Oxidizing Agents

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Hydrogen Peroxide and Di(hydroperoxy)propane Adducts of Phosphine Oxides as Stoichiometric and Soluble Oxidizing Agents

*Shin Hye Ahn, Kyle J. Cluff, Nattamai Bhuvanesh, and Janet Blümel**

Abstract: *Aqueous hydrogen peroxide is widely used as an oxidizing agent in industry and academia. Herein, the hydrogen peroxide adducts of phosphine oxides, $[tBu_3PO{\cdot}H_2O_2]_2$ and $[Ph_3PO{\cdot}H_2O_2]_2{\cdot}H_2O_2$, are described. Additionally, the corresponding di(hydroperoxy)propane adducts $R_3PO{\cdot}(HOO)_2CMe_2$ (R = Cy, Ph) were synthesized and characterized. All adducts could be obtained as large single crystals suitable for structural characterization by X-ray crystallography and solid-state NMR spectroscopy. The di(hydroperoxy)propane adducts are soluble in organic solvents which enables oxidation reactions in one phase. As the adducts are solid and molecular, they can easily be applied stoichiometrically. No loss of oxidizing power occurs upon long-term storage of the single crystals at room temperature or the powders at −20 °C.*

Hydrogen peroxide (H_2O_2) is a very important reagent for oxidation reactions in organic syntheses.[1] For example, Baeyer–Villiger oxidations,[2,3] sulfide oxidation processes,[4–6] and epoxidation reactions[7–9] are mainly performed using H_2O_2. Most importantly, since the rise of the new propylene oxide processes that use aqueous H_2O_2 as the oxidant, the reagent has become such an important commodity that world consumption has surpassed 2 million tons per year.[1a] Reactions with H_2O_2 are very selective and efficient, with fast and quantitative reactions taking place at low temperatures. Additionally, many oxidation reactions with H_2O_2, for example, the transformation of phosphines to their oxides,[10] do not require any catalyst.

Aqueous H_2O_2 is an enticing oxidizing agent in industrial settings because it is cheap, available on a large scale, and it can be applied in concentrations up to 85 wt %. Its major drawback, however, remains the water byproduct. Aqueous H_2O_2 solutions used in modern industrial processes are very pure and stable, with typical decomposition rates of 1 % per year. On the other hand, in academic settings 30 wt % aqueous solutions are usually purchased as a compromise between potency and safety regulations. In practice, with many users aqueous H_2O_2 decomposes at unpredictable rates, and the solutions have to be titrated[11] prior to each application when exact stoichiometry is needed. Furthermore, in cases where the reagents are not soluble in water, the oxidation has to be performed in a biphasic system, which entails a slow reaction at the phase boundary and a requirement for phase separation at the workup stage.

Different formulations of H_2O_2 are also in use, for example, urea hydrogen peroxide (UHP) adducts.[12] However, the UHP adducts are not stoichiometric in nature, and urea and water have to be removed after the reaction. Alternatively, alkali metal peroxocarbonates have been applied,[13–15] but like UHP, they are caustic. Unfortunately, H_2O_2 is much less stable under basic conditions. Additionally, many oxidations performed with H_2O_2 are cocatalyzed by acids.[1a] Besides these materials, encapsulated[16] and immobilized versions of hydrogen peroxide are known.[17,18] Again, the stoichiometry of these materials is not very well defined. Furthermore, H_2O_2 adducts of metal complexes have been characterized.[19] Organic and silicon-containing peroxides are important, but can be difficult to synthesize and remove from reaction mixtures.[20] Recently, bishydroperoxides have also received some attention.[21]

The ideal oxidizing agent is an easy to synthesize, solid, and molecular H_2O_2 adduct of reproducible stoichiometry that is soluble in organic solvents. Herein, we probe molecular H_2O_2 adducts of phosphine oxides. These adducts, in contrast to UHP[12] and alkali metal peroxocarbonates,[13–15] are only moderate Lewis bases, and they could also function as ligands for Mo or W centers in oxidation reactions,[22] therewith playing a dual role. The $P{:}H_2O_2$ ratio in the compounds is also investigated to determine whether the ratio, recently defined for the adduct $[Cy_3PO{\cdot}H_2O_2]_2$ by an X-ray crystal structure,[10] remains the same for different phosphine oxides. Next, a new class of oxidizing agents, di(hydroperoxy)propane adducts of phosphine oxides ($R_3PO{\cdot}(HOO)_2CMe_2$), are characterized. This characterization includes the quantification of their oxidative strengths, shelf lives under various conditions, and their solubilities in organic solvents. The general nature of the structures and their stoichiometric composition are also investigated. The potential of the adducts $R_3PO{\cdot}(HOO)_2CMe_2$ (R = Cy, Ph) as oxidizing agents for sulfide oxidations[23] is described.

To probe whether $[R_3PO{\cdot}H_2O_2]_2$ represents a general composition of hydrogen peroxide adducts of phosphine oxides, analogous compounds with different substituents (R = *t*Bu, Ph) have been synthesized as described previously.[10] The adduct $[tBu_3PO{\cdot}H_2O_2]_2$ (**1**) crystallized as a dimer with two H_2O_2 molecules hydrogen-bonded between two phosphine oxide groups in a chair conformation (Figure 1).[24] The tendency of P=O groups to form hydrogen bonds to H_2O_2 molecules,[10] H_2O, and silanols[25] has been described. Recently, hydrogen bonding between P=O and phenol OH groups has also been used to create dimeric motifs.[26]

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[*] S. H. Ahn, K. J. Cluff, Dr. N. Bhuvanesh, Prof. J. Blümel
Department of Chemistry, Texas A&M University
P.O. Box 30012, College Station, TX 77842-3012 (USA)
E-mail: bluemel@tamu.edu
Homepage: http://www.chem.tamu.edu/rgroup/bluemel

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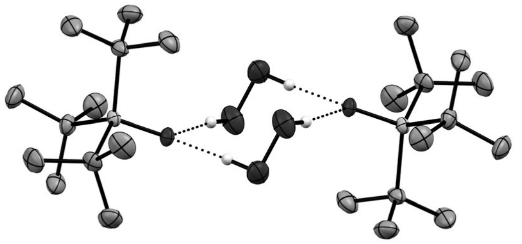


Figure 1. Single-crystal X-ray structure of $[t\mathrm{Bu_3PO{\cdot}H_2O_2}]_2$ (**1**).[24] Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

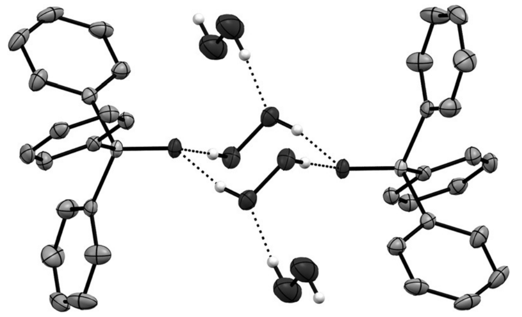
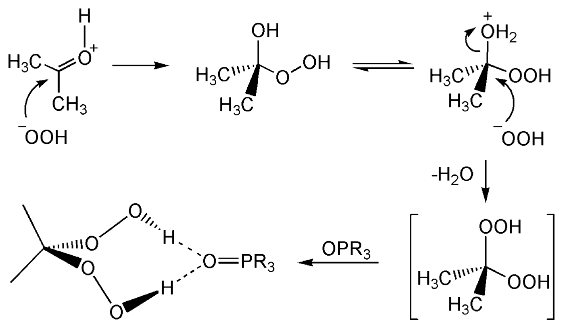


Figure 2. Single-crystal X-ray structure of $[\mathrm{Ph_3PO{\cdot}H_2O_2}]_2{\cdot}\mathrm{H_2O_2}$ (**2**).[24] The top H_2O_2 molecule belongs to the neighboring unit cell. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

Triarylphosphine oxide adducts differ in structure to that of **1**, and they can even lead to different adduct structures and stoichiometries for one given triarylphosphine oxide. For example, an adduct of Ph_3PO has been described earlier and its composition has been determined as $(\mathrm{Ph_3PO})_2{\cdot}\mathrm{H_2O_2}$ with H_2O_2 bridging two Ph_3PO molecules.[27] Our attempt to reproduce this result led to the formation of the new adduct $[\mathrm{Ph_3PO{\cdot}H_2O_2}]_2{\cdot}\mathrm{H_2O_2}$ (**2**; Figure 2).[24] Most probably, due to the rigid nature and sterics of the phenyl groups, additional H_2O_2 molecules can be accommodated in the space between the dimers.

Although the adducts **1** and **2** are active oxidizing agents, our search for molecular oxidants with known and reproducible numbers of active oxygen atoms led us to the preparation of the new di(hydroperoxy)propane adducts $\mathrm{Cy_3PO{\cdot}(HOO)_2CMe_2}$ (**3**; Cy = cyclohexyl) and $\mathrm{Ph_3PO{\cdot}(HOO)_2CMe_2}$ (**4**). Both compounds are obtained in nearly quantitative yield (see the Experimental Procedures in the Supporting Information) as giant crystals (Supporting Information, Figure S1) when the phosphine oxides are combined with aqueous H_2O_2 in the presence of acetone at ambient temperatures. Interestingly, the bishydroperoxides form without addition of a strong acid or catalyst.[21] A mechanism for the formation of **3** and **4** is proposed in Scheme 1. No triacetone triperoxide is generated in the process and it also does not form upon long-term storage of **3** or **4**.



Scheme 1. Suggested mechanism for the formation of the adducts $\mathrm{R_3PO{\cdot}(HOO)_2CMe_2}$. R = Cy (**3**), Ph (**4**).

To obtain dry compounds without decomposing the peroxide groups, the generated water is removed as an azeotropic mixture with ethanol under a mild vacuum at room temperature. The IR spectra of **3** and **4** (Figure S2) confirm that no water is present, which would manifest itself as a broad absorption at $3400\,\mathrm{cm^{-1}}$.[10] The IR ν(P=O) value ($1125\,\mathrm{cm^{-1}}$) is lower than that of adduct-free trialkylphosphine oxides ($1153\,\mathrm{cm^{-1}}$),[10] because the hydrogen bonds in **3** weaken the P=O double bond. The band is very narrow, indicating the well-defined and molecular nature of the adduct **3** (Figure S2). Accordingly, the ^{31}P NMR signals for **3** and **4** ($\delta = 55.59$ and 34.74 ppm) are shifted to lower field compared to Cy_3PO and Ph_3PO ($\delta = 49.91$ and 29.10 ppm).[10] In contrast to **1** and **2**, the di(hydroperoxy)propane adducts **3** and **4** possess diagnostic ^{13}C NMR signals for the quaternary carbons at $\delta = 108.91$ and 109.28 ppm.

X-Ray structures of the adducts **3** and **4** (Figure 3 and 4)[24] confirm that each P=O group forms two hydrogen bridges to one di(hydroperoxy)propane moiety. This means that there are two active oxygen atoms per P=O group, and thus the oxidative power (see below) is twice as high as for **1**.

Both adducts **3** and **4** could easily be obtained as very large single crystals (Figure S1). This rare opportunity[25,29] could be seized to perform single-crystal solid-state NMR measurements of **4**. The chemical shift anisotropy (CSA) obtained from the span of the ^{31}P wide-line NMR spectrum of polycrystalline **4** amounts to 166 ppm (Figure S3). Figure 5 displays the ^{31}P CP (cross-polarization) NMR spectra of

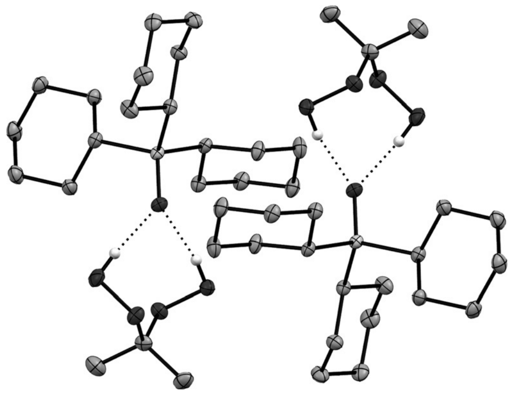


Figure 3. Single-crystal X-ray structure of $\mathrm{Cy_3PO{\cdot}(HOO)_2CMe_2}$ (**3**) showing two independent molecules.[24] Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

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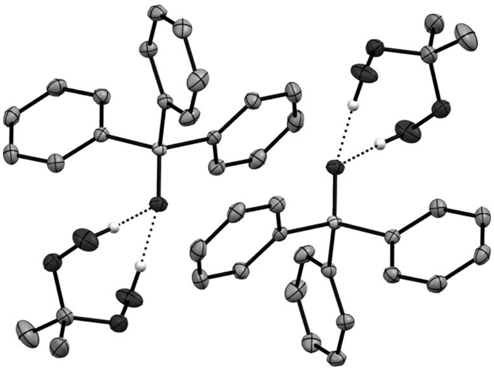

Figure 4. Single-crystal X-ray structure of $Ph_3PO{\cdot}(HOO)_2CMe_2$ (**4**) showing two independent molecules.[24] Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

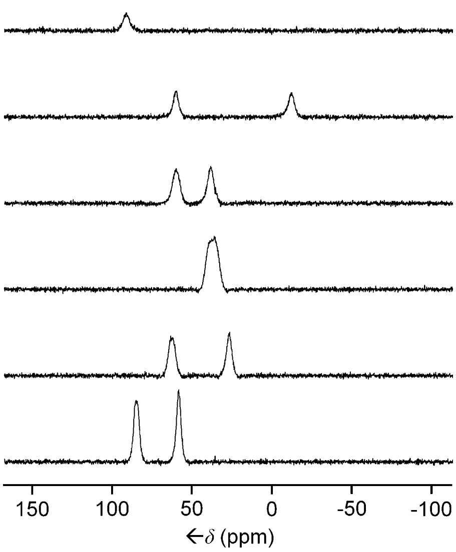

Figure 5. ^{31}P CP NMR spectra of a large single crystal of **4** at different random orientations with respect to the external magnetic field.

a single crystal of $Ph_3PO{\cdot}(HOO)_2CMe_2$ recorded with different orientations. Two signals, corresponding to two magnetically inequivalent ^{31}P nuclei in the unit cell, are obtained. The chemical shift changes of the two signals with the orientation of the crystal in the magnetic field is different, as described for other cases.[25,29]

To increase the number of active oxygen atoms per phosphine oxide mass and to probe the general structure of the di(hydroperoxy)propane adducts, 1,2-bisdiphenylphosphinoethane (dppe) was treated with acetone and aqueous H_2O_2. The expected di(hydroperoxy)propane adduct $[CH_2Ph_2PO{\cdot}(HOO)_2CMe_2]_2$ (**5**) was obtained. The X-ray structure of (**5**)[24,28] (Figure S4) matches the structural trend evident in **3** and **4** (Figure 3 and Figure 4).[24]

One of the most important advantages of the di(hydroperoxy)propane adducts of phosphine oxides with respect to their application as oxidizing agents is that they are very soluble in organic solvents, rendering biphasic reaction mixtures obsolete. The solubilities of **3** and **4** in representative organic solvents have been quantified (Figure 6; Table S1).

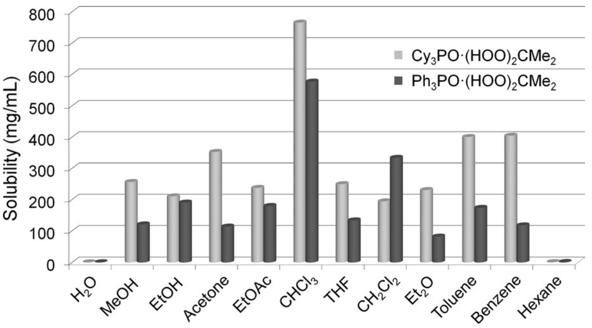

Figure 6. Solubilities of adducts $Cy_3PO{\cdot}(HOO)_2CMe_2$ (**3**) and $Ph_3PO{\cdot}(HOO)_2CMe_2$ (**4**) in representative solvents.

The solubilities of the compounds are remarkably high in chloroform, with 0.77 and 0.57 $g\,mL^{-1}$ for **3** and **4**, respectively. Importantly, the compounds are substantially soluble even in the aromatic solvents toluene and benzene.

We next probed the safety of the oxidizing reagents. The decomposition temperatures of neat **3** and **4**, with onset temperatures of 70 and 75 °C, respectively, are lower than those of the analogous H_2O_2 adducts (Table S2). However, it should be noted that no explosive triacetone triperoxide or other oligomers are formed during the decomposition. The adducts **3** and **4** have also been tested by applying mechanical stress. No sudden release of oxygen occurred during forceful grinding of the pure powders. This may be due to the low weight % of active oxygen in the molecules, which is 7.9% for $Cy_3PO{\cdot}(HOO)_2CMe_2$ and 8.3% for $Ph_3PO{\cdot}(HOO)_2CMe_2$. The ^{31}P NMR spectra before and after grinding only showed the starting materials. Thermogravimetric analyses (TGA) indicated that the di(hydroperoxy)propane moieties, as a whole or in fragments, are lost in one step upon heating, leaving the phosphine oxides behind.

Next, a straightforward standardized in situ test was developed to determine the number of active oxygen atoms per adduct in the starting material and assess the shelf lives of **3** and **4**. For this purpose, for example, a weighed amount of $Cy_3PO{\cdot}(HOO)_2CMe_2$ in a defined volume of solvent was placed into an NMR tube equipped with a centered capillary containing neat Ph_2PCl as the chemical shift and intensity standard. Then a weighed amount of Ph_3P in slight excess was added. The oxidation to Ph_3PO[30] was selective and instantaneous and a routine ^{31}P NMR spectrum with a sufficiently long relaxation delay (35 s) was subsequently recorded. The number of active oxygen atoms per adduct $Cy_3PO{\cdot}(HOO)_2CMe_2$ could be determined from the intensity ratio of the signals of residual Ph_3P and Ph_3PO. Adducts **3** and **4** contain two active oxygen atoms each, and the only reaction products are the water adducts of the phosphine oxides[10,25] and acetone. Oxidation of trialkylphosphines with **1**–**4** yields the corresponding phosphine oxides but with no oxygen insertion into P–C bonds, as observed with air as oxidant.[10]

This method was also used to probe the long-term stability of powders of **3** and **4** (Figure 7; Figure S5). At −20 and 4 °C, both adducts retain their oxidative power over months. Exposure to light did not influence the decomposition, whereas the temperature played a dominant role. Further-

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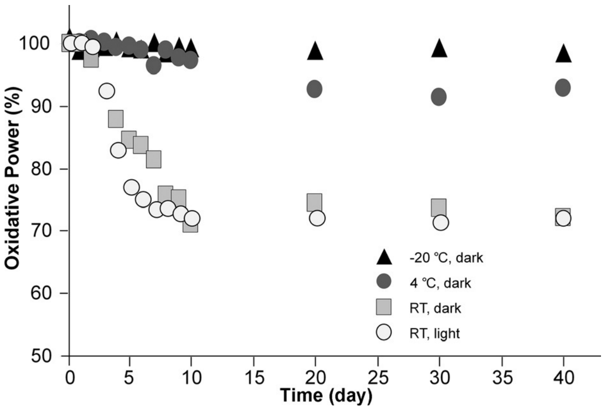

Figure 7. Oxidative power of $Cy_3PO{\cdot}(HOO)_2CMe_2$ (**3**) after being stored under the indicated conditions. 100% oxidative power is equivalent to 2 moles of active oxygen per mole of **3**.

more, the exposed surface area of the materials made a difference. For example, large crystals ($3\times3\times1$ mm^3) of **3** retained 99% oxidative power after 100 days exposed to the ambient atmosphere and light at room temperature. Under these conditions, the polycrystalline materials retain 60 to 70% of their oxidative power over several months. Since the surface area plays a role, it might be assumed that acetone and H_2O_2 (boiling point 150.2 °C) evaporate over time. ^{13}C NMR spectra of the exposed material indicate that indeed acetone is gradually lost.

Even in solution, the di(hydroperoxy)propane adducts **3** and **4** are remarkably stable in the absence of a reducing agent. For example, heating a benzene solution of **4** to 90 °C and monitoring the solution with ^{13}C NMR spectroscopy showed that 3 days were necessary to decompose about 80% of **4**. The main products were $Ph_3PO{\cdot}H_2O$[10,25] and acetone in addition to traces of isopropanol, formic acid, and acetic acid. After one day a transient species with low intensity signals at $\delta = 109.44$ and 21.24 ppm was visible that could either be assigned to $(HO)_2CMe_2$, or $(HOO)(HO)CMe_2$, hydrogen bonded to Ph_3PO.

In addition to the use of **3** and **4** in the classical organic syntheses mentioned above, another important application targets sulfide oxidation.[7–9,31] When **3** or **4** were combined with THT (tetrahydrothiophene) in a molar ratio of 1:2 in benzene, THT was selectively and quantitatively oxidized to the sulfoxide at ambient temperatures within two hours. The only other reaction products were acetone and the corresponding phosphine oxides of **3** and **4**. The water molecule remained firmly hydrogen bonded to the phosphine oxide group.[10,25] This fast and clean reaction in one organic phase compares favorably to earlier studies which required biphasic mixtures and added catalysts.[7–9]

In summary, we report herein a number of key results and observations. a) We demonstrated that the H_2O_2 adducts of trialkylphosphine oxides crystallize readily and reproducibly in a dimeric structure with a chair-type arrangement of the H_2O_2 moieties. Interestingly, triarylphosphine oxide adducts can be composed with different numbers of H_2O_2 molecules. b) When phosphines or phosphine oxides are treated with aqueous H_2O_2 in the presence of acetone, the di(hydroperoxy)propane adducts **3** and **4** are obtained in high yields without addition of acids or catalysts. Their large single crystals are amenable to X-ray and solid-state NMR analyses. Even chelating phosphine oxides reproducibly result in one di(hydroperoxy)propane moiety per phosphine oxide group (**5**). c) Both peroxy groups in **3** and **4** each release one active oxygen atom. d) All adducts are safe and robust towards mechanical stress and elevated temperatures. Large crystals have shelf lives of months at ambient temperature. e) The described adducts are very soluble in representative organic solvents, allowing oxidation reactions in a single organic phase. f) Adducts **3** and **4** selectively oxidize phosphines instantaneously and THT within two hours, respectively, in organic phases at room temperature. g) The oxidation reactions are well-defined because of the stoichiometric nature and ease of administration of the oxidizing agents. h) The H_2O formed in the oxidation reactions remains strongly bound to the phosphine oxides and is less prone to provoke unwanted follow-up reactions than the excess of H_2O in an aqueous solution. i) The phosphine oxides as coproducts of the oxidation reactions are inert. As previous work showed, one option for the removal of the phosphine oxides from the reaction mixtures is the strong but reversible adsorption on solid oxide materials, such as molecular sieves or silica.[10,25] Once the phosphine oxides are retrieved from the support by washing with polar solvents,[25] they can be reused after being "recharged" with acetone/aqueous H_2O_2 to form **1**, **3**, or **4**.

In conclusion, this contribution describes an important new class of materials that has bright future prospects, with the potential to make a significant impact in diverse fields of synthetic chemistry. The ease of handling, transport, and storage of the described di(hydroperoxy)propane adducts render them attractive oxidizing agents. In future work our highest priority will be generating silica-immobilized versions for recycling of the phosphine oxide carrier, and to probe the potential of these new oxidizing agents for different applications.

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[24] CCDC 1033533 (**1**), 1033531 (**2**), 1033530 (**3**), 1033532 (**4**), and 1044831 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Unit cell parameters for $C_{12}H_{27}O_1P_1\cdot H_2O_2$ (**1**): $a = 8.266(2)$, $b = 15.032(4)$, $c = 12.467(4)$, space group $= P2_1/n$; for $(C_{18}H_{15}O_1P_1)_2\cdot(H_2O_2)_3$ (**2**): $a = 9.6284(3)$, $b = 16.8881(6)$, $c = 10.9317(4)$, space group $= P2_1/n$; for $(C_{18}H_{33}O_1P_1)\cdot(C_3H_8O_4)$ (**3**): $a = 10.158(3)$, $b = 10.645(3)$, $c = 11.169(3)$, space group $= P\bar{1}$; for $(C_{18}H_{15}O_1P_1)\cdot(C_3H_8O_4)$ (**4**): $a = 9.1646(19)$, $b = 21.719(5)$, $c = 10.053(2)$, space group $= P2_1/n$; for $[(C_{26}H_{24}O_2P_2)\cdot(C_3H_8O_4)_2]$ (**5**): $a = 10.8389(17)$, $b = 19.838(3)$, $c = 15.277(2)$, space group $= P2_1/c$.

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