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Electroreduction of tetra-coordinate phosphonium derivatives; one-pot transformation of triphenylphosphine oxide into triphenylphosphine

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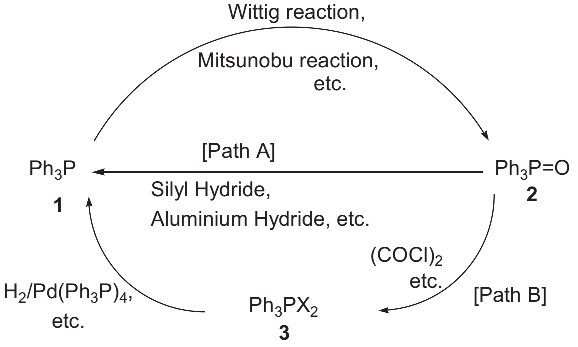
ABSTRACT

Electroreduction of triphenylphosphine dichloride in acetonitrile was performed successfully in an undivided cell fitted with an aluminium sacrificial anode and a platinum cathode, wherein Al^{3+}, which was electrogenerated at the anode would react as a Lewis acid with triphenylphosphine dichloride to afford tetra-coordinate chlorotriphenylphosphonium species and subsequent two-electron reduction at the cathode would give triphenylphosphine. One-pot transformation of triphenylphosphine oxide to triphenylphosphine was achieved successfully by the treatment of triphenylphosphine oxide with oxalyl chloride and subsequent electroreduction. In a similar manner, some tetra-coordinate triphenylphosphonium species derived from triphenylphosphine oxide were reduced electrochemically to triphenylphosphine in moderate yields.

1. Introduction

In modern organic synthesis, triphenylphosphine **1** is an important reagent for various reactions, e.g., Wittig reaction,[1] Mitsunobu reaction,[2] Mukaiyama–Corey lactonization,[3] Appel reaction[4] and Staudinger reaction.[5] In these reactions, **1** is turned into triphenylphosphine oxide **2**, which is a stable and flame-resistant chemical. As a result, a significant amount of **2** has been stored as a troublesome waste. Facile methods for reducing **2** to **1** have been in great demand from a viewpoint of treatment of the troublesome waste and recycling of phosphine resources[6,7] (Scheme 1). Indeed, many procedures for the reduction of **2** to **1** have been reported thus far. Direct reduction of **2** to **1** was performed with silyl hydrides ($HSiCl_3$,[8] $HSi(OMe)_3/Ti(O\text{-}i\text{-}Pr)_4$,[9] $PhSiH_3$,[10] etc.) and aluminium hydrides ($LiAlH_4$,[11] $LiAlH_4/CeCl_3$,[12] AlH_3,[13] $NaAlH_4/NaAlCl_4$,[14] $HAl(i\text{-}Bu)_2$,[15] etc.) (Scheme 1, path A). Low-valent metals (Si_2Cl_6,[16] SmI_2/HMPA,[17] Cp_2TiCl_2/Mg,[18] etc.) and non-metallic organic reagents (hydrocarbon/activated carbon,[19] $(Et_2N)_3P/POCl_3$,[20] etc.) have also been used for the reduction of **2** to **1**. However, the procedures reported thus far are not practical since they always require stoichiometric amounts of the reductants that are expensive, explosive, not easy to handle and form a significant amount of wastes.



Scheme 1. Recycling use of triphenylphosphine **1**.

Electrochemical reactions, which do not require any reductants/oxidants and can be carried out under mild conditions, are highly promising candidate[21] for reagent-free, environmentally benign and straightforward access, and several electrochemical processes have been used successfully in industry. Upon electrochemical reduction of **2**, however, the reductive cleavage of the P–C bond mainly occurred to produce a complex mixture of diphenylphosphine oxide, diphenylphosphine, phenylphosphine oxide, benzene, 1,3-cyclohexadiene, cyclohexene, etc., and no appreciable amount of **1** was obtained (Scheme 2).[22] It is likely that the P=O bond of **2** ($Cl_3P{=}O$ 510 kJ/mol)[23] is so strong to cleave that, accordingly, P–C bond fission occurred predominantly to give diphenylphosphine oxide, benzene, etc.

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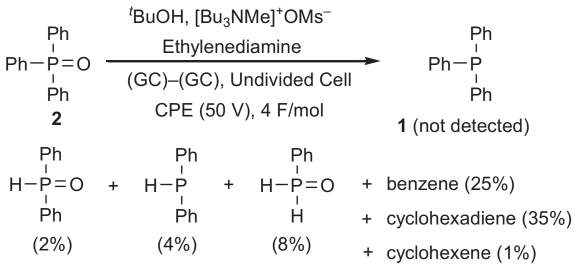


Scheme 2. Electroreduction of **2**.[22]

Triphenylphosphine dichloride (Ph_3PCl_2, **3a**) is easily prepared by treatment of **2** with chlorinating reagents such as $COCl_2$ and $(COCl)_2$.[11,24,25] Compared with reduction of **2**, the reduction of **3a** to cleave P–Cl bond is expected to proceed more smoothly than that of **2** to cleave P=O bond since P–Cl bond is far weaker (H_2P–Cl, 315.1 kJ/mol)[26] than P=O bond (Scheme 1, path B). Therefore, reduction of **3a** has been intensively investigated as an alternative access to **1**. Indeed, reduction of **3a** to **1** proceeded by hydrogenation under high temperature and/or high pressure in the presence of transition metal catalysts (Pt, Rh and Pd).[27,28] Reduction of **3a** with several metals such as sodium,[29] aluminium,[30] silicon[31] and iron[32] has also been reported. However, the reported procedures are not necessarily satisfactory since each process requires tedious pre-treatment of the metals and/or special care of the explosive nature of the activated metals or hydrogen under vigorous conditions.

Recently, we found that electrochemical reduction of triphenylphosphine dihalides **3** (Ph_3PX_2, X=Cl (**3a**), Br (**3b**) and I (**3c**)) proceeded smoothly to give **1** in an undivided cell fitted with an aluminium sacrificial anode. We also developed one-pot transformation of triphenylphosphine oxide **2** to **1** through **3**.[33,34] During the study, we found that tetra-coordinate phosphonium species $[Ph_3P–X]^+$ **4** would be a reactive intermediate of this reduction. Herein, we describe the details on the electroreduction of **3** as well as the 'one-pot' conversion of **2** to **1** and further applications to the electroreduction of some tetra-coordinate phosphonium compounds **5**–**7** derived from **2** in situ (Scheme 3).

$[Ph_3P–Cl]^+[PO_2Cl_2]^-$ **5** $[Ph_3P–OMe]^+OTf^-$ **6** $[Ph_3P–OSiMe_3]^+OTf^-$ **7**

Scheme 3. Tetra-coordinate phosphonium salts **5**–**7**.

2. Results and discussion

Cyclic voltammogram of triphenylphosphine oxide **2** in acetonitrile (MeCN) (Fig. 1b) shows no detectable waves between −0.2 to −2.5 V versus Ag/Ag$^+$ (supporting electrolyte: 0.1 M of tetrabutylammonium triflate (Bu_4NOTf)), indicating that direct electroreduction of **2** would not occur smoothly. On the other hand, an irreversible reduction wave is observed at −0.8 V in cyclic voltammogram of triphenylphosphine dibromide (**3b**), suggesting that two-electron reduction of **3b** followed by P–Br bond fission would occur to produce **1** (Fig. 1c). These results prompted us to investigate electroreduction of Ph_3PX_2 **3** (X=Cl (**3a**), Br (**3b**) and I (**3c**)).

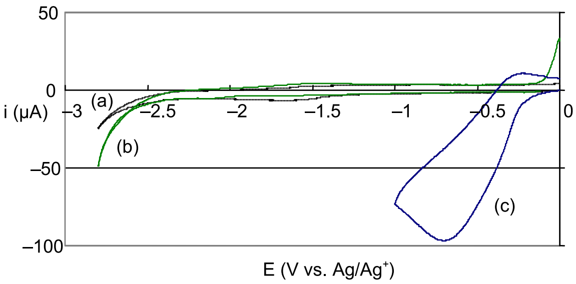
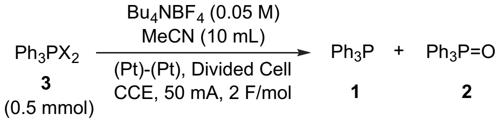


Fig. 1. Cyclic voltammograms of $Ph_3P=O$ **2** and Ph_3PBr_2 **3b**. (a) Background, (b) **2** (10 mM), (c) **3b** (10 mM) in Bu_4NOTf (0.1 M)/MeCN; working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/Ag$^+$; scan rate: 300 mV/s.

Electroreduction of **3b** was carried out in a divided cell fitted with a platinum plate anode and cathode (1.5×1.0 cm^2 each) (Table 1, entry 1). A solution of **3b** (0.5 mmol) in MeCN (10 mL) containing tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.05 M) and an MeCN (10 mL) solution of Bu_4NBF_4 (0.05 M) were placed in the cathodic and the anodic chambers, respectively. A constant current (50 mA) was supplied until 2 F/mol-**3b** of electricity was passed. Gas chromatography (GC) analysis of the reaction mixture in the cathodic chamber showed the formation of triphenylphosphine **1** (38%) together with triphenylphosphine oxide **2** (62%), which would be formed by hydrolysis of unreacted **3b** during the course of electroreduction and/or work-up process. Among thus far examined solvents, MeCN was the only solvent effective for the present purpose; thus, electroreduction of **3b** to **1** hardly occurred in tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl formamide (DMF) and 1,4-dioxane, resulting in the exclusive formation of **2**.

Table 1
Electroreduction of Ph_3PX_2 in a divided cell



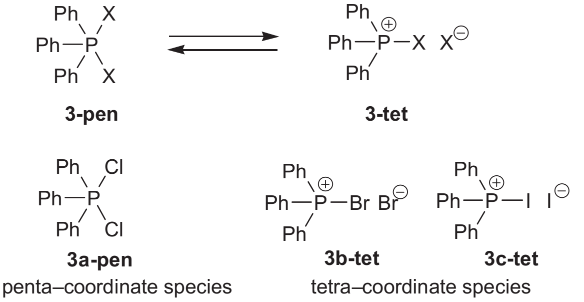
Entry	Ph_3PX_2		Yield[a]/%	
		X	**1**	**2**
1	**3b**	Br	38	62
2	**3c**	I	40	60
3	**3a**	Cl	2	98

[a] Determined by GC.

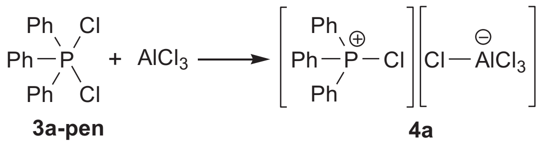
It is of interest to note that electroreduction of **2** under similar conditions gave no detectable amount of **1**, resulting in the recovery of most of **2**. Electroreduction of triphenylphosphine diiodide (**3c**) was similarly performed to give **1** and **2** in 40% and 60% yields, respectively (entry 2), whereas electroreduction of Ph_3PCl_2 **3a** hardly proceeded to give **1** in only 2% yield together with **2** (98% yield) (entry 3). In all entries in Table 1, other by-products such as diphenylphosphine oxide and diphenylphosphine were not detected, which were derived from the reductive C–P bond fission of **3**.

The significant difference between the electroreduction of **3a** and that of **3b** and **3c** can be reasonably explained by assuming that Ph_3PX_2 **3** exists in penta-coordinate form **3**-pen and/or tetra-coordinate form **3**-tet (Scheme 4).[35] ^{31}P NMR studies of **3** revealed that **3c** dissociated completely in a polar organic solvent such as MeCN to form tetra-coordinate iodotriphenylphosphonium iodide **3c**-tet, whereas penta-coordinate **3a** scarcely ionizes to form an equilibrium mixture of **3a**-pen and **3a**-tet favouring **3a**-pen. In this regard, Godfrey and co-workers reported the X-ray crystal structures of **3**,[36–38] showing that compounds **3b** and **3c** are ionic tetra-coordinate tetrahedral phosphonium salts, whereas **3a** is a penta-coordinate trigonal bipyramidal phosphorus compound.

Above all, we assumed that the cationic forms (**3b**-tet and **3c**-tet) are reduced more easily than the neutral form (**3a**-pen). This assumption, in turn, spurred us to investigate the formation of tetra-coordinate phosphonium salt **4a** from **3a** by the aid of aluminium chloride ($AlCl_3$) as a Lewis acid (Scheme 5).



Scheme 4. Dissociation equilibrium of Ph_3PX_2 **3a**–**3c**.



Scheme 5. Tetra-coordinate complex **4a** derived from **3a**.

The formation of ionic tetra-coordinate chlorotriphenylphosphonium salt **4a** was supported by ^{31}P NMR spectra of **3a** in the absence and in the presence of $AlCl_3$ (Fig. 2). In ^{31}P NMR spectrum of **3a** alone in MeCN, a single peak appeared at 50.1 ppm (external standard H_3PO_4, δ=0) (d). Significant low-field shift to 58.2 (Fig. 2c) and 64.6 ppm (Fig. 2b) was observed when 0.5 and 1 mol equiv of $AlCl_3$ was added, respectively, and further addition of $AlCl_3$ did not result in appreciable low-field shift any more (Fig. 2a). These results suggest that the electron density on the central phosphorus atom of **3a** decreased significantly by the formation of a one-to-one tetra-coordinate complex **4a**; thereby reducing the reduction potential significantly.

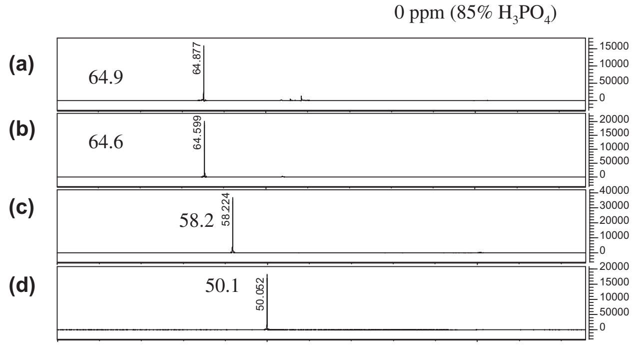


Fig. 2. ^{31}P NMR spectra of Ph_3PCl_2 **3a**/$AlCl_3$. (a) **3a**+$AlCl_3$ 2 equiv, (b) **3a**+$AlCl_3$ 1 equiv, (c) **3a**+$AlCl_3$ 0.5 equiv, (d) **3a**.

Electroreduction of **3a** in the presence of $AlCl_3$ was performed in a divided cell in a manner similar to that described above. A mixture of **3a** and $AlCl_3$ (1 mol equiv) in MeCN containing Bu_4NBF_4 (0.05 M) was electrolyzed under a constant current condition (50 mA). Electricity (2 F/mol-**3a**) was passed to give **1** in 37% yield together with **2** (47%), suggesting that electroreduction of **3a** proceeded smoothly through the in situ generated tetra-coordinate chlorotriphenylphosphonium species **4a**.

Electroreduction of **3a** through **4a** was performed more efficiently and conveniently in an undivided cell fitted with an Al sacrificial anode, wherein the anodic reaction would supply the required Al salts (Fig. 3) and in turn give tetra-coordinate phosphonium **4a** by the reaction with **3a**. Two-electron reduction at the cathode of thus formed cation species **4a** would give **1** together with $AlCl_3$ (a hard acid), which would associate more efficiently with **3a** (a hard base) than with **1** (a soft base), as the results, generating **4** again in situ.

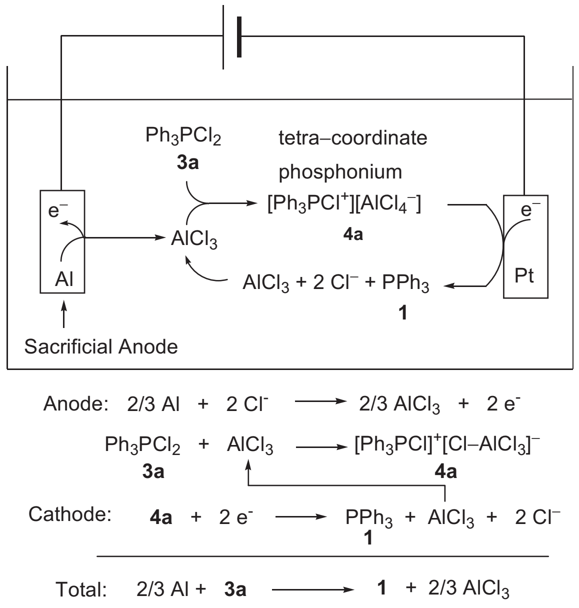
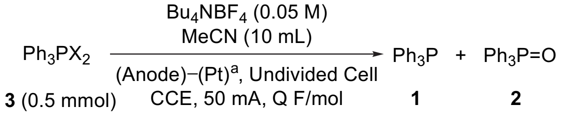


Fig. 3. Sacrificial anode: a source of Lewis acid.

In fact, the electroreduction of **3a** proceeded without addition of $AlCl_3$; thus, a solution of **3a** in MeCN containing Bu_4NBF_4 (0.05 M) was electrolyzed in a beaker-type undivided cell fitted with an Al plate anode ($1.5\times1.0\ cm^2$) and a Pt plate cathode ($1.5\times1.0\ cm^2$). Passage of 2 F/mol-**3a** of electricity (50 mA) gave **1** and **2** in 34% and 46% yields, respectively (Table 2, entry 1). When 3 F/mol-**3a** of electricity was passed, the yield of **1** increased to 46% (entry 2). Notably, when the electrolysis was carried out by use of a magnesium rod (6 mmϕ) or a zinc plate ($1.5\times1.0\ cm^2$) as a sacrificial anode, the yield of **1** decreased to 7–10% (entries 3 and 4). The Mg^{2+} and Zn^{2+} salts, generated in situ from the sacrificial anodes, are rather weak Lewis acids and would not efficiently form the tetra-coordinate chlorotriphenylphosphonium salts ($[Ph_3P–Cl]^+[MgCl_3]^-$ and $[Ph_3P–Cl]^+[ZnCl_3]^-$). In a similar manner, the electroreduction of **3b** and **3c** proceeded smoothly to provide **1** in 45% and 61% yields, respectively.

Table 2
Electroreduction of Ph_3PX_2 **3** in an undivided cell using sacrificial anode



$$\underset{\mathbf{3}\ (0.5\ \text{mmol})}{Ph_3PX_2}\ \xrightarrow[\text{(Anode)–(Pt)}^{a}\text{, Undivided Cell}\\ \text{CCE, 50 mA, Q F/mol}]{Bu_4NBF_4\ (0.05\ M)\\ \text{MeCN (10 mL)}}\ \underset{\mathbf{1}}{Ph_3P}\ +\ \underset{\mathbf{2}}{Ph_3P{=}O}$$

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

[a] Pt: $1.5\times1.0\ cm^2$, 33.3 mA/cm^2.
[b] Yields of the isolated products.
[c] Plate ($1.5\times1.0\ cm^2$).
[d] Rod (6 mmϕ).

The yield of **1** was significantly improved by the increase of the concentration of **3a** (Table 3, entry 2). When the concentration of **3a** increased from 0.05 M to 1 M, **1** was obtained in 68% yield. In place of Bu_4NBF_4, Bu_4NOTf and tetrabutylammonium bromide (Bu_4NBr) were used as supporting electrolytes without appreciable change in the yield of **1** (entries 3 and 4).

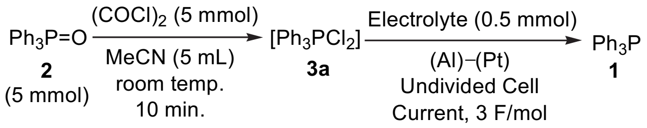
Table 3
Effect of concentration of **3a** and supporting electrolyte[a]

Entry	**3a** (mmol)	MeCN (mL)	Concn **3a** (mol/L)	Supporting electrolyte (0.1 M)	Yield[b]/%	
					1	**2**
1	0.5	10	0.05	Bu_4NBF_4	46	33
2	5.0	5	1.0	Bu_4NBF_4	68	11
3	5.0	5	1.0	Bu_4NOTf	68	7
4	5.0	5	1.0	Bu_4NBr	62	16

[a] (Al)-(Pt): 1.5×1.0 cm^2, undivided cell, 50 mA, 3 F/mol.
[b] Yields of the isolated compounds.

Since Ph_3PX_2 **3** is highly moisture sensitive, and is easily hydrolyzed to give **2**, we next examined the one-pot conversion of **2** to **1** in which chlorination of **2** to **3a** with oxalyl chloride in situ and subsequent electrochemical reduction of **3a** were performed. A typical procedure is as follows. To a solution of **2** (5 mmol) and Bu_4NOTf (0.5 mmol) in MeCN (5 mL) was added oxalyl chloride (0.43 mL, 5 mmol) at ambient temperature, and the mixture was stirred for 10 min. An Al anode (1.5×1.0 cm^2) and a Pt cathode (1.5×1.0 cm^2) were immersed in the mixture, and a constant current (50 mA) was supplied until 3 F/mol-**2** of electricity was passed. Usual work-up gave **1** (3.7 mmol, 74%) and **2** (0.3 mmol, 6%) (Table 4, entry 3). Current did not affect on the yields of **2** (entries 1–3). Ph_3P **1** was obtained from $Ph_3P{=}O$ **2** in 74, 72 and 82% yields when the current was set at 50, 100 and 200 mA, respectively. In place of Bu_4NOTf, $AlCl_3$ and $AlBr_3$ were used efficiently as supporting electrolytes to produce **1** in 74% and 84% yields, respectively (entries 4 and 5). It is interesting to note that even without addition of the supporting electrolytes, the electroreduction proceeded smoothly to give **1** in 73% yield (entry 6). In the initial stage of the electrolysis, chloride contaminants, e.g., hydrogen chloride and aluminium chloride, which were derived from oxalyl chloride and/or a small amount of the ionic form of **3a**, would act as a supporting electrolyte, and then aluminium salts generated in situ from the sacrificial anode would work as a supporting electrolyte and Lewis acid. These results demonstrated the feasibility of the one-pot procedure for the conversion of **2** to **1**; thereby, offering a practical recycling system for **1**.

Table 4
One-pot conversion of **2** to **1** via **3a**

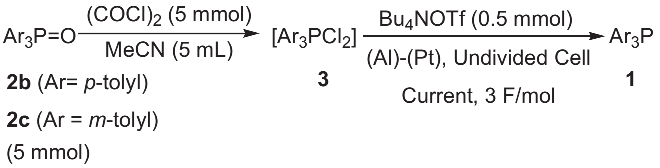


Entry	Electrolyte	Current/mA	Yield[a]/%
			1
1	Bu_4NOTf	200	82
2	Bu_4NOTf	100	72
3	Bu_4NOTf	50	74
4	$AlCl_3$	50	74
5	$AlBr_3$	50	84 (72)[b]
6	None	50	73

[a] Determined by GC.
[b] Yields of the isolated **1**.

Electroreduction of other triarylphosphine oxides such as tri(*p*-tolyl)phosphine oxide (Ar=*p*-MeC_6H_4) **2b** and tri(*m*-tolyl)phosphine oxide (Ar=*m*-MeC_6H_4) **2c** proceeded smoothly in a similar manner as described above to give tri(*p*-tolyl)phosphine **1b** and tri(*m*-tolyl) phosphine **1c** in 60% and 76% yields, respectively (Table 5).

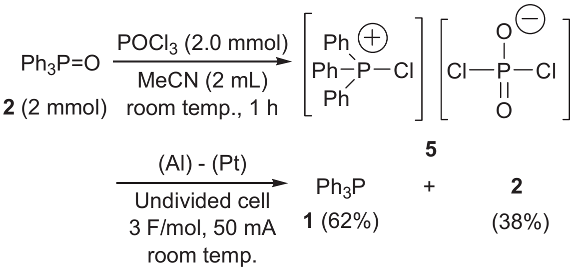
Table 5
Electroreduction of triarylphosphine oxides



Entry	Ar	Current/mA	Yield[a]/%
			1
1	*p*-Tolyl (**2b**)	50	**1b**, 60
2	*p*-Tolyl (**2b**)	200	**1b**, 59
3	*m*-Tolyl (**2c**)	50	**1c**, 76
4	*m*-Tolyl (**2c**)	200	**1c**, 72

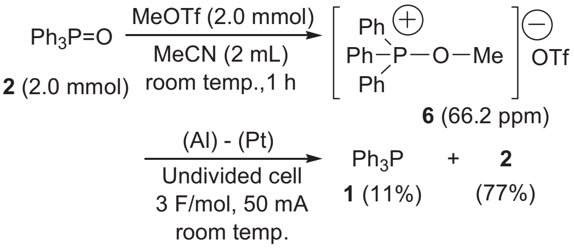
[a] Yields of the isolated compounds.

Electroreduction of **5**–**7** was also investigated. To an MeCN (2 mL) suspension of **2** (2.0 mmol) was added $POCl_3$ (2.0 mmol), and the mixture was stirred at room temperature for 1 h to give a clear solution of $[Ph_3PCl]^+[PO_2Cl_2]^-$ **5** (Scheme 6).[39] To the solution were immersed an Al anode (1.0×1.5 cm^2) and a Pt cathode (1.0×1.5 cm^2), and the mixture was electrolyzed under constant current conditions (50 mA, 93 min, 3 F/mol-**2**) to give **1** in 62% yield.



Scheme 6. Synthesis and electroreduction of $[Ph_3PCl]^+[Cl_2PO_2]^-$ **5**.

Methoxytriphenylphosphonium triflate $[Ph_3P{-}OMe]^+[OTf]^-$ **6** was generated from **2** by treatment with methyl triflate (MeOTf) (Scheme 7). A mixture of MeCN (2 mL), **2** (2 mmol) and MeOTf (2 mmol) was stirred at room temperature for 1 h. ^{31}P NMR of the mixture showed a single peak of **6** (^{31}P NMR: δ 66.2 ppm, 100%), suggesting that **6** was obtained as a tetra-coordinate phosphonium species. To the mixture were immersed an Al anode (1.0×1.5 cm^2) and a Pt cathode (1.0×1.5 cm^2), and the mixture was electrolyzed (50 mA, 93 min, 3 F/mol-**2**) to give **1** and **2** in 11% and 77% yields, respectively.[40]



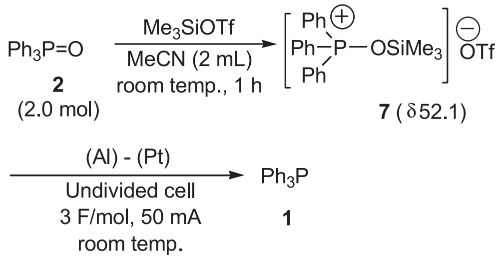
Scheme 7. Synthesis and electroreduction of $[Ph_3P{-}OMe]^+[OTf]^-$ **6**.

$[Ph_3P{-}O{-}SiMe_3]^+[OTf]^-$ **7**[41] was prepared by treatment of **2** with Me_3SiOTf. A mixture of MeCN (2 mL), **2** (2.0 mmol) and Me_3SiOTf (2.0 mmol) was stirred at room temperature for 1 h to give a solution of **7** whose ^{31}P NMR showed a single peak at δ 52.1 ppm. The mixture was electrolyzed (Al anode (1.0×1.5 cm^2), Pt cathode (1.0×1.5 cm^2), 50 mA, 93 min, 3 F/mol-**2**) to give **1** and **2** in 35% and 47% yields, respectively (Table 6, entry 1). By increasing of Me_3SiOTf to 6 mmol, yield of **1** increased up to 65% (entry 3).

In conclusion, the electrochemical reduction of triphenylphosphine dihalides **3** was performed efficiently in an undivided cell fitted with an aluminium sacrificial anode and a platinum cathode, wherein in situ generated $AlCl_3$ interacted with **3** and thus formed tetra-coordinate ionic species ($[Ph_3PCl]^+[AlCl_4]^-$) suffered two-electron reduction at the cathode to provide **1** in good yields. The one-pot conversion of **2** to **1** through **3a** (Ph_3PCl_2) was achieved successfully by the treatment of **2** with oxalyl chloride in MeCN and the subsequent electrochemical reduction of the mixture with an Al anode and a Pt cathode.

Table 6

Synthesis and electroreduction of $[Ph_3P{-}OSiMe_3]^+[OTf]^-$ **7**[a]



Entry	Me_3SiOTf (mL, mmol)	Ratio,[b] **1/2**
1	0.37, 2.0	35:47
2	0.73, 4.0	48:44
3	1.11, 6.0	65:35
4	1.47, 8.0	66:34

[a] Compound **2** (2.0 mmol), room temp.

[b] Determined by ^{31}P NMR.

3. Experimental section

3.1. General

^1H and ^{13}C NMR spectra were recorded on a Varian MERCURY 300 (^1H: 300 MHz, ^{13}C: 75 MHz) spectrometer in $CDC1_3$ (^1H: Me_4Si (δ=0), ^{13}C: $CDCl_3$ (δ=77.0)). ^{31}P NMR spectra were recorded on a Varian MERCURY 300 (120 MHz) spectrometer in $CDC1_3$ and/or CH_3CN/C_6D_6 (85% H_3PO_4 (δ=0) as an external standard). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analysis was executed on Perkin–Elmer PE 2400 Series II CHNS/O analyzer. Gas chromatography (GC) was performed with SHIMADZU GC-2014 instrument equipped with two packed columns (Silicon SE-52 (5%), Chromosorb W 80-100 AW-DMCS, 2.1 m×3.2 mm I.D.) using N_2 gas as an eluent. Analytic thin layer chromatography was performed on Merck, pre-coated plate silica gel 60 F_{254} (0.25 mm thickness). Column chromatography was performed on KANTO CHEMICAL silica gel 60N (40–50 μm).

Cyclic voltammetry (CV) was measured on the BAS 100B/W potentiostat (BAS, Tokyo, JAPAN). A platinum electrode (3 mmϕ), a platinum wire electrode (1 mmϕ) and an Ag/Ag$^+$ electrode (Ag wire in 0.01 M MeCN solution of $AgNO_3$, and Bu_4NClO_4) were used as a working, a counter and a reference electrode, respectively. The working electrode was polished with 5 μm diamond slurry and with 0.5 μm alumina slurry, successively, and washed with deionized water and acetone.

Unless otherwise noted, all materials were purchased from commercial suppliers, and reagent grade materials were used without further purification. All reactions were performed in dry solvents under argon atmosphere. MeCN and DMF were distilled from CaH_2. THF and 1,4-dioxane were distilled from sodium benzophenone ketyl under argon atmosphere.

3.2. Electroreduction of Ph_3PCl_2 3a in a divided cell (Table 1, entry 3)

In the cathodic chamber of an H-type divided cell equipped with a stirring bar was placed an MeCN (10 mL) solution of Ph_3PCl_2 (**3a**, 167 mg, 0.5 mmol) and Bu_4NBF_4 (165 mg, 0.5 mmol), and in the anodic chamber was placed an MeCN (10 mL) solution of Bu_4NBF_4 (165 mg, 0.5 mmol). In each chamber, Pt plate electrodes (1.5×1.0 cm^2) were immersed. The solutions were electrolyzed at room temperature under constant current conditions (50 mA, 33 mA/cm^2) until 2.0 F/mol-**3a** of electricity was passed (32 min). The mixture was poured into 5% aq HCl (5 mL) and extracted with ethyl acetate (AcOEt) (10 mL×3). The combined extracts were washed with satd aq $NaHCO_3$ and brine, successively, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was diluted with acetone (10 mL) containing 1,4-di-*iso*-propylbenzene (92 mg, 0.6 mmol) as an internal standard and analyzed by GC, showing that Ph_3P (**1**, 2%) and $Ph_3P{=}O$ (**2**, 98%) were obtained.

In a similar manner, electroreduction of Ph_3PX_2 **3** in a divided cell was carried out under several electroreduction conditions. The results are summarized in Table 1.

3.3. Electroreduction of 3a in an undivided cell (Table 2, entry 1)

Into an undivided cell equipped with an Al plate anode (1.5×1.0 cm^2), a Pt plate cathode (1.5×1.0 cm^2) and a stirring bar was placed an MeCN (10 mL) solution of Ph_3PCl_2 (**3a**, 167 mg, 0.5 mmol) and Bu_4NBF_4 (165 mg, 0.5 mmol). The solution was electrolyzed at room temperature under constant current conditions (50 mA, 33 mA/cm^2) until 2 F/mol-**3a** of electricity was passed (32 min). After work-up as described above, purification by column chromatography (SiO_2, hexane/AcOEt=5:1, 1:1) afforded **1** (45 mg, 0.17 mmol, 34%) as colourless solids.

*3.3.1. Triphenylphosphine (**1**).* Colourless solids; R_f=0.80 (hexane/AcOEt=1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.28–7.35 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.45 (d, J=6.8 Hz), 128.66, 133.69 (d, J=19.5 Hz), 137.10 (d, J=9.8 Hz); ^{31}P NMR (120 MHz, $CDCl_3$) δ −4.91; IR (KBr) 3066, 1638, 1308, 1281, 1155 cm^{-1}.

In a similar manner, electroreduction of Ph_3PX_2 in an undivided cell was carried out under several conditions. The results are summarized in Tables 2 and 3.

3.4. One-pot conversion of 2 to 1 by chlorination/electroreduction (Table 4, entry 1)

Into an undivided cell equipped with an Al plate anode (1.5×1.0 cm^2), a Pt plate cathode (1.5×1.0 cm^2) and a stirring bar was placed an MeCN (5 mL) solution of **2** (1391.1 mg, 5 mmol) and Bu_4NOTf (195.8 mg, 0.5 mmol). To the solution was added oxalyl chloride (0.43 mL, 5 mmol) at room temperature, and the mixture was stirred for 10 min. The solution was electrolyzed at room temperature under constant current conditions (50 mA, 33 mA/cm^2) until 3 F/mol-**2** of electricity was passed (8 h). Work-up and purification by column chromatography (SiO_2, hexane/AcOEt=5:1, 1:1) afforded **1** (970 mg, 3.7 mmol, 74%) as colourless solids, and **2** (83 mg, 0.3 mmol, 6%) was recovered.

In a similar manner, one-pot conversion of **2** was carried out under several conditions. The results are summarized in Table 4.

3.5. Synthesis and electroreduction of $[Ph_3PCl]^+[PCl_2O_2]^-$ 5

Into a Schlenk flask equipped with a magnetic stirring bar, a three-way cock and a rubber septum was placed triphenylphosphine oxide **2** (565 mg, 2.0 mmol). The whole apparatus was purged with argon. To the mixture were added MeCN (2 mL) and $POCl_3$ (0.18 mL, 2.0 mmol), successively, at room temperature. The mixture was stirred at room temperature for 1 h. The electrolysis was carried out using an aluminium plate anode (1.5×1.0 cm^2) and a platinum plate cathode (1.5×1.0 cm^2) under constant current (50 mA, 93 min, 3 F/mol-**2**) conditions. The reaction mixture was poured into a mixture of ice and aq 5% HCl, and extracted with AcOEt (3×10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was analyzed by ^{31}P NMR (120 MHz, $CDCl_3$) to find that triphenylphosphine **1** (δ −5.02) and **2** (δ 29.6) were obtained in 62:38 ratio.

*3.5.1. Tris(p-tolyl)phosphine (**1b**).* Colourless solids; R_f=0.63 (hexane/AcOEt=5:1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.55–7.13 (m, 12H), 2.34 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.38, 134.63, 134.38, 134.14, 132.46, 130.18, 128.19, 20.82; ^{31}P NMR (120 MHz, $CDCl_3$) δ −4.73; IR (KBr) 3068, 3013, 2971, 2920, 2865, 2732, 2359, 1917, 1814, 1658, 1595, 1496, 1450, 1394, 1352, 1307, 1272, 1211, 1186, 1118, 1104, 1090, 1038, 1019, 971, 846, 811, 711, 640, 624, 605, 516, 505, 476 cm^{-1}.

*3.5.2. Tris(m-tolyl)phosphine (**1c**).* Colourless solids; R_f=0.63 (hexane/AcOEt=5:1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.17 (m, 12H), 2.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.74, 137.64, 137.16, 137.01, 134.44, 134.15, 130.69, 130.46, 129.31, 128.23, 128.15, 21.26; ^{31}P NMR (120 MHz, $CDCl_3$) δ −7.38; IR (KBr) 3074, 3046, 3020, 2994, 2951, 2917, 2360, 1952, 1884, 1693, 1589, 1474, 1449, 1400, 1305, 1269, 1216, 1169, 1103, 1038, 998, 884, 781, 696, 542, 519 cm^{-1}.

3.6. Synthesis and electroreduction of $[Ph_3POMe]^+OTf^-$ 6

Into a Schlenk flask equipped with a magnetic stirring bar, a three-way cock and a rubber septum was placed triphenylphosphine oxide **2** (568 mg, 2.0 mmol). The whole apparatus was purged with argon. To the mixture were added MeCN (2 mL) and MeOTf (0.22 mL, 2.0 mmol), successively, at room temperature to give compound **6** (^{31}P NMR δ 66.2 ppm). The mixture was stirred at room temperature for 1 h. The electrolysis was carried out using an aluminium plate anode (1.5×1.0 cm^2) and a platinum plate cathode (1.5×1.0 cm^2) under constant current (50 mA, 93 min, 3 F/mol-**2**) condition. The reaction mixture was poured into a mixture of ice and aq 5% HCl, and extracted with AcOEt (3×10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was analyzed by ^{31}P NMR (120 MHz, $CDCl_3$) to find that triphenylphosphine **1**, **2** and an unidentified compound **8** (δ 21.1) were obtained in 11:77:12 ratio.

3.7. Synthesis and electroreduction of $[Ph_3POSiMe_3]^+OTf^-$ 7

Into a Schlenk flask equipped with a magnetic stirring bar, a three-way cock and a rubber septum was placed triphenylphosphine oxide **2** (568 mg, 2.0 mmol). The whole apparatus was purged with argon. To the mixture were added MeCN (2 mL) and Me_3SiOTf (1.47 mL, 8.0 mmol), successively, at room temperature to give compound **7** (^{31}P NMR δ51.3).[40] The mixture was stirred at room temperature for 1 h. The electrolysis was carried out using an aluminium plate anode (1.5×1.0 cm^2) and a platinum plate cathode (1.5×1.0 cm^2) under constant current (50 mA, 93 min, 3 F/mol-**2**) conditions. The reaction mixture was poured into a mixture of ice and aq 5% HCl, and extracted with AcOEt (3×10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was analyzed by ^{31}P NMR (120 MHz, $CDCl_3$) to find that **1** and **2** were obtained in 66:34 ratio.

3.8. Cyclic voltammetry of Ph_3PBr_2 3b (Fig. 1b)

The working, counter and reference electrodes were dipped into an MeCN solution of Ph_3PBr_2 **3b** (10 mM) containing Bu_4NOTf (0.1 M) as a supporting electrolyte in a beaker-type electrochemical cell. The solution was degassed with argon for 10 min before measurement. Cyclic voltammogram was measured in a potential range from 0.0 V to −2.8 V versus Ag/Ag^+ at a scan rate of 300 mV/s.

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