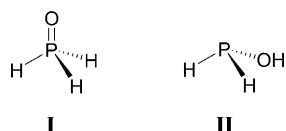


Experimental Evidence of Phosphine Oxide Generation in Solution and Trapping by Ruthenium Complexes**

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In memory of Massimo Di Vaira

Phosphorus oxides, oxyacids, and their esters are important chemicals for industry. Apart from playing a role in most organisms in ruling their energy transformations, they find wide and diverse applications, such as fertilizers, pesticides, herbicides, lubricants, flame retardants, additives for special plastics and materials, and drugs for different diseases.^[1] Little attention has however been paid to lower-oxidation-state species, such as PO, HPO, and P₂O, for which synthetic isolation procedures and even direct evidence of their existence are scarce.^[2] One of the most elusive species in this regard is phosphine oxide, H₃PO (**I**; Scheme 1). This molecule was first observed by reacting atomic oxygen with



Scheme 1. Phosphine oxide (**I**) and its tautomer, phosphinous acid (**II**).

PH₃ using a discharge–flow system equipped with molecular-beam sampling mass spectrometry.^[3] Alternatively, red-light photolysis of co-deposited PH₃/O₃ onto an argon matrix at 12–18 K was used to generate and trap **I** in a very diluted concentration together with its tautomer phosphinous acid H₂P(OH) (**II**), which was identified by FTIR.^[4] Finally, Ault and Kayser observed the formation of H₃PO in argon matrices after photochemical irradiation of a mixture of VOCl₃, CrO₂Cl₂, and PH₃.^[5]

Both molecules have been studied by theoretical methods.^[6] Application of an adequate phosphorus basis set has recently shown that, in contrast with previous ab initio studies,^[7] **I** is more stable than **II** by only about 1 kcal mol⁻¹ in the gas phase.^[8] In contrast, computational analysis in aqueous solution showed that upon solvation **I** is largely preferred by about 10 kcal mol⁻¹ owing to stronger hydrogen bonding with the highly polar P^{δ+}→O^{δ-} bond.^[8] The possible involvement of H₃PO in the oxidative polymerization of phosphine to give polyhydride phosphorus P_xH_y polymers has been also proposed.^[9]

Herein we show that the previously unknown P⁻¹ species H₃PO (**I**) can be easily generated in solution by electrochemical methods, and we provide evidence of its solution stability, its characterization by conventional NMR spectroscopy, and its trapping as a ligand in the coordination sphere of hydrosoluble ruthenium complexes after tautomerization to **II**.

The electrochemical generation of H₃PO was performed in a single electrochemical cell with a lead cathode and a sacrificial zinc anode using P₄ melted in a slightly acidic water/ethanol solution (2:1 volume ratio, water acidified with HCl, 2M) at 60°C (Supporting Information, Figures S1, S2). The overall electrochemical process may be divided in two parts. In the first step, the electrochemical generation of PH₃ on the lead cathode takes place as previously described,^[10,11] while in the second step, mild oxidation of PH₃ to H₃PO occurs at the anodic surface of the zinc electrode. In agreement with cyclic voltammetry experiments showing an irreversible oxidation wave, PH₃ is electrochemically active in the anodic potential range +0.80–1.25 V (vs. Ag/AgNO₃, 0.01M in CHCN₃) and can be therefore oxidized in acidic water/ethanol 2:1 solution to H₃PO (Supporting Information, Figure S3). Scheme 2 shows the overall electrochemical process resulting in the cathodic reduction of P₄ to PH₃ and anodic oxidation of PH₃ to H₃PO ($E = +1.24$ V vs. Ag/AgNO₃, 0.01M in CHCN₃).

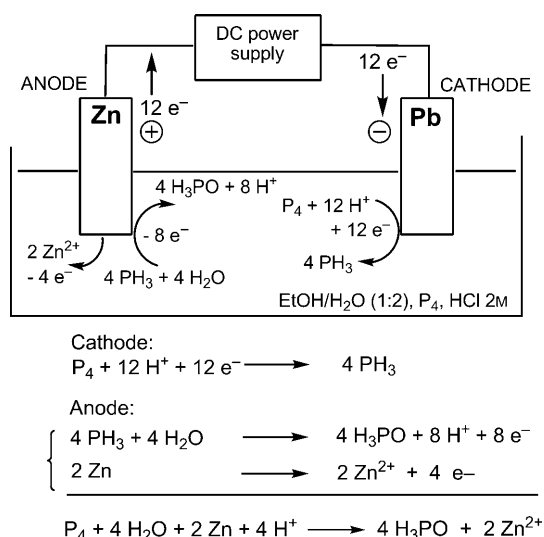
Different working conditions were investigated to optimize the production of H₃PO. The best performance was

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Scheme 2. Electrochemical generation of H₃PO in acidic H₂O/EtOH solution from P₄.

obtained by dissolving 70 mg of solid P₄ in 30 mL of a mixture of water and ethanol 2:1 in the electrochemical cell heated to 60 °C. A current of 150 mA was applied for 30 min, and during this time HCl (2 mL, 2 M) was added. The presence of water played a crucial role: in pure ethanol, only the reduction of P₄ to PH₃ was observed, in keeping with a previous report from Tomilov.^[10]

The optimized process (see the Supporting Information) resulted in the complete conversion of P₄ to three products identified by ³¹P{¹H} NMR signals at $\delta = -243.05$ ppm and $\delta = 4.97$ ppm (Figure 1 a), which were easily attributed to phosphine (PH₃, 15.1 %) and (H₃PO₂, 16.1 %) respectively, while the singlet at $\delta = -17.55$ ppm was assigned to phosphine oxide, H₃PO (68.8 %). Turning off the ¹H decoupler (Figure 1 b) converted the latter singlet into a quartet, as expected for three protons directly bonded to phosphorus (¹J_{PH} = 512.2 Hz).^[12] Moreover, the presence of a clear cross-peak in the ³¹P{¹H}, ¹H HMQC 2D NMR spectrum (Figure 2) showed unambiguously direct bonding between the nuclei giving rise to the ³¹P resonance attributed to H₃PO with the doublet centered at $\delta = 7.00$ ppm (¹J_{PH} = 512.2 Hz).^[13]

Solutions of electrogenerated H₃PO slowly disproportionate to PH₃ and H₃PO₂ [Equation (1)]. At -30 °C, the process is rather slow, and after 20 days at -20 °C the concentration of H₃PO is about half of the original value. At room temperature, the transformation is much faster (*t*_{1/2} ≈ 345 min) and a complete disproportionation to PH₃ and H₃PO₂ occurs in about two days.



Attempts to isolate the phosphine oxide in pure form from the water/ethanol solution were unsuccessful. Removal of all the volatile species, that is, the solvent and PH₃, left an oily residue that, taken with H₂O and analyzed by ³¹P{¹H} NMR spectroscopy, showed the presence of H₃PO together with a variable amount of H₃PO₂, which could not be completely eliminated.

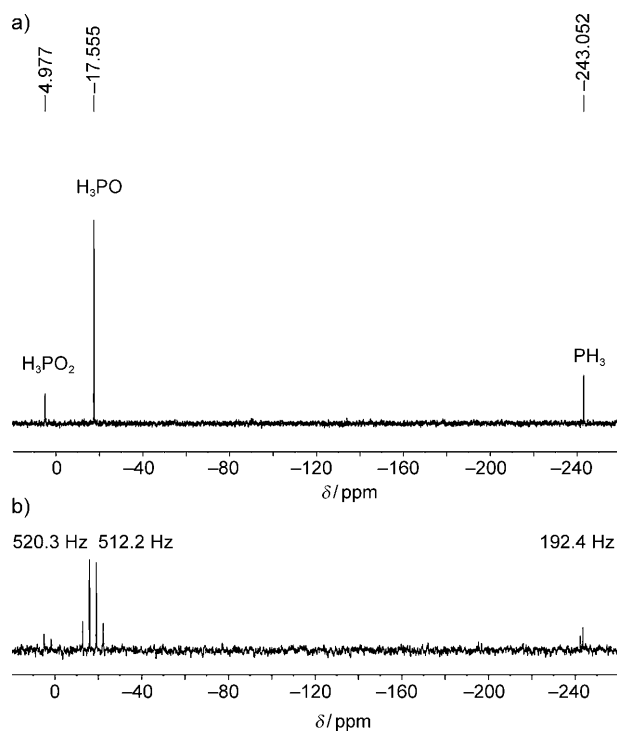


Figure 1. a) ³¹P{¹H} NMR and b) ³¹P NMR spectra (D₂O, RT) of an acidic H₂O/EtOH 2:1 solution of P₄ after electrolysis (30 min).

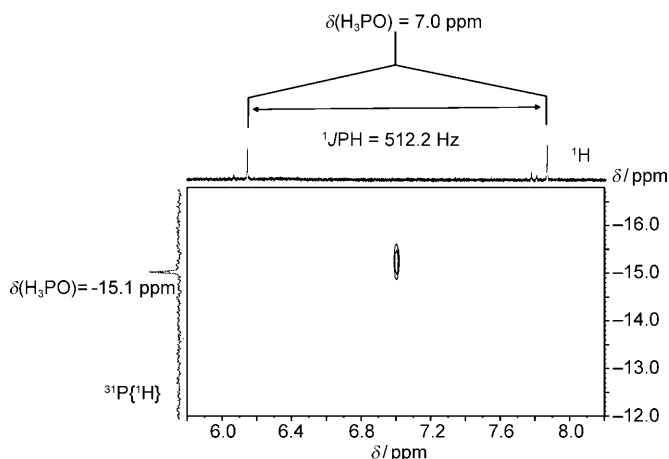
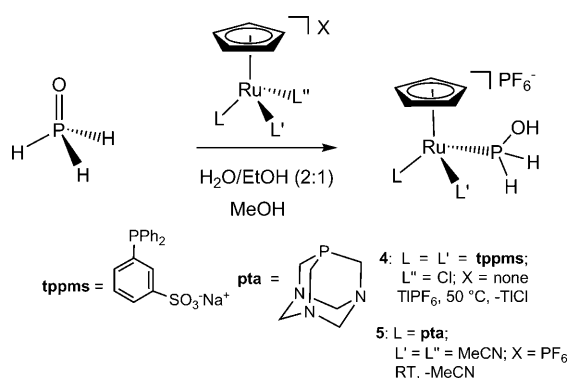


Figure 2. Section of the ³¹P{¹H}-¹H HMQC (phase-sensitive, with pre-saturation) 2D NMR spectrum (161.97 MHz, 25 °C) of the electrolyzed solution of P₄ in H₂O/EtOH 2:1 obtained in an Evans tube containing D₂O. The ¹H NMR spectrum was recorded using a WATERGATE (water suppression by gradient-tailored excitation) pulse sequence to suppress the H₂O peak at $\delta = 4.9$ ppm.

Confirmation for the electrochemical generation of **I** was obtained by trapping this molecule as a thermally stable derivative. A perusal of the literature available on the metal-mediated reactivity of white phosphorus^[14] indicated that the ruthenium(II) complex [CpRu(PPh₃)₂Cl] (**1**) is able, after chloride removal, to coordinate both white phosphorus and phosphine,^[15] and also to stabilize the hydrolysis products of coordinated P₄,^[16] including the lower phosphorus oxyacids H₃PO₂ and H₃PO₃.^[17] These can work as ligands following

ruthenium-promoted isomerization to the phosphine-like tautomers $\text{PH}(\text{OH})_2$ and $\text{P}(\text{OH})_3$, respectively.^[17] Thus, we reasoned that a water-soluble version of complex **1** could react with a water/ethanol solution of the electrogenerated H_3PO by stabilizing the putative phosphinous acid, $\text{H}_2\text{P}(\text{OH})$, assisting the energetically favored H_3PO tautomerization at ruthenium.

In keeping with this working hypothesis, reaction of crude **1** with the ruthenium complexes $[\text{CpRu}(\text{tppms})_2\text{Cl}]^{[\text{18}]}$ (**2**) [Cp = cyclopentadienyl, $\text{tppms} = m\text{-SO}_3\text{C}_6\text{H}_4\text{PPh}_2^{(-)}\text{Na}^{(+)}$] and $[\text{CpRu}(\text{pta})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (**3**)^[19] ($\text{pta} = 1,3,5\text{-triazadiazaphosphadamantane}$) gave as products the organometallic complexes $[\text{CpRu}(\text{tppms})_2\{\text{H}_2\text{P}(\text{OH})\}]\text{PF}_6$ (**4**) and $[\text{CpRu}(\text{pta})(\text{CH}_3\text{CN})\{\text{H}_2\text{P}(\text{OH})\}]\text{PF}_6$ (**5**) after simple workup (Scheme 3; see the Supporting Information for details).^[20]



Scheme 3. Synthesis of $[\text{CpRu}(\text{tppms})_2\{\text{H}_2\text{P}(\text{OH})\}]\text{PF}_6$ (**4**) and $[\text{CpRu}(\text{pta})(\text{CH}_3\text{CN})\{\text{H}_2\text{P}(\text{OH})\}]\text{PF}_6$ (**5**) from H_3PO trapping.

The formation of complexes **4** and **5** confirmed that the electrogenerated phosphine oxide may be trapped before disproportionation by coordination of its tautomer, $\text{H}_2\text{P}(\text{OH})$, to ruthenium. Both compounds were characterized by ESI-MS, IR and NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a triplet centered at $\delta = 70.3$ ppm for **4** ($^2J_{\text{PP}} = 51.3$ Hz), while that of **5** has a doublet at $\delta = 74.1$ ppm ($^2J_{\text{PP}} = 63.0$ Hz) for the coordinated phosphinous acid. Switching off the proton decoupler gave triplets with identical $^1J_{\text{PH}}$ couplings (366.0 Hz), thus providing confirmation for a $\text{H}_2\text{P}(\text{OH})$ coordinated species. Complexes **4** and **5** are the first compounds incorporating phosphinous acid and may be related to the crystallographically authenticated sulfur analogue, that is, $[\text{CpRu}(\text{PPh}_3)_2\{\text{H}_2\text{P}(\text{SH})\}]\text{PF}_6$ (**6**), obtained by controlled hydrolysis of the P_4S_3 dinuclear sandwich complex $[\{\text{CpRu}(\text{PPh}_3)_2\}_2(\mu, \eta^{1,1}\text{-P}_{\text{ap}}, \text{P}_{\text{bas}}\text{-P}_4\text{S}_3)](\text{PF}_6)_2$.^[21] Both **4** and **5** are air-stable orange microcrystalline materials that share most of their chemophysical properties with **6** and the other known $[\text{CpRu}(\text{PPh}_3)_2\{\text{PH}_{(3-x)}(\text{OH})_x\}]^+$ derivatives ($x = 2, 3$).^[17]

In conclusion, the elusive and poorly investigated phosphine oxide H_3PO (**1**) has been generated by simple electrochemical methods based on a two-step process involving first the electroreduction of white phosphorus to PH_3 in an acidic water/ethanol mixture at a lead electrode, followed by PH_3 oxidation at the zinc anode yielding H_3PO in about 70 %

maximum yield. Spontaneous disproportionation of **1** to PH_3 and H_3PO_2 acid takes place even at low temperature and hampers the isolation of H_3PO as a pure product. Nonetheless, H_3PO , the first defined compound of phosphorus in the -1 oxidation state, was characterized in solution by NMR spectroscopy and trapped in the coordination sphere of ruthenium(II) by tautomerization to phosphinous acid, $\text{H}_2\text{P}(\text{OH})$, to afford stable organometallic cationic complexes. Studies are in progress to explore the reactivities of both free H_3PO and coordinated $\text{H}_2\text{P}(\text{OH})$.

Experimental Section

CAUTION: Both white phosphorus and phosphine are very toxic, flammable, and hazardous compounds (see the Supporting Information).

H_3PO was electrogenerated in a 50 mL home-made electrochemical cell (see Supporting Information for details).^[22] White phosphorus (70 mg, 0.56 mmol) was suspended in $\text{H}_2\text{O}/\text{EtOH}$ 2:1 (30 mL) and warmed to 60°C under nitrogen to ensure dissolution (ca. 30 min). HCl (0.5 mL, 2 M) was then added to the mixture and an electrical current with intensity $i = 150$ mA (current density 5.0 mA cm^{-2}) was applied for about 30 min while keeping the temperature constant at 60°C . During the experiment, the mixture became cloudy and a yellowish suspension formed. Further addition of HCl (1.5 mL, 2 M) and vigorous stirring at 60°C gave an almost colorless solution. The overall potential on the cell was -1.5 – 2.5 V.

A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of an aliquot showed complete conversion of P_4 into PH_3 , H_3PO , and H_3PO_2 , with signals at $\delta(\text{PH}_3) = -243.05$ ppm (s); $\delta(\text{H}_3\text{PO}) = -17.55$ ppm (s); $\delta(\text{H}_3\text{PO}_2) = 4.97$ ppm (s). The relative amount depends from several factors such as reaction time, temperature, and acidity. In the experiment described above, the highest production of H_3PO was obtained with the following ratios: PH_3 (15.1%), H_3PO (68.8%), and H_3PO_2 (16.1%).

Synthesis of $[\text{CpRu}(\text{tppms})_2\{\text{H}_2\text{P}(\text{OH})\}]\text{PF}_6$ (**4**): $[\text{CpRu}(\text{tppms})_2\text{Cl}]$ (**2**, 28 mg, 0.0301 mmol) was dissolved in dry MeOH (15 mL) and reacted with one equiv of solid TIPF_6 (10.5 mg, 0.0301 mmol) at room temperature under stirring. After 4 h, the solution was filtered by cannula to remove TiCl , giving a clear yellow solution of $[\text{CpRu}(\text{tppms})_2(\text{CH}_3\text{OH})]\text{PF}_6$. A $\text{H}_2\text{O}/\text{EtOH}$ 2:1 solution (14.0 mL) of H_3PO , prepared as described above, was transferred to a Schlenk flask and evaporated under vacuum to half of the volume to remove the solvent and the volatiles (PH_3). The resulting colorless solution, containing only H_3PO (70%) and H_3PO_2 (30%), was then added dropwise to the solution of $[\text{CpRu}(\text{tppms})_2(\text{CH}_3\text{OH})]\text{PF}_6$, and the stirred suspension was warmed to 50°C for 1 h, after which a clear yellow solution was obtained. Evaporation of the solvent to dryness left a yellow solid, which was washed with Et_2O (2×5 mL) and filtered under vacuum. Yield 19.6 mg (60%, based on complex **2**). H_3PO_2 is left unreacted, as formation of $[\text{CpRu}(\text{tppms})_2\{\text{PH}(\text{OH})_2\}]\text{PF}_6$ (**4c**) was not observed. See the Supporting Information for an independent synthesis of **4c** and $[\text{CpRu}(\text{TPPMS})_2(\text{PH}_3)]\text{PF}_6$ (**4b**).

^1H NMR (400.13 MHz, CD_3OD , 20°C): $\delta = 4.6$ (s, Cp, 5H), 6.9–8.2 ppm (m, aromatic, 28H). The signal for to the two $\text{H}_2\text{P}(\text{OH})$ protons could not be directly observed as it is masked by the aromatic proton signals, but it was identified indirectly by ^1H , ^{31}P HMQC 2D-NMR, which correlated the phosphorus resonance with a doublet at ca. 7.5 ppm ($^1J_{\text{HP}} = 366.0$ Hz; Supporting Information, Figure S6). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.97 MHz, CD_3OD , 20°C): $\delta = 70.3$ (t, $^2J_{\text{PP}} = 51.3$ Hz, $\text{H}_2\text{P}(\text{OH})$), 46.7 (d, $^2J_{\text{PP}} = 51.3$ Hz, tppms), -145.1 ppm (sept, $^1J_{\text{PF}} = 705.9$ Hz, PF_6); ^{31}P NMR (161.97 MHz, CD_3OD , 20°C): $\delta = 70.3$ (tt, $^1J_{\text{HP}} = 366.0$ Hz, $^2J_{\text{PP}} = 51.3$ Hz, $\text{H}_2\text{P}(\text{OH})$), 46.7 (br d, $^2J_{\text{PP}} = 51.3$ Hz, tppms), -145.1 ppm (sept, $^1J_{\text{PF}} = 705.9$ Hz, PF_6). IR

(MeOH): $\nu(\text{POH})$ 2488 (m), $\nu(\text{PH})$ 2240 (w), $\nu(\text{P=O})$ 1250 (s), $\nu(\text{SO}_3)$ 1191 (vs), $\nu(\text{PF}_6)$ 854 cm^{-1} (s). ESI-MS: $\text{C}_{41}\text{H}_{36}\text{O}_7\text{P}_3\text{S}_2\text{Ru}$, m/z 899, $m/z - \text{H}_2\text{P}(\text{OH})$ 848.9.

Complex **5** was similarly prepared using $[\text{CpRu}(\text{pta})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (**3**) instead of **2** (see the Supporting Information).

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