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ROYAL SOCIETY OF CHEMISTRY
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DOI: 10.1039/C7NJ03717A

Journal Name

ARTICLE

Electrooxidative CH/PH Functionalization as a Novel Way to Benzo[*b*]phosphole Oxides Mediated by Catalytic Amounts of Silver Acetate

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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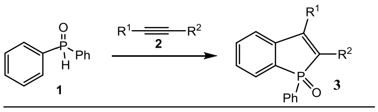
Electrochemical joint oxidation of diphenylphosphine oxide with acetylenes in presence of silver acetate (10%) as catalyst yields to benzo[*b*]phosphole oxide derivatives in mild conditions at room temperature without additional oxidants or initiators and with high yields up to 100%. Redox properties of key intermediate of 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 the reaction precursors to form phosphinoyl radical $Ph_2P(=O)^\bullet$ fixed as a spin-adduct by ESR. Thus radical mechanism type going throught Ag^+/Ag^0 couple was developed for electrocatalytic conditions.

Introduction

Phosphorus-containing heterocycles have become of great interest to the 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, the 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 urgent need in the new effective, atom-economical catalytic routes of their synthesis.



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 benzophosphol oxide derivatives

Since 2013 a lot of various one-stage methods for the synthesis of benzo[*b*]phosphole oxide derivatives **3** through dehydrogenative annulation (Scheme 1) have been demonstrated.[15-20] Disadvantages of all described methods are high temperature and using excess of oxidants, such as $Mn(OAc)_3$ or AgOAc (4 equiv) by Satoh, [15] Ag_2O (2 equiv) or $Pd(OAc)_2$ with threefold excess of Ag salts and equivalent amount of metal nitrates by Duan,[16] AgOAc (2 equiv) by Ackermann,[17] TBHP (2 equiv) with $CuSO_4$[18] or $K_2S_2O_8$ (5 equiv) by Zhao.[19] Catalytic amounts of metal derivatives (2% $CuSO_4$[18], 5% Ag_2O[16], 2.5% Cp^*RhCl_2[16] or $Pd(OAc)_2$[16] perform well only in conditions of excess of 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 oxides preparation was used only in some instances. Thus, only Lakhdar synthesized benzo[*b*]phosphole oxides under photocatalytic conditions by using eosin Y as the catalyst and N-ethoxy-2-methylpyridinium tetrafluoroborate as the oxidant at lower temperature, 35°C, [20] and Satoh used room temperature in the presence of 4 equiv of $Mn(OAc)_3$[15], but the yields were lower than at 100°C. The use of additional reagents (oxidants, bases), typical for the traditional reactions, leads to the increase of product's costs, complicates their separation and increases the wastes.

The mechanism of the most Ag-catalyzed reactions is proposed as radical type based on the absence of target product when some equivalent of TEMPO presents in 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 itself by the applied oxidant $K_2S_2O_8$, for example. Moreover, if TEMPO was taken in equivalent amount or two-fold excess over the oxidant, the entire oxidant was spent by the side reaction of TEMPO oxidation, which is easily oxidized to about 0 V ref. Fc^+/Fc or +0.42 V ref.Ag/AgCl.[21-22] But in 2017 Li group[23] described novel Mn(II)-promoted tandem phosphorylation/cyclization reaction with phosphine oxides and suggested that unlike all the previously discussed reactions, the

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DOI: 10.1039/C7NJ03717A

formation of P-cycle is carried out by an ionic, not radical, path. As a rule, proposed cycles are tentative and can’t explain the use of silver salt excess for example.[15,16]

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

Results and Discussion

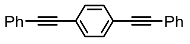
Electrocatalytic oxidative synthesis

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

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

Table 1 Yields of 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

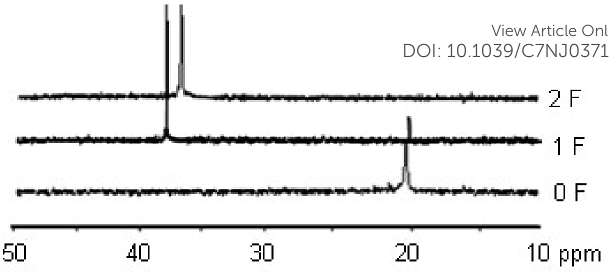


Fig. 1 ^{31}P NMR monitoring of electrochemical oxidation of diphenylphosphine oxide and diphenylacetylene mixture before and after 1 and 2 F electricity was passed

Cyclic voltammetry

For the detailed investigations of reaction pathway the methods of cyclic voltammetry (CV), electron-spin resonance spectroscopy (ESR) were used. At first redox properties of AgOAc, Ph$_2$P(O)Ag – key intermediate of catalytic cycle (formed from AgOAc and diphenylphosphine oxide), acetylenes and Ph$_2$P(O)H have been studied by cyclic voltammetry. Acetylenes and Ph$_2$P(O)H are not redox active.

CVs of AgOAc contain one reduction and two oxidation peaks at -0.48 V and -0.16, 1.43 V (vs. Fc$^+$/Fc) for Ag(I/0) and Ag(0/I/II), respectively in CH$_3$CN (Fig. 2).There is little data on oxidation potentials for Ag^0/Ag$^+$/Ag^{2+} couples in organic media in literature. Silver (II) high standard potential in acidic water (E^0 = 1.98 V vs. normal hydrogen electrode, NHE)[37] is found. Potentials for Ag$^+$/Ag^0 couple (strongly dependant on solvent and counter-ions) is 0.04 in acetonitrile.[38] AgBF$_4$ reveals the following peaks at -0.28, 0.016, 1.40 V (vs. Fc$^+$/Fc) for Ag(I/0) and Ag(0/I/II) in similar conditions. Thus, the excess of Bu$_4$NBF$_4$ supporting electrolyte does not substitute OAc$^-$ in silver salt AgOAc and is suitable for investigation.

We proposed that one key step of 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 numerous publications postulate the instant formation of a phosphinoyl radical in the reaction of Ag(I) with Ph$_2$P(O)H. [39-41] However, at room temperature, when protected from visible light, this compound is stable and does not change the properties when stored at least for several months. Sometimes the participation of AgP(O)Ph$_2$ was assumed, but was not proved, for example in [16,35]. We obtained Ph$_2$(O)PAg through previously reported method[47-49] and characterized spectrally. The investigation of redox properties of key Ph$_2$(O)PAg intermediate by cyclic voltammetry was not carried out yet. CVs of Ph$_2$P(O)Ag contain only two oxidation peaks at 0.05 and 1.85 V (Fig. 2). The first oxidation peak of Ph$_2$P(O)Ag is close to 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$_2$P(O)Ag.

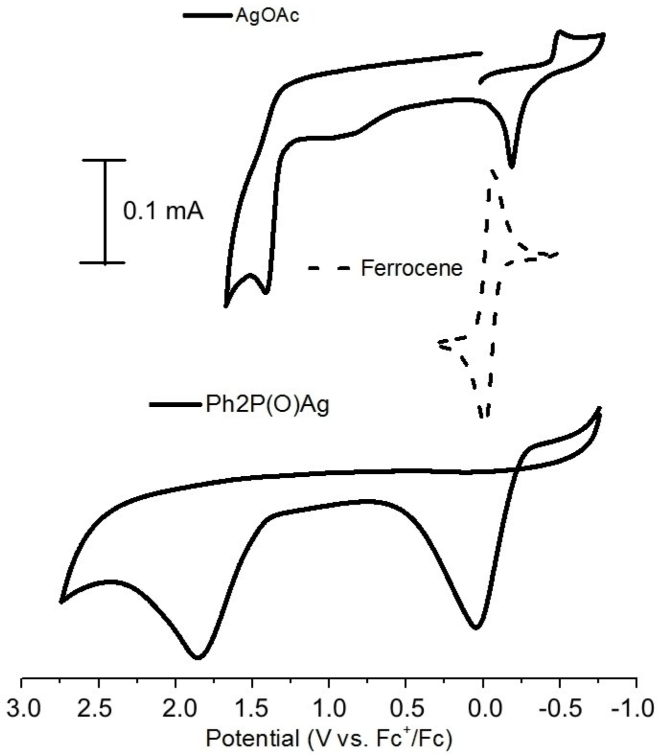


Fig. 2 CVs of AgOAc and $Ph_2(O)PAg$ in CH_3CN. Conditions: 0.1 V/s scan rate, 0.1 M Bu_4NBF_4, WE:GC, RE:Pt.

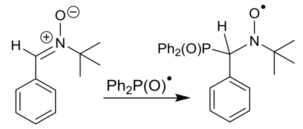
ESR study and mechanistic considerations

Thus the oxidation of $Ph_2(O)PAg$ salt at 0.05 V (vs. Fc^+/Fc) is the key step of 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 ESR-spectroelectrochemical cell is characterized by appearance and increase in intensity of ESR signal from the PBN-bound radical species of $Ph_2P(O)$ adduct (Fig.3, Scheme2).

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 = ½, which is the nucleus of phosphorus in the β-position. The magnetic resonance parameters were obtained as a result of the simulation: g = 2.0059, a^N= 14.5 G, a^H=4.3 G, a^P = 14.9 G. The observed g values at about g = 2.006 indicate at 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 phosphinoyl $Ph_2P(=O)^\bullet$ radicals, but are slightly different from them since they were obtained elsewhere in other conditions.[42-45]

For example, in[56] the presence of PBN/phosphinoyl radical adduct $Ph_2P(O)$-PBN was revealed, but the presence of the benzoyl radical was also detected and spectra are complicated. In [45] they observed the spectrum of phenyl-PBN radical adduct, formed after phenyl – radical generation, as a precursor to phosphinoyl radical. 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] are used as oxidants and photosensibilisators. Thus, on the way to phosphinoyl radical different types of radicals (phenyl, benzoyl, etc.) have been observed. This fact complicates the estimation of true PBN/phosphinoyl 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 phosphinoyl radical.

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



Scheme 2 Trapping of phosphorus-centered radical by PBN.

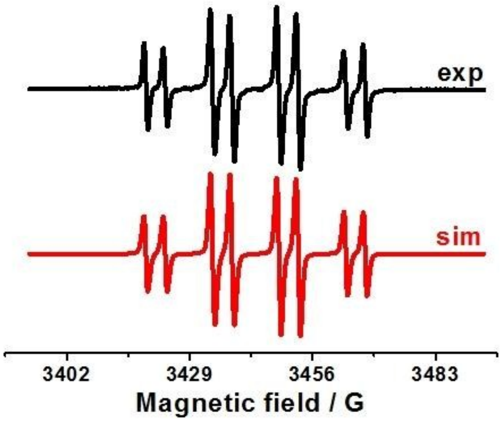


Fig 3. ESR spectra obtained during anodic joint electrolysis of $Ph_2P(O)Ag$ and spin trap PBN solution (left) at 0.05V (vs. Fc^+/Fc) in CH_3CN, recorded at 293 K with simulations.

The result suggested that this reaction follows 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 on the bottom of the cell.

Interestingly, the addition of diphenylacetylene does not qualitatively change the type of the ESR spectra recorded during electrolysis of this mixture at potential of 0.15 V. However, 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).

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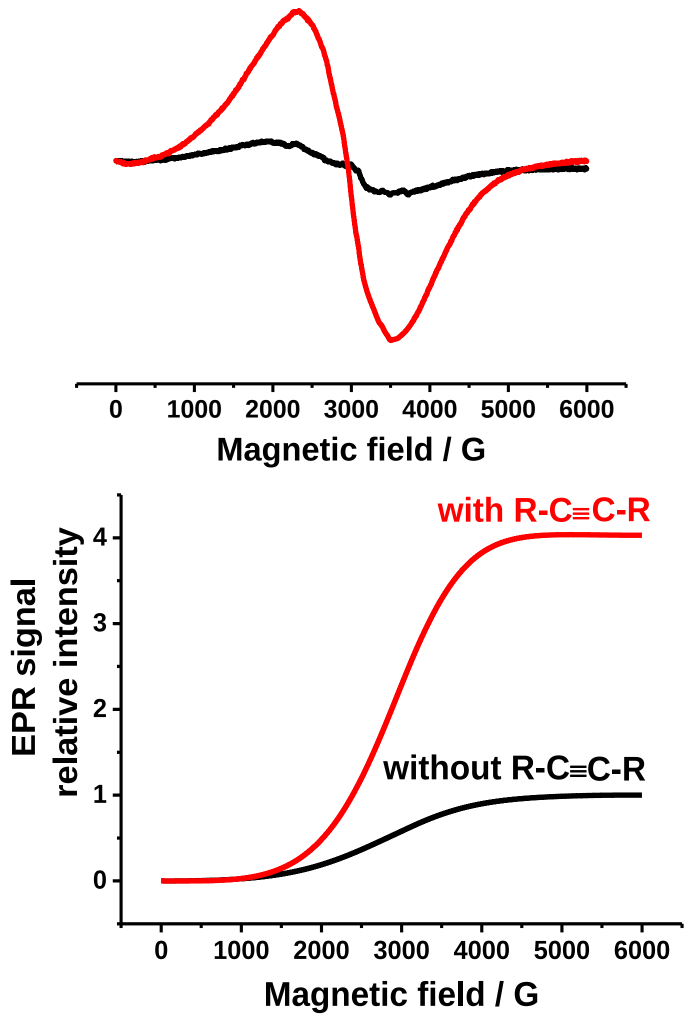
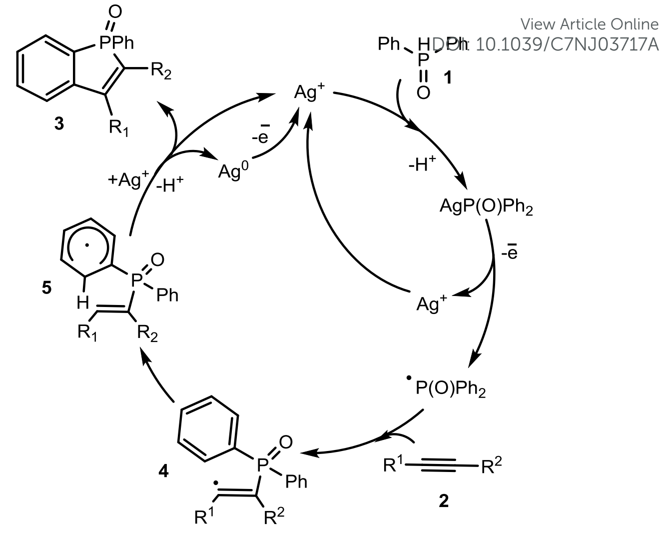


Fig. 4 Comparison of Ag(0) signals in the presence (red) or absence(black) of diphenylacetylene (upper), and the intensities of these signals (lower).

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 give noticeable ESR spectra.

Thus, catalytic cycle on Scheme 3 was suggested based on ESR and CV experiments. The proposed catalytic pathway includes the formation of the $Ph_2P(O)Ag$ at the first step; its oxidation leads to $Ph_2P(O)^{\bullet}$ radical and Ag^+ regeneration. Then the radical addition to the 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**. Ag^0-intermediate is formed in the presence of acetylene at the transient step, as it was detected by ESR. Keeping in mind 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). In contrast to methods from the literature, for example, the Duan protocol,[16] Ag(I) completely regenerates during catalytic cycle, since it is easily oxidized at anode rather than precipitates.



$$(C_6H_5)_2P(O)H + RCCR \xrightarrow{-2\bar{e}} (C_6H_4)P(O)C_6H_5CRCR\ +2H^+$$

Scheme 3 Proposed catalytic cycle

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

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

The ESR spectra were registered on 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 working electrode, platinum filament was used as auxiliary electrode, and Ag/AgCl was used as reference electrode. Prior to each experiment, helium was passed for 5 min through solution in the cell. When passing was complete, the cell was filled with helium. The spectra were registered 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

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separation of the anode and cathode compartments. The potential value of the working electrode was recorded 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 amounted to 48.00 cm^2. A ceramic plate with the pore size of 900 nm was used as a 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 in order to remove any traces of oxygen and other gaseous impurities. $PyHBF_4$ was used as supporting electrolyte.

Electrochemical cell contained 0.4 mmol of diphenylphosphine oxide (CAS 4559-70-0), 0.4 mmol of appropriate acetylene and 0.04mmol of AgOAc in 20 ml of CH_3CN with 0.1 M of PyHBF4, the solution was agitated with a magnetic stirrer. 2 F of electricity per one mole of diphenylphosphine oxide (22 mA for 0.4 mmol) was passed through the solution. The electrolysis potential is 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 electrolysis time is over the reaction mixture was filtered and concentrated under vacuum. Then 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 cyclization products are consistent with the literature data.[16,53] $PyHBF_4$ can be further purified by recrystallization from alcohol and used again.

3a: ^1H 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: ^1H 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: ^1H 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: ^1H 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: ^1H 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: ^1H 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: ^1H 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. ^1H 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 catalyst. The yield of target benzo[b]phosphole oxide is up to 100%. The redox properties of key intermediate were investigated. The oxidation of $Ph_2P(O)Ag$ with the formation of phosphinoyl 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.

Acknowledgements

The work is supported by Russian Science Foundation (grant № 14-23-00016).

Conflicts of interest

There are no conflicts to declare.

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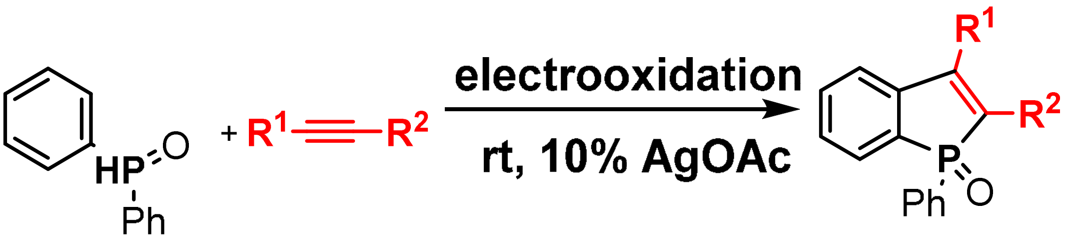
DOI: 10.1039/C7NJ03717A



Electrochemical oxidation synthesis of benzo[*b*]phosphole oxides has been performed at room temperature with catalytic amounts of AgOAc.