylphosphine dihalides **3**–**5** to triphenylphosphine **1** in a divided cell[a]



Entry	Ph_3PX_2		Yield of **1**[b] (%)	Recovery of **2**[b] (%)
		x		
1	**3**	Cl	2	98
2	**4**	Br	38	62
3	**5**	I	40	60

[a] Pt: 1.5 × 1.0 cm^2, 33 mA/cm^2.
[b] Determined by GC.

Table 2
Electroreduction of triphenylphosphine dihalides in an undivided cell[a]



Entry	Ph_3PX_2		Anode	F/mol	Yield of **1**[b] (%)	Recovery of **2**[b] (%)
		X				
1	**3**	Cl	Al	2	34	46
2	**3**	Cl	Al	3	46	33
3	**3**	Cl	Mg	2	7	55
4	**3**	Cl	Zn	2	10	88
5	**4**	Br	Al	2	45	39
6	**5**	I	Al	2	61	20

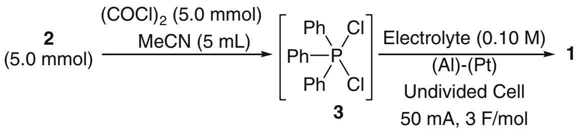
[a] Pt: 1.5 × 1.0 cm^2, 33.3 mA/cm^2.
[b] Yields of the isolated compounds.

Table 3
Effect of concentration of **3** and electrolyte[a]

Entry	**3**		Electrolyte	Yield of **1** [b] (%)	Recovery of **2**[b] (%)
	(mmol)	(M)			
1	0.5	0.05	Bu_4NBF_4	46	33
2	5.0	1.00	Bu_4NBF_4	68	11
3	5.0	1.00	Bu_4NOTf	68	7
4	5.0	1.00	Bu_4NBr	62	16

[a] Pt: 1.5 × 1.0 cm^2, 33.3 mA/cm^2.
[b] Yields of the isolated compounds.

Table 4
One-pot conversion of Ph_3PO **2** to Ph_3P **1**



Entry	Electrolyte	Yield of **1**[a] (%)	Recovery of **2**[a] (%)
1	Bu_4NOTf	74	6
2	$AlCl_3$	74	12
3	$AlBr_3$	84 (72)[b]	12 (8)[b]
4	None	73	14

[a] Determined by GC.
[b] Yields of the isolated compounds.

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