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Electrooxidative CH/PH functionalization as a novel way to synthesize benzo[*b*]phosphole oxides mediated by catalytic amounts of silver acetate

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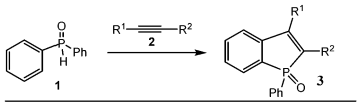
Electrochemical joint oxidation of diphenylphosphine oxide with acetylenes in the presence of silver acetate (10%) as a catalyst yields benzo[*b*]phosphole oxide derivatives under mild conditions at room temperature without additional oxidants or initiators and with yields up to 100%. The redox properties of the key intermediate of the catalytic cycle have been investigated by cyclic voltammetry and EPR spectroscopy. The $Ph_2P(O)Ag$ intermediate oxidizes easier (+0.05 V *vs.* Fc^+/Fc) than all reaction precursors to form the phosphinyl radical $Ph_2P(=O)^\bullet$, fixed as a spin-adduct by ESR. Thus, a radical mechanism type through the Ag^+/Ag^0 couple was developed for electrocatalytic conditions.

Introduction

Phosphorus-containing heterocycles have attracted significant interest from synthetic chemists over the last few years because of their wide application in organic synthesis, medicinal chemistry, and materials science.[1–5] Among them, benzo[*b*]phosphole oxide derivatives, phosphorus-containing π-conjugated compounds, have attracted significant attention as promising organic optoelectronic materials due to their unique physical and photoelectric properties.[6–14] This explains the urgent need to develop new effective, atom-economical catalytic routes for their synthesis.

Since 2013, various one-stage methods for the synthesis of benzo[*b*]phosphole oxide derivatives **3** through dehydrogenative annulation (Scheme 1) have been demonstrated.[15–20] The disadvantages of all the described methods are requirement of high temperature and excessive use of oxidants such as $Mn(OAc)_3$ or AgOAc (4 equiv.), as reported by Satoh,[15] Ag_2O (2 equiv.) or $Pd(OAc)_2$ with three-fold excess of Ag salts and an equivalent amount of metal nitrates, as reported by Duan,[16] AgOAc (2 equiv.), as reported by Ackermann,[17] and TBHP (2 equiv.) with $CuSO_4$[18] or $K_2S_2O_8$ (5 equiv.), as reported by Zhao.[19] Metal derivatives (2% $CuSO_4$,[18] 5% Ag_2O,[16] 2.5% Cp*$RhCl_2$[16] or $Pd(OAc)_2$[16]) in catalytic amounts perform well only under conditions of excess various oxidants, with the product yield dependent on the nature of the latter (therefore, for each condition, a screening is required), as well as at elevated temperatures and often in excess of diphenylphosphine oxide.[15,16,18] Low temperature for benzo[*b*]-phosphole oxide preparation was used only in some instances. Only Lakhdar synthesized benzo[*b*]phosphole oxides under photocatalytic conditions using Eosin Y as the catalyst and *N*-ethoxy-2-methylpyridinium tetrafluoroborate as an oxidant at a lower temperature, 35 °C,[20] and Satoh used 4 equiv. of $Mn(OAc)_3$15 at room temperature, but the yields were lower than those obtained at 100 °C. The use of additional reagents (oxidants and bases), typical for traditional reactions, leads to an increase in the production cost, complicates the separation, and increases waste.



Reaction conditions

A: $Mn(OAc)_3$ $2H_2O$ (4 eqv) or AgOAc (4 eqv), DMF, 100°C (*Satoh*); [15]
B: 5% Ag_2O / 1 eq. $Zn(NO_3)_2.6H_2O$, DMF, 100-120°C (*Duan*);[16]
C: AgOAc (2 eqv), DMSO, 120°C (*Ackermann*);[17]
D: $CuSO_4$ $5H_2O$ (2 mol%), TBHP (2 eqv), NH_3 H_2O (0.25 ml), MeCN, 60°C, air (*Zhao*);[18]
E: $K_2S_2O_8$ (5 eqv), MeCN, 90°C (*Zhao*);[19]
F: Eosin Y (4 mol%), Green LED (525 nm), Oxidant (1.5 eqv), $NaHCO_3$ (1.2 eqv), DMF, 35°C (*Lakhdar*).[20]

Scheme 1 Synthesis of benzophosphole oxide derivatives.

The mechanism of most Ag-catalyzed reactions is proposed to be radical type based on the absence of the target product when some equivalent of TEMPO is present in the reaction mixture. However, the failure of the reaction in the presence of TEMPO can be explained by the fact that the latter is easily oxidized by the applied oxidant, for example, $K_2S_2O_8$. Moreover, if TEMPO was taken in an equivalent amount or two-fold excess over the oxidant, the entire oxidant was spent by the side

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reaction of oxidation of TEMPO, which is easily oxidized to about 0 V ref. Fc^+/Fc or +0.42 V ref. Ag/AgCl.[21,22] However, in 2017, Li's group[23] described a novel Mn(II)-promoted tandem phosphorylation/cyclization reaction with phosphine oxides and suggested that unlike all the previously discussed reactions, the formation of a P-cycle was carried out by an ionic, not radical path. As a rule, the proposed cycles are tentative and cannot explain the use of excess of silver salt for example.[15,16]

In recent years, a series of successful electrocatalytic reactions with C–C, C–P bond formation catalyzed by metal complexes in reductive or oxidative conditions have been performed.[24–33] In the present study, the synthesis of benzo[*b*]phosphole oxides from diphenylphosphine oxide and acetylenes catalyzed by Ag salt (0.1 equiv.) at room temperature under electrochemical conditions has been demonstrated. In this case, an excess of oxidant or Ag salt is not required due to electrochemical regeneration of the catalyst's active form near the electrode surface.

Results and discussion

Electrocatalytic oxidative synthesis

AgOAc is frequently used as an oxidant or a catalyst for successful Ag-mediated CH/PH functionalization of diphenylphosphine oxide by acetylenes.[15–17,34,35]

It has been found that joint electrochemical oxidation of diphenylphosphine oxide and acetylene in the presence of 0.1 equiv. AgOAc at room temperature leads to the formation of benzo[*b*]phosphole oxide **3** with mild to high yields (Table 1).

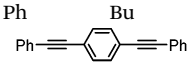
^{31}P NMR monitoring of the electrochemical oxidation of the reaction mixture revealed the need for 2 F electricity per 1 mole of diphenylphosphine oxide **1** for conversion of **1** into the target cyclization product **3** with yields up to 100% (Table 1 and Fig. 1). The electrolysis potential was 0.15–0.35 V (*vs.* Fc^+/Fc). Thus, the diphenylphosphine oxide **1** (commercially available, δ = 22.07)[36] is fully converted into benzo[*b*]phosphole oxide after passing 2 F electricity per 1 mole of phosphine oxide with δ = 37.0–40.0.[16] The result of ^{31}P NMR spectra monitoring is demonstrated in Fig. 1. The yield of the target benzo[*b*]-phosphole oxides is 85–100% in the case of symmetric acetylenes and 40–50% for asymmetric acetylenes. In the case of **3d–f**, only one cyclization product is formed.

Cyclic voltammetry

For the detailed investigation of the reaction pathway, the methods of cyclic voltammetry (CV) and electron-spin resonance spectroscopy (ESR) were used. At first, the redox properties of AgOAc and $Ph_2P(O)Ag$ – a key intermediate of the catalytic cycle (formed from AgOAc and diphenylphosphine oxide), acetylenes, and $Ph_2P(O)H$ – were studied by cyclic voltammetry. Acetylenes and $Ph_2P(O)H$ are not redox active.

The CVs of AgOAc contain one reduction and two oxidation peaks at −0.48 V and −0.16 and 1.43 V (*vs.* Fc^+/Fc) for Ag(I/0) and Ag(0/I/II), respectively, in CH_3CN (Fig. 2). There is little data on the oxidation potentials for $Ag^0/Ag^+/Ag^{2+}$ couples in organic media in literature. High standard potential of silver(II) in acidic water (E^0 = 1.98 V *vs.* normal hydrogen electrode, NHE)[37] is found. The potential for the Ag^+/Ag^0 couple (strongly dependent on solvent and counter-ions) is 0.04 in acetonitrile.[38] $AgBF_4$ reveals peaks at −0.28, 0.016, and 1.40 V (*vs.* Fc^+/Fc) for Ag(I/0)

Table 1 Yields of the isolated benzo[*b*]phosphole oxides and conversion based on ^{31}P NMR monitoring (R^1, R^2 from Scheme 1)

Compound	R^1	R^2	Spectral yield, %	Isolated yield, %
3a	Ph	Ph	100	90
3b	*p*-NO_2–Ph	*p*-NO_2–Ph	90	85
3c	Pr	Pr	85	80
3d	Ph	Et	50	40
3e	Ph	Pr	40	35
3f	Ph	Bu	40	35
3g			55	35

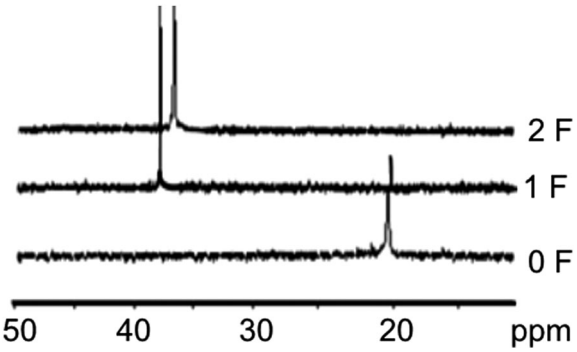


Fig. 1 ^{31}P NMR monitoring of electrochemical oxidation of diphenylphosphine oxide and diphenylacetylene mixture before and after 1 and 2 F electricity was passed.

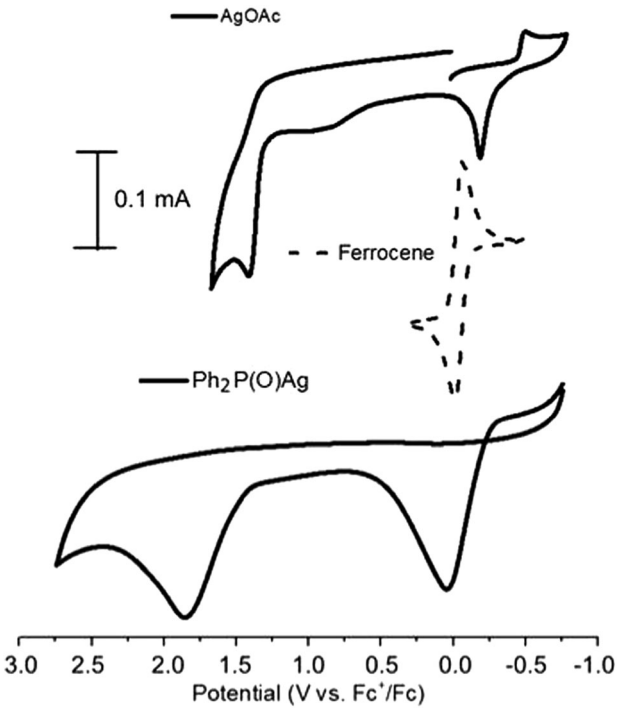


Fig. 2 CVs of AgOAc and $Ph_2(O)PAg$ in CH_3CN. Conditions: 0.1 V s^{-1} scan rate, 0.1 M Bu_4NBF_4, WE:GC, RE:Pt.

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and Ag(0/I/II) under similar conditions. Thus, the excess of the Bu_4NBF_4 supporting electrolyte does not substitute OAc^- in the silver salt AgOAc and is suitable for investigation.

We proposed that one key step in the investigated catalytic cycle should be $AgP(O)Ph_2$ oxidation.[16,35] Some contradictions should be noted in the studies of Ag-catalyzed C–H phosphonations. Most of the studies postulate the instant formation of a phosphinyl radical in the reaction of Ag(I) with $Ph_2P(O)H$.[39–41]

However, at room temperature, when protected from visible light, this compound is stable and does not change its properties when stored even for several months. Sometimes, the participation of $AgP(O)Ph_2$ was speculated, but it was not proved in studies reported in literature.[16,35] We obtained $Ph_2(O)PAg$ through a previously reported method[47–49] and characterized it spectrally. The investigation of the redox properties of the key $Ph_2(O)PAg$ intermediate by cyclic voltammetry has not been carried out to date. The CVs of $Ph_2P(O)Ag$ contain only two oxidation peaks at 0.05 and 1.85 V (Fig. 2). The first oxidation peak of $Ph_2P(O)Ag$ is close to the potential of electrolysis, which involves electrochemical phosphonation/cyclization. Thus, it was confirmed that the preparative electrochemical oxidation of diphenylphosphine oxide with acetylenes proceeds at the potential of the first oxidation peak of $Ph_2P(O)Ag$.

ESR study and mechanistic considerations

Thus, the oxidation of $Ph_2(O)PAg$ salt at 0.05 V (*vs.* Fc^+/Fc) is the key step in the electrochemical reaction. To establish the character of the catalytic cycle and the intermediate P(O)–Ag bond scission (ionic or radical type), we carried out a number of ESR experiments under anaerobic conditions. Joint oxidation of $Ph_2P(O)Ag$ and spin trap PBN (PBN = *N-tert*-butyl-α-phenylnitrone) mixture at 0.05 V (*vs.* Fc^+/Fc) in an ESR-spectroelectrochemical cell is characterized by appearance and increase in the intensity of the ESR signal from the PBN-bound radical species of the $Ph_2P(O)$ adduct (Fig. 3 and Scheme 2).

The ESR spectrum of the PBN adduct includes the splitting on the nuclei of nitrogen and hydrogen (in the α-position) and a significant splitting on the nucleus with nuclear spin I = 1/2, which is the nucleus of phosphorus at the β-position. The magnetic

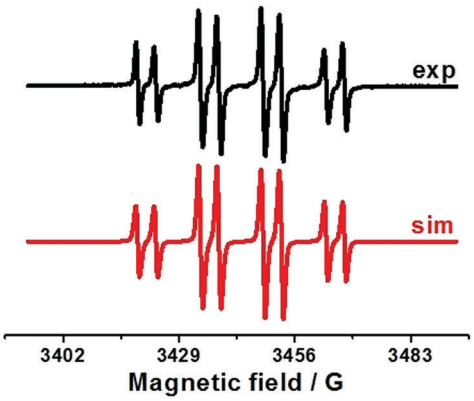
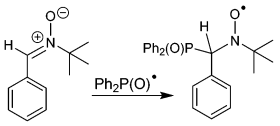


Fig. 3 ESR spectra obtained during anodic joint electrolysis of $Ph_2P(O)Ag$ and spin trap PBN solution (left) at 0.05 V (*vs.* Fc^+/Fc) in CH_3CN, obtained at 293 K with simulations.



Scheme 2 Trapping of phosphorus-centered radical by PBN.

resonance parameters were obtained as a result of the simulation: $g = 2.0059$, $a^N = 14.5$ G, $a^H = 4.3$ G, and $a^P = 14.9$ G. The observed g values at about $g = 2.006$ indicate the formation of PBN-bound radical species, and other magnetic resonance parameters are characteristic of phosphorus-containing PBN spin adducts.[50,51] These parameters are close to those reported for the phosphinyl $Ph_2P(=O)^\bullet$ radicals, but are slightly different from those since they were obtained elsewhere under other conditions.[42–46]

For example, in literature,[44] the presence of the PBN/phosphinyl radical adduct, $Ph_2P(O)$–PBN was revealed, but the presence of the benzoyl radical was also detected, and the spectra obtained were complicated. In literature,[45] the spectrum of the phenyl–PBN radical adduct, formed after phenyl – radical generation, as a precursor to the phosphinyl radical has been reported. Ph_2I^+OTf (form Ph radical),[45] camphorquinone (CQ)/diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide (TPO)/amine photoinitiating systems (form benzoyl radical),[44] benzophenone, 2-isopropylthioxanthone, camphorquinone, 2,4,6-(4-methoxyphenyl)thiopyrylium tetrafluoroborate, and Eosin-Y[42] were used as oxidants and photosensibilisators. Thus, on the way to phosphinyl radical, different types of radicals (phenyl, benzoyl, *etc.*) have been observed. This fact complicates the estimation of true PBN/phosphinyl radical adduct parameters. The data closest to our parameters were described by Buettner.[52] Thus, electrooxidative conditions (without additional oxidants) for $Ph_2P(O)Ag$ oxidation are the most correct for the detection of the phosphinyl radical.

Thus, we can conclude that $Ph_2P(=O)^\bullet$ reacts readily with the spin trap, and the spin adduct is quite stable.

The result suggested that this reaction followed a radical pathway. It should be noted that in addition to this spectrum (Fig. 3), a very wide line with $g = 2.34$ and ΔH peak–peak = 1200 G (the black line in Fig. 4) was observed. This signal can be apparently assigned to the metallic Ag(0),[42] the particles of which precipitate at the bottom of the cell.

Interestingly, the addition of diphenylacetylene does not qualitatively change the type of the ESR spectra obtained during electrolysis of this mixture at the potential of 0.15 V. However, the intensity of the spectrum of $Ph_2P(O)^\bullet$–PBN decreases, but the intensity of the Ag(0) signal increases (Fig. 4) approximately four times. This circumstance well confirms the possible mechanism of the catalytic cycle including the observed intermediates $Ph_2P(O)Ag$, $Ph_2P(O)^\bullet$, and Ag(0).

A mixture of $Ph_2P(O)H$ and PBN or $Ph_2P(O)Ag$ and PBN in the absence of applied potential at room temperature does not exhibit noticeable ESR spectra.

Thus, catalytic cycle in Scheme 3 was suggested based on the ESR and CV experiments. The proposed catalytic pathway includes the formation of $Ph_2P(O)Ag$ in the first step; its oxidation leads to $Ph_2P(O)^\bullet$ radical and Ag^+ regeneration. Then, the radical addition

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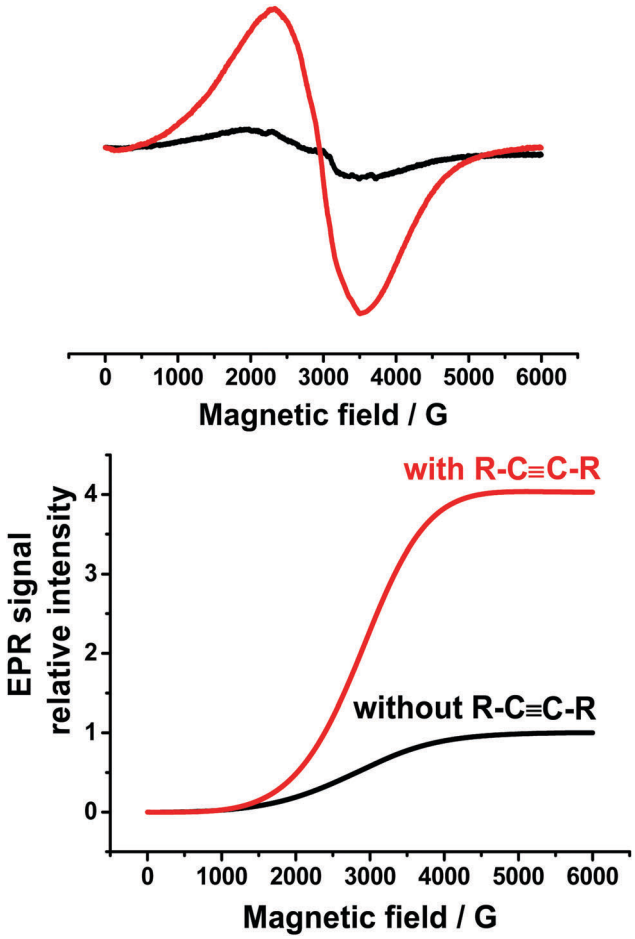
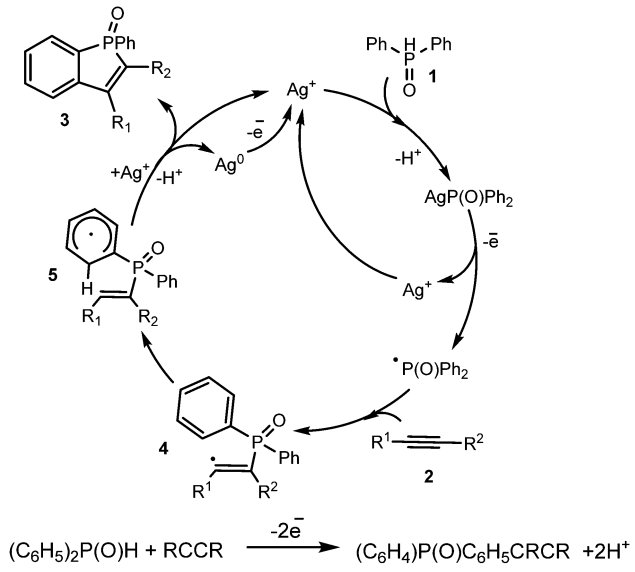


Fig. 4 Comparison of Ag(0) signals in the presence (red) or absence (black) of diphenylacetylene (upper), and the intensities of these signals (lower).



Scheme 3 Proposed catalytic cycle.

to alkyne affords an alkenyl radical 4. Next, the intramolecular addition of the alkenyl radical 4 to the aryl ring at the *ortho* position of the phosphorus atom, followed by the oxidation with Ag^+ and the elimination of a proton, affords the phosphorus heterocycle 3. The Ag^0-intermediate is formed in the presence of acetylene in the transient step, as detected by ESR. Considering these details, it is possible to explain the decrease of $^{\bullet}P(O)Ph_2$ ESR signal intensity in the presence of alkyne (concurrent radical trapping with this substrate) and subsequent increase of ESR signal of silver aggregates (due to oxidation of resulting cyclization product). Contrary to the methods reported in the literature, for example, the Duan protocol,[16] Ag(I) completely regenerates during catalytic cycle since it is easily oxidized at anode rather than precipitated.

Experimental

Solvents were purified, dried, and distilled before use. The supporting electrolyte Bu_4NBF_4 used for electrochemical studies was purchased from Sigma-Aldrich and dried overnight at 100 °C under vacuum prior to use. Anhydrous acetonitrile (>99.8%) used for electrochemistry was purchased from Sigma-Aldrich.

Cyclic voltammetry measurements were performed using the E2P potentiostat of BASi Epsilon (USA) composed of a measuring block, Dell Optiplex 320 computer with installed Epsilon ES-USB-V200 program, and C3 electrochemical cell. A stationary glassy-carbon electrode (3.0 mm diameter) was used as the working electrode. Platinum wire of 0.5 mm diameter was used as an auxiliary electrode. Ag/AgCl was used as the reference electrode. Ferrocenium was used as an internal standard. The potential of Fc^+/Fc is 0.45 V *vs.* Ag/AgCl. Measurements were performed under argon.

All NMR experiments were performed using the Bruker AVANCE-400 spectrometer. Frequencies, 400.13 MHz, in ^{1}H NMR, 161.90 MHz in ^{31}P NMR were referenced to the residual signal of the solvent. ^{31}P chemical shifts were referenced to the signals of 85% H_3PO_4 (0.00 ppm).

The ESR spectra were obtained using a Brucker Elexsys E500 X-range spectrometer with an ESR electrolysis cell operating in the three-electrode scheme placed into the resonator. Platinum spiral was used as the working electrode, platinum filament was used as the auxiliary electrode, and Ag/AgCl was used as the reference electrode. Prior to each experiment, helium was passed for 5 min through the solution in the cell. When passing was complete, the cell was filled with helium. The spectra were obtained in the potentiostatic mode. The spectra were simulated by WinSim.

The preparative electrolysis was performed using a direct current source B5-49 in a three-electrode cell with 40 ml volume with a separation of the anode and cathode compartments. The potential value of the working electrode was obtained using a direct-current V7-27 voltmeter in relation to the Ag/AgCl (0.01 M, NaCl) reference electrode that had two sections separated with Vycor, the second of which contained a saturated solution of the background salt in CH_3CN. The surface area of the working platinum (Pt) U-shaped electrode was measured to be 48.00 cm^2. A ceramic plate with the pore size of 900 nm was used as a

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membrane. During the preparative synthesis, the electrolyte was continuously stirred using a magnetic stirrer with a continuous inflow of inert gas that was run through a purification system to remove any traces of oxygen and other gaseous impurities. $PyHBF_4$ was used as the supporting electrolyte.

The electrochemical cell contained 0.4 mmol of diphenylphosphine oxide (CAS 4559-70-0), 0.4 mmol of appropriate acetylene, and 0.04 mmol of AgOAc in 20 ml of CH_3CN with 0.1 M of $PyHBF_4$. The solution was agitated using a magnetic stirrer. Then, 2 F of electricity per one mole of diphenylphosphine oxide (22 mA for 0.4 mmol) was passed through the solution. The electrolysis potential was 0.15–0.35 V *vs.* Fc^+/Fc. The electrolysis time is just over an hour. All syntheses were carried out at ambient temperature. After the electrolysis was over, the reaction mixture was filtered and concentrated under vacuum. Then, the dry residue was dissolved in $CHCl_3$ and $PyHBF_4$ (poorly soluble in $CHCl_3$) was filtered off. The reaction mixture in $CHCl_3$ was concentrated under vacuum again, and the residue was purified by silica gel chromatography with hexane/ethyl acetate = 1/1 to afford the product as a white to yellow color solid. The spectra of the cyclization products are consistent with the literature data.[16,53] $PyHBF_4$ can be further purified by recrystallization from alcohol and used again.

3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.80 (m, 2H), 7.75–7.70 (m, 5H), 7.55–7.60 (m, 1H), 7.55–7.50 (m, 5H), 7.40–7.35 (m, 6H). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 38.0 (s).

3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 3H), 7.65 (m, 2H), 7.50 (m, 3H), 7.35 (m, 7H), 7.00 (m, 2H). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 38.0 (s).

3c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 3H), 7.45 (m, 2H), 7.35 (m, 4H), 3.15 (m, 2H), 2.30 (m, 1H), 2.05 (m, 2H), 1.97 (m, 2H), 1.60 (m, 1H), 1.30 (t, J^{HH} = 7.3, 3H), 0.94 (t, J^{HH} = 7.3, 3H). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 39.2 (s).

3d: ^{1}H NMR (400 MHz, $CDCl_3$): 7.80–7.70 (m, 4H), 7.50–7.45 (m, 4H), 7.40–7.35 (m, 6H), 3.25–3.20 (m, 2H), 1.35 (t, J^{HH} = 7.3, 3H). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 39.7(s).

3e: ^{1}H NMR (400 MHz, $CDCl_3$): 7.80 (m, 4H), 7.62 (m, 2H), 7.44 (m, 8H), 3.17 (m, 2H), 2.15 (m, 1H), 2.01 (m, 1H), 1.30 (t, J^{HH} = 7.3, 3H). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 39.5(s).

3f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.57 (m, 6H), 7.57–7.47 (m, 4H), 7.43–7.40 (m, 4H), 3.16 (t, J^{HH} = 7.0, 2H), 1.50–1.35 (m, 2H), 1.30 (t, J^{HH} = 7.3, 3H), 0.97–0.85 (m, 2H). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 38.7 (s).

3g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.68 (m, 6H), 7.51–7.50 (m, 4H), 7.15–7.12 (m, 6H), 7.07–7.02 (m, 6H). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 37.1 (s), 37.5 (s).

$AgP(O)Ph_2$ was obtained by mixing and stirring of 1 equiv. of AgOAc and 1 equiv. of diphenylphosphine oxide at room temperature overnight in CH_3CN. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.69 (m, 4H), 7.46–7.42 (t, 2H), 7.36–7.32 (m, 4H). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 32.9(s).

Conclusions

Thus, the electrochemical oxidation of diphenylphosphine oxide with acetylene in equal amounts was performed without chemical oxidants and additives at room temperature with 0.1 equivalent of Ag salt as a catalyst. The yield of the target benzo[*b*]phosphole oxide was up to 100%. The redox properties of the key intermediate were investigated. The oxidation of $Ph_2P(O)Ag$ with the formation of phosphinyl radical is a key catalytic step for electrochemical reaction. The total regeneration of Ag(I) during electrolysis leads to the use of catalytic amounts of Ag salt.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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