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Authors: Janet Bluemel, Shin Hye Ahn, and Nattamai Bhuvanesh

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Di(hydroperoxy)alkane Adducts of Phosphine Oxides: Safe, Solid, Stoichiometric, and Soluble Oxidizing Agents

Shin Hye Ahn,[a] Nattamai Bhuvanesh[a] and Janet Blümel*[a]

Abstract: The di(hydroperoxy)alkane adducts of phosphine oxides $Ph_3PO{\cdot}(HOO)_2CMe_2$ (**1**), $Cy_3PO{\cdot}(HOO)_2CMe_2$ (**2**), $Ph_3PO{\cdot}(HOO)_2CMeEt$ (**3**), $Cy_3PO{\cdot}(HOO)_2CMeEt$ (**4**), $Cy_3PO{\cdot}(HOO)_2CEt_2$ (**5**), $Cy_3PO{\cdot}(HOO)_2C(CH_2)_5$ (**6**), and $Cy_3PO{\cdot}(HOO)_2CMePh$ (**7**), $(Ph_2P(O)CH_2CH_2P(O)Ph_2){\cdot}((HOO)_2CEt_2)_2$ (**8**), and $Ph_2P(O)CH_2P(O)Ph_2{\cdot}(HOO)_2CMe_2$ (**9**), are synthesized and fully characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy. Single crystal X-ray structures are reported for **3**-**9**. Different one-pot synthetic pathways, starting from R_3P, R_3PO, $R_3PO{\cdot}H_2O$, and $R_3PO{\cdot}H_2O_2$ are explored and discussed and a mechanism for the formation of the di(hydroperoxy)alkane adducts of phosphine oxides is suggested. The longevity of the adducts is tested by monitoring the oxidation of Ph_3P with quantitative NMR. The solubilities of the adducts in organic solvents are presented, and their applicability as stoichiometric oxidizing agents for the selective oxidation of sulfides to sulfoxides is reported.

Introduction

Oxidation reactions are crucial for many synthetic processes, and various inorganic and organic peroxides, either solo or in the presence of catalysts play a central role.[1] Recent examples include the oxidation of amines to amides,[2] alkane activation,[3] and epoxidation reactions.[4] Additionally, the selective oxidation of sulfides to sulfones[5-7] and the classical Baeyer-Villiger oxidations are important in academia as well as industry.[8]

Many other groups study the practical and theoretical aspects of the transformation of phosphines to their oxides, and *vice versa*, which do not need any catalyst.[9-11] The interest of our group in phosphines and phosphine oxides stems from the application of the former for immobilizing homogeneous catalysts on solid supports,[12] and the analysis of P(V) surface species that come into existence under unfavorable immobilization conditions.[13] Furthermore, the adsorption of solid phosphine oxides on silica surfaces leads to interesting mobility effects that can be probed with solid-state NMR.[14]

For these studies, being able to cleanly oxidize phosphines to their oxides without overoxidation to phosphinic and phosphonic acid esters is crucial.[15] The best option for transforming the phosphines into their oxides selectively was the oxidation with aqueous H_2O_2 in a biphasic system.[15] Aqueous H_2O_2 is an enticing oxidizing agent in academic settings because it is relatively inexpensive and under present safety regulations available for laboratories in concentrations up to 30 wt%. Its major drawback, however, remains the abundance of water in the reaction mixture which can lead to unwanted secondary reactions. Another, in academia less known ingredient of commercial aqueous H_2O_2 solutions is nitric acid, which is used to adjust the pH value to 1 to 2. The nitric acid serves as stabilizer because within this pH range the H_2O_2 has the longest life time. Furthermore, in labs with many users aqueous H_2O_2 decomposes at unpredictable rates, and the solutions have to be titrated[16] prior to each application when exact stoichiometry is needed. Additionally, in case the reagents are not water soluble, like most unmodified phosphines, the oxidation reaction has to be performed in a biphasic system, which entails a phase separation requirement in the workup.

Other, water free formulations of H_2O_2 are also used, for example, urea hydrogen peroxide (UHP) adducts.[17] However, the stoichiometry of this material is not very well defined, it is not well soluble in organic solvents, and urea and water have to be removed after the reaction. Other approaches include encapsulated[18] and immobilized versions of hydrogen peroxide.[19,20] Furthermore, H_2O_2 adducts of metal complexes have been characterized.[21] Silicon-containing and organic peroxides are important, too, but they can be difficult to synthesize and remove after the reactions.[22] Recently, bishydroperoxides have also received some attention.[23]

The ideal oxidizing agent is an easy to synthesize peroxide of reproducible stoichiometry that is soluble in organic solvents. It should be mechanically and thermally stable at ambient temperature over prolonged time periods, while retaining its oxidizing power. Additionally, a solid oxidizing agent would be preferred due to the ease of handling and application. We recently reported on a new class of materials, hydrogen peroxide adducts of phosphine oxides, for example, $(Cy_3PO{\cdot}H_2O_2)_2$.[7,15] These adducts already fulfill many of the points on the above wish list, and additionally, no acid has to be added to prolong the H_2O_2 life time, since the phosphine oxides serve as stabilizers. However, our quest for alternative oxidizing agents with lower phosphine oxide carrier weight led us to yet another class of adducts. The new di(hydroperoxy)alkane adducts of phosphine oxides incorporate two active oxygen atoms per P=O group, while they still come close to the "ideal oxidizing agent" described above. Two representatives, $R_3PO{\cdot}(HOO)_2CMe_2$ (R = Cy, Ph), have been communicated recently.[7]

The goal of this contribution is to demonstrate that this new substance class is of a general nature and that many different compounds with the general composition $R_3PO{\cdot}(HOO)_2CR'R''$, incorporating virtually any combination of alkyl and aryl substituents R, R', and R'', can easily be synthesized and characterized. Overall, nine representatives of new di(hydroperoxy)alkane adducts of phosphine oxides will be presented, their structural and spectroscopic data are discussed,

[a] S. H. Ahn, Dr. N. Bhuvanesh, Prof. J. Blümel
Department of Chemistry, Texas A&M University
College Station, TX, 77842-3012 (USA)
Fax: (+1) 979-845-5629
E-mail: bluemel@tamu.edu

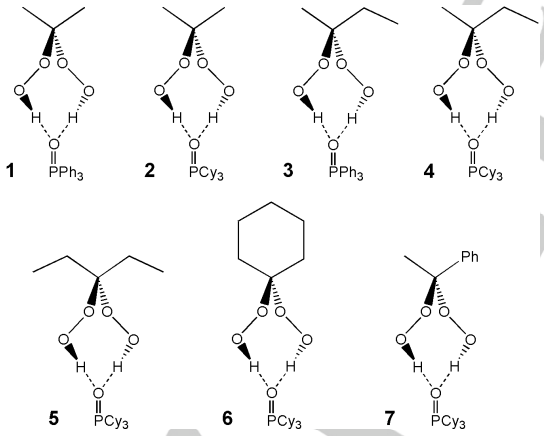
and their chemical behavior and oxidizing power will be probed.

For this purpose, first it will be demonstrated that the active oxygen content and the structural mode stay the same for different phosphine oxides. This includes the characterization of the adducts by single crystal X-ray diffraction, and the quantification of their oxidative strengths, shelf lives under various conditions, and their solubilities in organic solvents. The potential of the adducts **1**-**9** (Schemes 1 and 2) as oxidizing agents for sulfide oxidations[5-7] is described.

In summary, it will be demonstrated that di(hydroperoxy)alkane adducts of phosphine oxides are of a general nature and that they can be fine-tuned and obtained in a large number of easily synthesized and purified representatives. This new class of solid, safe, stoichiometric, and soluble oxidizing agents should have important future applications in academic and industrial settings, especially in cases where abundant water or the nitric acid stabilizer are problematic.

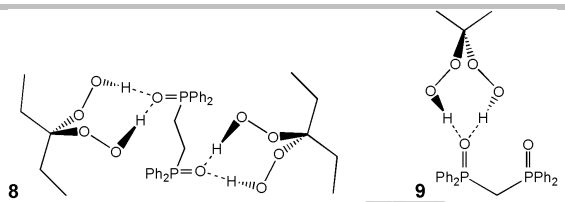
Results and Discussion

Since the discovery that phosphine oxides form stable adducts with di(hydroperoxy)alkanes at room temperature and in the absence of metal catalysts, only two representatives, **1** and **2** (Scheme 1), have been communicated.[7] Therefore, our primary goal in this contribution is to demonstrate that this type of adduct is of a general nature and can be synthesized using a wide variety of different phosphine oxide carriers and ketones. Adducts **1**-**7** which are based on monophosphine oxides, are displayed in Scheme 1.



Scheme 1. Di(hydroperoxy)alkane adducts of phosphine oxides **1**-**7**.

The adducts **8** and **9** (Scheme 2) represent a first step towards reducing the relative weight of the carrier by using diphosphine dioxides. For their synthesis the mixed alkyldiarylphosphine oxides $[Ph_2P(O)CH_2]_2$ ($dppeO_2$, **10**) and $Ph_2P(O)CH_2P(O)Ph_2$ ($dppmO_2$, **11**) are used as educts to give the corresponding adducts (Scheme 2).

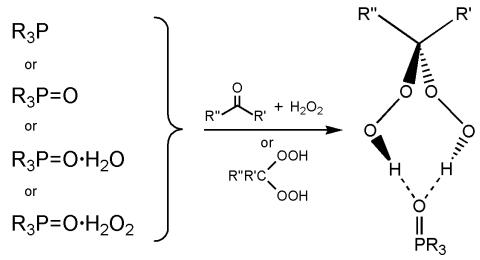


Scheme 2. Di(hydroperoxy)alkane adducts **8** and **9**.

The applicable ketones are not limited to acetone, but so far include butanone, 3-pentanone, cyclohexanone, and acetophenone (Schemes 1 and 2). All adducts are obtained cleanly in the displayed 1 : 1 ratio of di(hydroperoxy)alkane and phosphine oxide. The large number of adducts with the same composition and structural motif, irrespective of their different substituents at phosphorus and the quaternary carbon atoms, corroborates the assumption that the two strong hydrogen bridges lead to a favorable geometry that stabilizes the adducts. In fact **1**-**9** are safe oxidizing agents which melt smoothly without sudden release of oxygen or other violent outbursts. The adducts are also robust towards sudden mechanical impact and grinding with a mortar and pestle. It should also be mentioned that phosphine oxides are flame retardants and they are basically non-toxic.[24]

Syntheses of the New Adducts

Di(hydroperoxy)alkane adducts of phosphine oxides can be synthesized in a variety of different ways (Scheme 3). One option is starting from the phosphines R_3P and treating them with a ketone in the presence of aqueous H_2O_2. In this case, an excess of H_2O_2 is needed because one oxygen atom of the oxidant is consumed to generate the phosphine oxide first. Furthermore, it has to be taken into account that starting from alkylphosphines entails the risk of formation of other unwanted products from oxygen insertion into the P-C bonds as described earlier.[15] Therefore, oxygen from the atmosphere needs to be excluded in this approach.

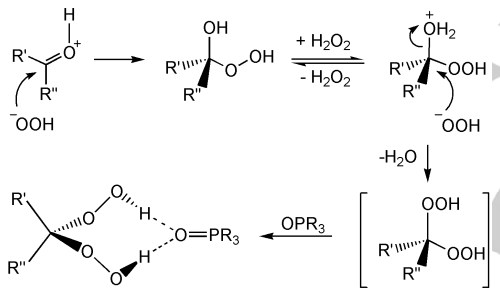


Scheme 3. General synthesis routes for di(hydroperoxy)alkane adducts of phosphine oxides.

When phosphine oxides are the educts for synthesizing di(hydroperoxy)alkane adducts, air does not have to be excluded, and it is not critical, whether they are used in pure form as R_3PO, or as the corresponding H_2O or H_2O_2 adducts. In any case, when combined with a ketone and aqueous H_2O_2, the desired adducts shown in Scheme 3 will be generated. Phosphine oxides readily form water adducts with one hydrogen

bridge, as demonstrated earlier,[14] and some phosphine oxides like Me_3PO are even hygroscopic.[15] However, H_2O_2 is more strongly bound by twofold hydrogen bonding and replaces the water molecule at the P=O group.[7,15]

The general mechanism for the reaction of phosphine oxides with ketones and aqueous H_2O_2 is displayed in Scheme 4. H_2O_2 with a pK_a of 11.8[25a] is more acidic than water (pK_a = 14.0). However, the nitric acid contained in the commercial aqueous H_2O_2 (see above) is most probably responsible for protonating and activating the ketones, for example, acetone (pK_a = 19.2)[25b] in the first step of the proposed mechanism. In the next step, H_2O_2 performs a nucleophilic attack at the carbonyl carbon. This process is repeated with the hydroperoxy(hydroxy)alkane to yield the di(hydroperoxy)alkane, which is immediately scavenged and stabilized by forming two hydrogen bonds with the phosphine oxide carrier (Scheme 4). The viability of this last step has been proven by synthesizing the free di(hydroperoxy)alkane $(HOO)_2C(CH_2)_5$[26] and binding it to Cy_3PO to generate the adduct **6** (Scheme 1 and Exper. Section). The di(hydroperoxy)alkane $(HOO)_2C(CH_2)_5$ is bound more strongly to phosphine oxide carriers than H_2O or H_2O_2, and therefore, the water and hydrogen peroxide adducts of phosphine oxides can also function as educts for the synthesis of the di(hydroperoxy)alkane adducts. Again, in case a phosphine is used as starting material, one oxygen atom of the di(hydroperoxy)alkane is sacrificed in the process of forming the phosphine oxide first.



Scheme 4. Suggested mechanism for the formation of di(hydroperoxy)alkane adducts of phosphine oxides.

The adducts **1**-**9** are obtained in nearly quantitative yields by all procedures discussed above (Scheme 3 and Experimental section). In order to obtain dry compounds without decomposing the peroxide groups, the water can be conveniently removed as an azeotropic mixture with ethanol in a mild vacuum at room temperature. All adducts are easy to purify by crystallization and often form giant single crystals (Figure 1). Importantly, the di(hydroperoxy)alkane adducts are generated at ambient temperature and in the absence of any metal catalyst.[21] These conditions prevent the formation of potentially dangerous cyclic peroxide trimers. Additionally, no explosive cyclic trimers or other oligomers are formed during forced decomposition of **1**-**9**.

The adducts **1**-**9** have been tested by applying high temperatures and mechanical stress. In fact, none of the adducts displayed any violent decomposition during grinding and hammering, or being stored over months, or heated up. No sudden release of oxygen occurred during melting point determinations or forceful grinding of the pure powders. The ^{31}P NMR spectra before and after the procedures only indicated the presence of the starting materials. With respect to the safety aspect of future applications it should be noted that phosphine oxides are efficient flame retardants[24a,b] and that they are not toxic.[24c]

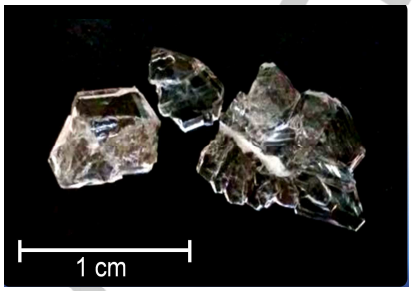


Figure 1. Single crystals of $Cy_3PO{\cdot}(HOO)_2CMeEt$ (**4**).

Characterization of the Adducts

All di(hydroperoxy)alkane adducts **1**-**9** (Scheme 1) are amenable to the most powerful analytical methods. These confirm that the adducts possess unique characteristics that are distinctly different from those of the pure phosphine oxides. In the following IR and NMR spectroscopy of the adducts **1**-**9**, as well as X-ray crystallographic data will be discussed in detail.

IR Spectroscopy

IR Spectrocopy confirms that the di(hydroperoxy)alkane adducts are very different from the pure phosphine oxides.

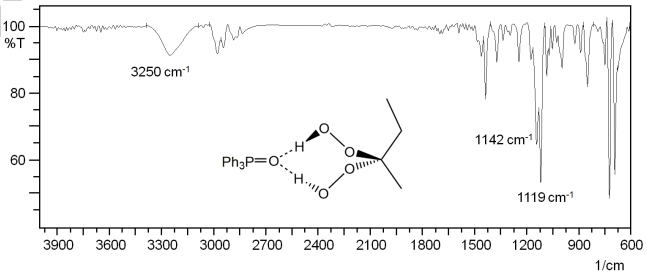


Figure 2. IR spectrum of polycrystalline $Ph_3PO{\cdot}(HOO)_2CMeEt$ (**3**).

Regarding the IR spectra of the di(hydroperoxy)alkane adducts **1**-**9** there are in general three strong stretching bands that are characteristic and valuable analytically, ν(O−H), ν(C−O), and ν(P=O). All these IR data are summarized in Table 1.

The ν(O-H) band of the di(hydroperoxy)alkane moiety hydrogen-bonded to the PO groups is rather broad and intensive and appears between 3200 and 3300 cm^{-1}. Fortunately, this value is distinctly different from the position of the ν(O-H) stretching band of PO-adsorbed water at around 3400 cm^{-1}.[14,15] Comparing, for example, the spectra of pure Ph_3PO with the corresponding di(hydroperoxy)butane adduct **3**, one can conclude that the IR spectrum of **3** (Figure 2) stems from a

water-free adduct. Additionally, a rather prominent overtone band that would be expected at about 1647 cm^{-1} from water bound to the phosphine oxide is absent.[15,27]

The IR stretching bands v(P=O) of the adducts have in general lower values (1113-1163 cm^{-1}) than those of the adduct-free phosphine oxides (1157-1188 cm^{-1}).[7,15] The reason for the diminished values of the adducts is that the hydrogen bonding in **1**-**9** weakens the P=O double bonds of the pure phosphine oxides and therefore decreases the frequencies of the stretching bands. The differences Δv(P=O) between the stretching band wavenumbers of the free phosphine oxides versus the corresponding adducts cover a rather narrow range of values from 22 to 44 cm^{-1} (Table 1). Within this limited range there is no obvious trend for the wavenumbers depending on aryl versus alkyl substitution at phosphorus or at the quaternary carbon of the di(hydroperoxy)alkane moiety. As it is the case for the pure phosphine oxides, the v(P=O) stretching bands of all adducts **1**-**9** are very narrow, as the example of **3** in Figure 2 shows.

In addition to the v(P=O) bands, in the narrow region from 1097 to 1118 cm^{-1} in all IR spectra of the adducts **1**-**9** an additional strong absorption is found. This band can be assigned to the v(C−O) band of the di(hydroperoxy)carbon moiety. For example, acetals and ketals display IR absorptions between 1035 and 1190 cm^{-1}.[28] The related structural element of secondary alcohols show IR bands between 1090 and 1120 cm^{-1}.[28] Furthermore, neat $(HOO)_2C(CH_2)_5$ displays a strong sharp peak at 1113 cm^{-1}. Overall, these narrow and characteristic bands in IR spectroscopy show that all adducts are well-defined and of a molecular and crystalline nature throughout the bulk material.

Table 1. Stretching bands v(O-H) and v(C-O), and comparison of the v(P=O) IR stretching band values of the pure phosphine oxides Ph_3PO, Cy_3PO, $Ph_2P(O)CH_2CH_2P(O)Ph_2$ (**10**), and $Ph_2P(O)CH_2P(O)Ph_2$ (**11**) with those of the adducts **1**-**9**, given as Δv(P=O).

Species	v(O−H) (cm^{-1})	v(C−O) (cm^{-1})	v(P=O) (cm^{-1})	Δv(P=O) (cm^{-1})
1	3256	1118	1152	30
2	3192	1099	1125	32
3	3250	1118	1142	40
4	3196	1101	1124	33
5	3194	1103	1126	31
6	3252	1103	1113	44
7	3176	1101	1123	34
8	3275	1097	1150	22
9	3291	1099	1163	25
Ph_3PO	-	-	1182	-
Cy_3PO	-	-	1157[15]	-
10	-	-	1172	-
11	-	-	1188	-

X-Ray Crystallography

The most important feature of the di(hydroperoxy)alkane adducts **1**-**9** is their formation of multiple hydrogen bonds between the (HOO−) and the P=O groups. We have previously described the tendency of P=O groups to form hydrogen bonds to H_2O_2 molecules,[7,15] H_2O,[14] and silanols.[14] Two X-ray structures of the di(hydroperoxy)propane adducts **1** and **2**, incorporating hydrogen bonds, have been communicated.[7] Recently, hydrogen bonding between P=O and the OH groups of a phenol moiety has successfully been applied to create novel dimeric motifs.[29]

The main interest in the following structural characterization of the new adducts is to probe whether the same arrangements of hydrogen bonds to the P=O groups will be established, and whether the packing motif of the adducts displays similar trends.

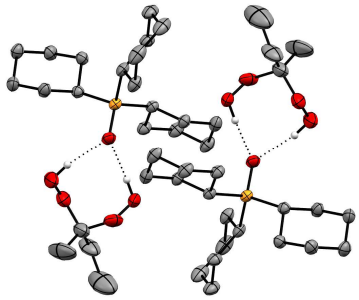


Figure 3. Single crystal X-ray structure of $Cy_3PO{\cdot}(HOO)_2CMeEt$ **4** (two independent molecules). Thermal ellipsoids are shown at the 50% probability level. Only the hydrogen-bonded H atoms are shown for clarity.[31]

All di(hydroperoxy)alkane adducts of phosphine oxides crystallize easily in the form of large colorless single crystals, one representative specimen being shown in Figure 1. Therefore, the single crystal X-ray structures of all adducts **1**-**9**[7,30-36] (Figures 3-8) could be obtained in high quality. The structures of **1**-**8** confirm that each P=O group forms two hydrogen bridges to one di(hydroperoxy)alkane 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 the H_2O_2 adducts of phosphine oxides presented previously.[7]

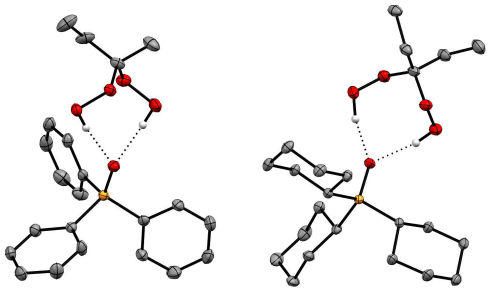


Figure 4. Single crystal X-ray structures of $Ph_3PO{\cdot}(HOO)_2CMeEt$ (**3**, left)[30] and $Ph_3PO{\cdot}(HOO)_2CEt_2$ (**5**, right).[32] Thermal ellipsoids are shown at the 50% probability level. Only the hydrogen-bonded H atoms are shown for clarity.

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The recurring and characteristic packing motif consists of two adduct assemblies being arranged in a manner so that the P=O groups point in opposite directions, as seen, for example, for the adducts **4**, **5**, **6**, and **7** in Figures 3, 4, 5, and 6, respectively. Even in the case of the adduct **10** (Figure 7), where the two P=O groups are connected by an ethylene bridge, this structural packing motif is preferred. The only exception to this rule so far is adduct **3** which does not form this dimer assembly (Figure 4). The reason for this might be that the phenyl rings of the Ph_3PO carriers do not form an arrangement that would be free of strain when they stack. This can be seen, for example, in the structure of **1**,[7] where the di(hydroperoxy)propane units are pushed away from the area of the aligned phenyl rings, in order to accommodate this stacking. In contrast to this, the cyclohexyl rings allow for unstrained stacking, with the di(hydroperoxy)alkane moieties being more centered on top of the P=O groups for **4**-**7**.

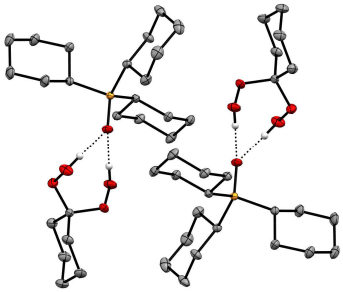

Figure 5. Single crystal X-ray structure of $Cy_3PO{\cdot}(HOO)_2C(CH_2)_5$ (**6**, two independent molecules).[33] Thermal ellipsoids are shown at the 50% probability level. Only the hydrogen-bonded H atoms are shown for clarity.

So far, **5** is the only representative of the di(hydroperoxy)alkane adducts of phosphine oxides found that displays polymorphism. It has been obtained in orthorhombic[32a] and columnar[32b] crystals. However, in both polymorphs of **5** the adduct assemblies still follow the general composition $Cy_3PO{\cdot}(HOO)_2CEt_2$. Therefore, the polymorphism will not impede any later application as stoichiometric oxidizing agent.

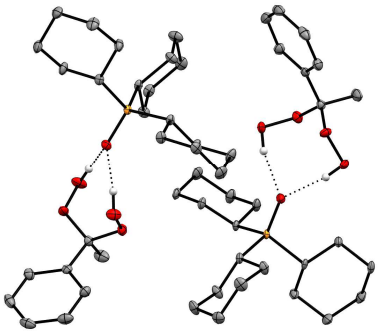

Figure 6. Single crystal X-ray structure of $Cy_3PO{\cdot}(HOO)_2CMePh$ (**7**, two independent molecules).[34] Thermal ellipsoids are shown at the 50% probability level. Only the hydrogen-bonded H atoms are shown for clarity.

In order to increase the number of active oxygen atoms per phosphine oxide carrier mass, and to further probe the general nature of the di(hydroperoxy)alkane adducts, 1,2-bisdiphenylphosphinoethane (dppe) has been treated with 3-pentanone and aqueous H_2O_2. The expected di(hydroperoxy)pentane adduct $[CH_2Ph_2PO{\cdot}(HOO)_2CEt_2]_2$ (**8**) was obtained.[35] Again, the large single crystals allowed for structural characterization (Figure 7). The two di(hydroperoxy)pentane moieties are bound to the P=O groups pointing in opposite directions.

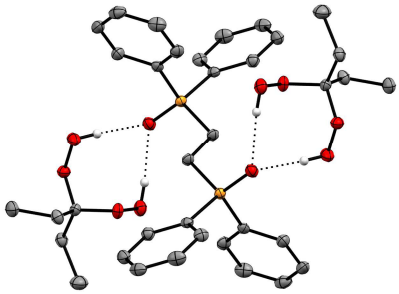

Figure 7. Single crystal X-ray structure of $(Ph_2P(O)CH_2CH_2P(O)Ph_2){\cdot}((HOO)_2CEt_2)_2$ (**8**).[35] Thermal ellipsoids are shown at the 50% probability level. Only the hydrogen-bonded H atoms are shown for clarity.

Next, we investigated whether offering two P=O groups in closer proximity as in $dppeO_2$ would lead to a different hydrogen bonding pattern. Interestingly, when $dppmO_2$ is reacted with acetone and aqueous H_2O_2 using the same procedure as for $dppeO_2$, only one P=O group per molecule carries the di(hydroperoxy)propane moiety (Figure 8).[36] The distances between the two P=O oxygen atoms and the terminal oxygen atom of one OOH group are practically identical with 2.816 and 2.817 Å. Therefore, one could imagine that the hydrogen atom interacts with both P=O oxygen atoms equally. However, the P=O bond lengths differ. The P=O bond of the group carrying the adduct is lengthened to 1.495 Å, while the free P=O bond remains in the typical range of P=O bond lengths with 1.488 Å.[14] The IR spectrum indicates that there is only one HO absorption present, which differs in its wavenumber from the water band at 3408 cm^{-1}.[15] In solution only an averaged chemical shift is obtained for both P=O groups of **9**, therefore it is possible that the hydrogen bond formation of the di(hydroperoxy)propane moieties with only one P=O group per diphosphine dioxide molecule is enforced by the favored packing of the assemblies in the crystal lattice.

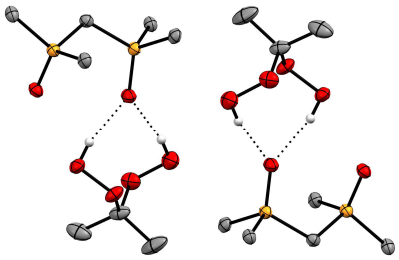

Figure 8. Single crystal X-ray structure of $Ph_2P(O)CH_2P(O)Ph_2{\cdot}(HOO)_2CMe_2$ (**9**, two independent molecules).[36] Thermal ellipsoids are shown at the 50% probability level. Only the hydrogen-bonded H atoms and *ipso* carbon atoms of the phenyl rings are shown for clarity.

Having obtained all single crystal X-ray structures of **1**-**9**, their crystallographic data can be compared and evaluated. First, the change of the P=O bond lengths which was expected from the shifts of the IR ν(P=O) bands to lower frequencies upon adduct formation (Table 1), was probed by the X-ray data (Table 2). According to expectation, in the adducts a qualitative lengthening of the P=O bonds, as compared to the respective pure phosphine oxides, is found. This result corroborates the weakening of the P=O bond due to the formation of two hydrogen bonds. The changes of bond lengths are in the range of those detected for hydrogen peroxide adducts of phosphine oxides. For example, when the adduct $[Cy_3PO{\cdot}H_2O_2]_2$ is generated from Cy_3PO, the two hydrogen bonds per PO group lead to an increase of the bond length by 0.015 Å.[15]

Table 2. Comparison of the P=O bond lengths (Å) of the adducts **1**-**9** with those of the pure phosphine oxides Ph_3PO, Cy_3PO, $Ph_2P(O)CH_2CH_2P(O)Ph_2$ (**10**), and $Ph_2P(O)CH_2P(O)Ph_2$ (**11**). Averaged bond length values are given for **3**, **9** and **10**.

Species	P=O bond lengths (Å)	Δ Bond lengths
1	1.502[7]	+0.023
2	1.507[7]	+0.017
3	1.506	+0.016
4	1.510	+0.020
5	1.508	+0.018
6	1.512	+0.022
7	1.510	+0.020
8	1.501	+0.010
9	1.492	+0.002
Ph_3PO	1.479[37]	-
Cy_3PO	1.490[38]	-
10	1.492[39]	-
11	1.491[40]	-

The formation of hydrogen bonds in **1**-**9** is corroborated by the O···H distances (Table 3). Average O···H distances in hydrogen bonds are in the order of 1.85 to 1.95 Å.[41,42] Most values for **1**-**9** lie well within this range, with only slightly longer distances for one hydrogen bond each in **8** and **9**. In these cases, most probably the strained geometries in the diphosphine dioxide carriers diminish the hydrogen bond strengths.

Another indication for the formation of strong hydrogen bonds are the comparatively short O···H−O distances between the oxygen atoms in **1**-**9** (Table 3). Average distances from 2.75 to 2.85 Å indicate hydrogen bond formation,[41,42] and the values of all adducts lie well within this range.

Table 3. Hydrogen bond lengths, O···O distances, and O−C−O angles of the di(hydroperoxy)alkane moieties in the adducts **1** to **9**. The values of one of the two independent molecules are given for **3**.

Adduct	O···H Distance (Å)	O···H−O Distance (Å)	O−C−O Angle (°)
1	1.777/1.874	2.686/2.771	110.8
2	1.841/1.873	2.677/2.720	111.5
3	1.874/1.974	2.706/2.733	110.7
4	1.838/1.848	2.615/2.749	108.5
5	1.835/1.846	2.679/2.687	110.5
6	1.864/1.876	2.705/2.723	112.0
7	1.825/1.888	2.664/2.719	111.7
8	1.902/1.981	2.751/2.827	110.7
9	1.909/1.985	2.742/2.816	110.7

Finally, it was considered whether the O−C−O angle in the di(hydroperoxy)alkane moiety of the adducts could serve as an indicator for strain in the assemblies due to the formation of the two hydrogen bonds. In fact, the angles deviate from the ideal tetrahedral angle of 109.5°, with most of the values being larger by about 1 to 2.5° (Table 3). Therefore, it seems like the O−C−O angles increase in order to accommodate the formation of the two hydrogen bonds per P=O group.

NMR Spectroscopy

The adducts **1**-**9** (Schemes 1 and 2) are highly soluble in organic solvents (see below). Therefore, they can conveniently be characterized by standard one- and two-dimensional solution NMR spectroscopy, and using these methods all resonances have been assigned unequivocally. The ^{1}H and ^{13}C NMR spectra show the signals expected for the phosphine oxide carriers, with characteristic chemical shifts and *J* coupling values that differ only minimally from those of the pure phosphine oxides.[15] However, the changes of the adduct moieties are substantial and they follow the expected trends when transforming ketones to di(hydroperoxy)alkanes.[7] Most valuable for the straightforward identification of the adducts is the appearance of a new resonance in the range of 108 to 115 ppm for the generated quaternary carbon atoms bound to two oxygen atoms (Table 4). This chemical shift range is very characteristic and fortunately it does not overlap with the typical spectral regions of aryl or alkyl carbon signals. As signals of quaternary carbon nuclei their ^{13}C NMR resonances are also easily identified by DEPT and $^{1}H,^{13}C$ COSY NMR spectra.

The ^{31}P NMR signals of all adducts **1**-**9** are shifted downfield as compared to those of the corresponding pure phosphine oxides Cy_3PO (49.91 ppm),[15] Ph_3PO (29.10 ppm),[15] $(CH_2(P(O)Ph_2)_2$ (32.68 ppm), and $CH_2(P(O)Ph_2)_2$ (24.86 ppm) (Table 4). This downfield shift indicates the deshielding of the phosphorus nuclei by the presence of two strong hydrogen bonds to the P=O oxygen atom. The Δδ values cover a relatively narrow range from 1.4 to 8.9 ppm without visible trend depending on the substituents at phosphorus or at the quaternary carbon atoms (Table 4).

Table 4. ^{13}C NMR chemical shifts of the quaternary carbon signals of the di(hydroperoxy)alkane moieties in **1**-**9**, ^{31}P NMR chemical shifts of the adducts and their corresponding pure phosphine oxides, and the ^{31}P NMR chemical shift differences. All values were obtained with $CDCl_3$ as the solvent.

Adduct	δ(^{13}C) of C_q (ppm)	δ(^{31}P) (ppm)	δ(^{31}P) of neat R_3PO (ppm)	Δδ (ppm)
1	109.28	34.74	29.16	5.64
2	108.91	55.59	49.91	5.68
3	111.56	30.52	29.16	1.42
4	111.26	58.77	49.91	8.86
5	113.76	58.35	49.91	8.44
6	109.52	58.01	49.91	8.10
7	110.18	58.31	49.91	8.40
8	114.13	39.42	32.68	6.74
9	109.21	30.33	24.86	5.47

Shelflives of the Adducts

Next, the shelf life of the representative adduct **4** has been monitored. For this purpose, a straightforward standardized *in situ* ^{31}P NMR test[7] was applied to determine the number of active oxygen atoms per adduct in the starting material and in the course of exposure to different conditions. Hereby, the oxidative power of **4** was determined at regular time intervals by adding a slight excess of Ph_3P to a weighed amount of **4**. PPh_3 was selected as the probe because it is not oxidized readily in air in the absence of a catalyst. However, di(hydroperoxy)alkane adducts transform Ph_3P into Ph_3PO selectively within minutes.[7] Therefore, the number of active oxygen atoms can be deduced from the intensity ratio of the quantitatively recorded ^{31}P NMR resonances of residual Ph_3P and Ph_3PO. As anticipated, the number of active oxygen atoms in **4** is two, and this number was used to define 100% oxidative power.

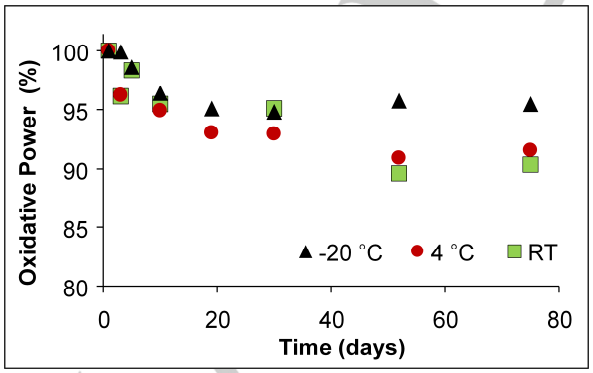

Figure 9. Oxidative power of polycrystalline $Cy_3PO{\cdot}(HOO)_2CMeEt$ (**4**) after being stored at the indicated temperatures. 100% oxidative power is equivalent to 2 moles of active oxygen per mole of **4**.

Subsequently, the long term stability of polycrystalline **4** was monitored under different conditions (Figure 9). As for **1** and **2**,[7] exposure to light did not alter the outcome of the experiments. However, the temperature had a large impact. While about 10% of the oxidative power of **4** is lost within 80 days of exposure at ambient temperature, moderate cooling at 4 °C helps the adduct to retain about 92% of active oxygen (Figure 9). Storage of polycrystalline **4** at −20 °C leads to a loss of only about 5% of oxidative power over the course of 80 days.

When large single crystals of the adducts **1**-**9** with volumes of about 10 mm^3 are exposed to ambient conditions for months, practically no decomposition and loss of oxidative power are detected. Therefore, the exposed surface area of the crystals is an important factor for the shelf life of the adducts.

Regarding the decomposition process, the two oxygen atoms per adduct assembly are most likely lost in a consecutive and not a simultaneous manner. To corroborate this assumption, we recently identified and characterized the intermediate hydroperoxy(hydroxy)alkane adduct of tricyclohexylphosphine oxide $Cy_3PO[(HOO)(HO)C(CH_2)_5]$.[43]

In order to further support this assumption, **4** has been dissolved in two different solvents (5 wt%) and the solutions were heated to 105 °C. At regular intervals the oxidizing power of the solutions was tested (Figure 10). In chlorobenzene the oxidizing power of **4** is diminished to 50% within 7h, in toluene within 8 hours. The decomposition curves reach a plateau at about 50% oxidative power, which means that most probably one of the two peroxo groups per adduct assembly is decomposing more easily at higher temperatures. The hydroperoxy(hydroxy)alkane adduct $Cy_3PO[(HOO)(HO)$-CMeEt][43] is more stable than the starting material **4**, and much higher temperatures are needed to decompose it in solution in a timely manner.[43]

Interestingly, the decomposition of **4** proceeds much faster in chlorobenzene than in toluene, which suggests that a radical process is dominant. This result, together with the fact that the adducts **1**-**9** incorporate two peroxo groups with different reactivities, points to a bright potential future of this class of materials not only as selective oxidizing agents, but also as hitherto unexplored radical initiators for polymerizations.

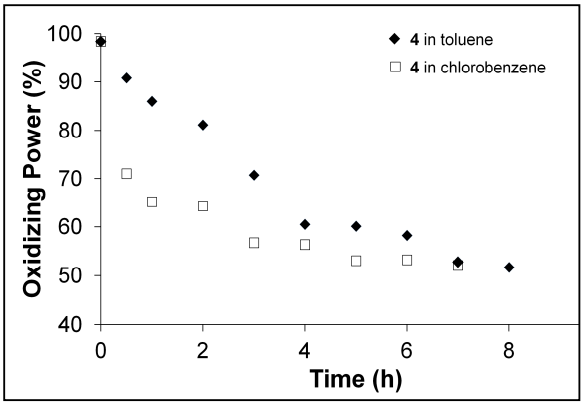

Figure 10. Oxidative power of $Cy_3PO{\cdot}(HOO)_2CMeEt$ (**4**), dissolved in toluene and chlorobenzene (5 wt%), while being heated to 105 °C. 100% oxidative power is equivalent to 2 moles of active oxygen per mole of **4**.

After complete loss of oxidizing power ^{13}C NMR spectra of the exposed materials indicate that the starting ketones are regenerated. No alcohols or other products have been found after complete decomposition of the adducts.

Solubilities of the Adducts

All di(hydroperoxy)alkane adducts of phosphine oxides are extremely soluble in organic solvents (Figure 11). This feature represents one of the most important advantages of these adducts with respect to their applications as oxidizing agents, because it allows oxidation reactions to be performed in one organic phase rendering a second aqueous phase obsolete. Therefore, transformations that would suffer from the presence of an excess of water can be undertaken in an organic phase. The one mole of water generated by using the two active oxygen atoms of the di(hydroperoxy)alkane moiety for oxidation processes will be retained by strong hydrogen bonding to the phosphine oxide and thus will not form a second aqueous layer.[14]

The solubilities in representative organic solvents have been quantified for four representative di(hydroperoxy)alkane adducts (Figure 11). All adducts are remarkably soluble in chloroform and dichloromethane. For example, more than 600 mg of **3** and nearly 400 mg of **4** can be dissolved in 1 mL of CH_2Cl_2. Even in the aromatic solvents toluene and benzene all solubilities are substantial and certainly allow oxidation reactions in these solvents.

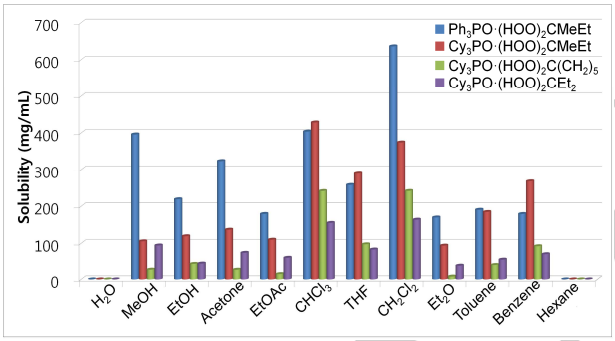

Figure 11. Solubilities of $Ph_3PO{\cdot}(HOO)_2CMeEt$ (**3**), $Cy_3PO{\cdot}(HOO)_2CMeEt$ (**4**), $Cy_3PO{\cdot}(HOO)_2CEt_2$ (**5**), and $Cy_3PO{\cdot}(HOO)_2C(CH_2)_5$ (**6**) in the indicated solvents.

Oxidation Reactions

The di(hydroperoxy)alkane adducts **1**-**9** are amenable to the classical H_2O_2 based organic syntheses mentioned above. Another important application targets the oxidation of sulfides for academic purposes, but also for the energy saving and efficient oxidative desulfurization of petroleum batches.[44] Once the fundamental insights about sulfide oxidation with **1**-**9** are gained, adducts of *P*-chiral phosphine oxides[10] could also be applied for the enantioselective synthesis of sulfoxides.[6]

In a first step towards this direction, selected di(hydroperoxy)alkane adducts (Table 5) were combined with THT (tetrahydrothiophene) in a molar ratio of 1 : 2 in benzene. In all cases, THT was selectively and quantitatively oxidized to the sulfoxide at ambient temperature within two to eight hours. The only other reaction products were the corresponding phosphine oxide carriers and the ketones. The water molecules remained attached to the phosphine oxides via hydrogen bonds.[14] No traces of the overoxidation product sulfone was detected, demonstrating how easily the solid adducts can be administered precisely with the proper stoichiometry. The fast and selective oxidation of THT in one organic phase compares favorably to studies performed previously with biphasic mixtures and added catalysts. [5a]

The time requirements of the oxidation reactions decreased for all adducts at the higher reaction temperatures of 50 °C and 60 °C (Table 5). For example, the adducts **1** and **2** oxidized the sulfide to the sulfoxide in less than half and hour, and even for the mildest oxidizing agent **5** the monoxidation was completed within 6 hours. Again, no overoxidation was found in any case, even at these elevated temperatures.

Table 5. Selective oxidation of THT (tetrahydrothiophene) to the sulfoxides (2 mol THT : 1 mol adduct). The time (h) required for the complete monoxidation at the given temperatures is reported.

Adduct	25 °C	50 °C	60 °C
$Ph_3PO{\cdot}(HOO)_2CMe_2$ (**1**)	2	0.5	0.4
$Cy_3PO{\cdot}(HOO)_2CMe_2$ (**2**)	2	0.5	0.4
$Ph_3PO{\cdot}(HOO)_2CMeEt$ (**3**)	5	2	1
$Cy_3PO{\cdot}(HOO)_2CMeEt$ (**4**)	8	3	1
$Cy_3PO{\cdot}(HOO)_2CEt_2$ (**5**)	8	7	6
$Cy_3PO{\cdot}(HOO)_2CMePh$ (**7**)	6	1	0.5

Conclusions

In this contribution, we widened the scope of di(hydroperoxy)alkane adducts of phosphine oxides and described new insights on this new class of materials. It could be demonstrated that (**a**) the substituents R in the phosphine oxides R_3PO can be aryl, alkyl, or mixed substituents, while adducts with di(hydroperoxy)alkanes are formed in each case. (**b**) The stoichiometry of the adducts is well-defined for all phosphine oxides, including those derived from the chelating phosphine dppe, with one di(hydroperoxy)alkane moiety per P=O group. Only in case the P=O groups are too close, just being separated from each other by a methylene group, they share one di(hydroperoxy)alkane unit. (**c**) The range of applicable starting ketones for the formation of the di(hydroperoxy)alkane moieties has been broadened to include butanone, 3-pentanone, cyclohexanone, and acetophenone. (**d**) Several different synthetic routes have been presented for generating all di(hydroperoxy)alkane adducts of phosphine oxides without addition of metal catalysts. (**e**) All adducts crystallize readily and reproducibly in large specimens which facilitates purification and single crystal X-ray analysis. The structures of the adducts and their packing motifs follow the same theme. (**f**) In general, there are two hydrogen bonds formed between the two hydroperoxy groups in the adduct and one P=O group. (**g**) Besides structural analysis in the solid state, NMR and IR spectroscopic studies

confirm the nature of the adducts. (**h**) One di(hydroperoxy)alkane moiety releases two active oxygen atoms in a consecutive manner. (**i**) All pure or dissolved adducts are safe and robust towards high temperatures and mechanical stress. At ambient temperatures shelf lifetimes of months have been determined. In solution 50% of the oxidative power is lost within about 8 hours for one representative adduct. (**j**) The high solubility of all adducts in the usual organic solvents allow oxidation reactions in one organic phase. (**k**) All solid, stoichiometric adducts can easily be administered and selectively oxidize phosphines to phosphine oxides instantaneously at ambient temperature. THT is transformed into the sulfoxide in organic phases at room temperature without overoxidation to the sulfone. Higher reaction temperatures lead to quantitative conversion of THT in most cases within one hour, without loss of selectivity. (**l**) The co-products of the oxidation reactions, ketones and phosphine oxides, are unreactive[24a,b] and non-toxic.[24c]

One option for the removal of the phosphine oxides from the reaction mixtures is the strong, but reversible adsorption on solids like molecular sieves or silica.[14,15] Once the phosphine oxides are retrieved from the support by washing with polar solvents,[15] they can be reused after being "recharged" with the desired ketone and aqueous H_2O_2 to form the di(hydroperoxy)alkane adducts. Alternatively, one can immobilize the adducts on silica by covalent tethering, like catalysts and linkers[12,13] in order to render the phosphine oxide carriers easily removable and recyclable by recharging them with a ketone and H_2O_2. We will further expand the scope of adduct molecules to include tripodal phosphines[45] and tetraphosphines[46] as oxide carriers to further increase their loading with peroxo groups. Additionally, diketones will be explored as educts. Finally, new applications for these stable, stoichiometric, and soluble di(hydroperoxy)alkane adducts of phosphine oxides will be explored. These will include the use of P-chiral phosphine oxides[10] and the enantioselective synthesis of sulfoxides.[6]

In conclusion, this contribution describes the general nature of an important new class of materials that has 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)alkane adducts render them attractive oxidizing agents that can be applied as an alternative to aqueous hydrogen peroxide.

Experimental Section

General Remarks

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 499.70, 125.66, and 202.28 MHz on a 500 MHz Varian spectrometer. The ^{13}C and ^{31}P{^{1}H} NMR spectra were measured with ^{1}H decoupling if not stated otherwise. Neat Ph_2PCl ($\delta(^{31}P)$ = +81.92 ppm) in a capillary centered in the 5 mm NMR tubes was used for referencing the ^{31}P chemical shifts of the compounds. For referencing the ^{1}H and ^{13}C chemical shifts the residual proton signals of the solvent $CDCl_3$ and the carbon signal have been used ($\delta(^1H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.00 ppm). All signal assignments were based on comparisons with analogous phosphine oxides[7,14,15] and two-dimensional ^{1}H,^{1}H and ^{1}H,^{13}C correlation NMR spectroscopy. Virtual couplings[47] are indicated in the data sections of the compounds. The IR spectra of the neat powders were recorded on a Shimadzu IRAffinity-1 FTIR instrument using a Pike Technologies MIRacle ATR plate. All reactions were carried out using standard Schlenk techniques, if not stated otherwise, although none of the materials described here is air-sensitive. Reagents purchased from Sigma Aldrich or VWR were used without further purification. Aqueous H_2O_2 solution (35%) was obtained from Acros Organics and used as received. Solvents were dried by boiling them over sodium, then they were distilled and stored under purified nitrogen. Acetone (Aldrich, ACS reagent grade) and ethanol (200 proof) were dried over 3 Å molecular sieves (EMD Chemical Inc.). Butanone, 3-pentanone, cyclohexanone and methylphenylketone were used as purchased.

Representative procedure to determine in general the oxidative power of adducts, described for the di(hydroperoxy)butane adduct of tricyclohexylphosphine oxide (**4**): 11 mg of **4** (0.026 mmol) and 43 mg of PPh_3 (0.164 mmol) are dissolved in 0.35 mL of $CDCl_3$ in an NMR tube under air (PPh_3 is not oxidized by oxygen from the air under these conditions, in the absence of a catalyst). The oxidation is monitored *in situ* via ^{31}P NMR spectroscopy and is complete within 20 min. The integral ratio between the signals of $OPPh_3$ and the remaining PPh_3 is used to calculate the oxidative power of **4**. For this particular reaction, 31% of the initial PPh_3 (0.051 mmol) is oxidized, which amounts to 2 molar equivalents of active oxygen per mole of **4**.

$Ph_3PO{\cdot}(HOO)_2CMe_2$ (**1**): Ph_3P (200 mg, 0.762 mmol) was weighed into a Schlenk flask and dissolved in acetone (100 mL) under nitrogen. Then aqueous H_2O_2 (1.0 mL, 10 mmol) was added and the reaction mixture was stirred for 3 h. The solution was concentrated to 5 mL *in vacuo*, then the product was allowed to crystallize at room temperature. $(Ph_3PO){\cdot}(HOO)_2CMe_2$ (**1**) was obtained in the form of colorless rectangular crystals (243 mg, 0.629 mmol, 83% yield).

NMR (δ, $CDCl_3$), ^{31}P 34.74 (s); ^{1}H 11.29-10.90 (br. s, OO*H*), 7.68-7.61 (m, 6H, H_o), 7.60-7.55 (m, 3H, H_p), 7.51-7.46 (m, 6H, H_m), 1.47 (m, 6H, CH_3); ^{13}C 132.57 (s, C_p), 132.10 (d, $^2J(^{31}P\text{-}^{13}C)$ = 10.7 Hz, C_o), 130.56 (d, $^1J(^{31}P\text{-}^{13}C)$ = 106.1 Hz, C_i), 128.77 (d, $^3J(^{31}P\text{-}^{13}C)$ = 12.6 Hz, C_m), 109.28 (s, CH_3C), 20.64 (s, CH_3).

NMR (δ, $(CD_3)_2CO$), ^{31}P 31.21 (s); ^{1}H 10.97 (br. s, OO*H*), 7.76-7.68 (m, 6H, H_o), 7.67-7.62 (m, 3H, H_p), 7.60-7.53 (m, 6H, H_m), 1.35 (s, CH_3); ^{13}C 133.14 (d, $^4J(^{31}P\text{-}^{13}C)$ = 2.3 Hz, C_p), 132.58 (d, $^2J(^{31}P\text{-}^{13}C)$ = 10.2 Hz, C_o), 132.51 (d, $^1J(^{31}P\text{-}^{13}C)$ = 104.7 Hz, C_i), 129.52 (d, $^3J(^{31}P\text{-}^{13}C)$ = 12.1 Hz, C_m), 109.03 (s, CH_3C), 20.97 (s, CH_3). IR: ν(PO) = 1151.5 cm^{-1}. mp (decomp.) 75 °C.

$Cy_3PO{\cdot}(HOO)_2CMe_2$ (**2**): Cy_3P (100 mg, 0.357 mmol) was weighed into a Schlenk flask inside a glove box. The flask was then sealed, brought outside, and the phosphine was dissolved in acetone (60 mL) under a nitrogen flow. After addition of aqueous H_2O_2 (0.5 mL, 5.1 mmol) the reaction mixture was stirred for 1 h. Then a large amount of EtOH (100 mL) was added to the flask, and the azeotropic mixture of EtOH and H_2O was removed *in vacuo* at ambient temperature. $(Cy_3PO){\cdot}(HOO)_2CMe_2$ (**2**) crystallized in the form of large colorless hexagonal specimens (126 mg, 0.311 mmol, 87% yield).

NMR (δ, $CDCl_3$), ^{31}P 55.59 (s); ^{1}H 1.97-1.80 (m, 15H, $PCH_{ax}CH_{eq}CH_{eq}$), 1.77-1.70 (s, 3H, $PCH(CH_2)_2CH_{eq}$), 1.49-1.36 (s, 12H, $PCHCH_{ax}$, CH_3), 1.36-1.21 (m, 9H, $PCHCH_2CH_{ax}CH_{ax}$); ^{13}C 108.91 (s, CH_3C), 34.79 (d, $^1J(^{31}P\text{-}^{13}C)$ = 60.9 Hz, P*C*), 26.74 (d, $^3J(^{31}P\text{-}^{13}C)$ = 12.7 Hz, $PCHCH_2CH_2$), 25.98 (d, $^2J(^{31}P\text{-}^{13}C)$ = 3.6 Hz, $PCHCH_2$), 25.92 (d, $^4J(^{31}P\text{-}^{13}C)$ = 1.8 Hz, $PCH(CH_2)_2CH_2$), 20.63 (s, CH_3).

NMR (δ, $(CD_3)_2CO$), ^{31}P 56.44 (s); ^{1}H 11.45 (br. s, OO*H*), 2.02-1.89 (m, 9H, $PCH_{ax}CH_{eq}$), 1.86-1.76 (m, 6H, $PCHCH_2CH_{eq}$), 1.74-1.66 (m, 3H, $PCH(CH_2)_2CH_{eq}$), 1.52-1.38 (m, 6H, $PCHCH_{ax}$), 1.37-1.19 (m, 9H, $PCHCH_2CH_{ax}CH_{ax}$), 1.30 (s, CH_3); ^{13}C 108.61 (s, CH_3C), 35.53 (d, $^1J(^{31}P\text{-}^{13}C)$ = 61.0 Hz, P*C*), 27.36 (d, $^3J(^{31}P\text{-}^{13}C)$ = 12.1 Hz, $PCHCH_2CH_2$), 26.74 (s, $PCH(CH_2)_2CH_2$), 26.73 (d, $^2J(^{31}P\text{-}^{13}C)$ = 2.8 Hz, $PCHCH_2$). IR: ν(PO) = 1124.5 cm^{-1}. mp (decomp.) 70 °C.

$Ph_3PO{\cdot}(HOO)_2CMeEt$ (**3**): Ph_3P (300 mg, 1.14 mmol) was placed in a round bottom flask and dissolved in toluene (40 mL). 2-Butanone (0.12 mL, 1.3 mmol) and aqueous H_2O_2 (0.5 mL, 5 mmol) were added, and the reaction mixture was stirred overnight. The solution was concentrated to about 3 mL in vacuum and the product was allowed to crystallize. Adduct **3** was obtained in the form of colorless crystals (294 mg, 65% yield).

NMR (δ, $CDCl_3$), ^{31}P 30.52 (s); ^{1}H 11.38 (s, 2H, OO*H*), 7.69-7.64 (m, 6H, H_o), 7.60-7.55 (m, 3H, H_p), 7.51-7.46 (m, 6H, H_m), 1.79 (q, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 2H, CH_2CH$_3$), 1.41 (s, 3H, CCH_3), 1.01 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 3H, CH$_2$CH_3); ^{13}C 132.32 (d, $^{4}J(^{31}P\text{-}^{13}C)$ = 2.7 Hz, C_p), 132.08 (d, $^{2}J(^{31}P\text{-}^{13}C)$ = 10.0 Hz, C_o), 131.29 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 105.4 Hz, C_i), 128.66 (d, $^{3}J(^{31}P\text{-}^{13}C)$ = 12.3 Hz, C_m), 111.56 (s, CH$_3$*C*), 26.09 (s, *C*H$_2$CH$_3$), 17.46 (s, CCH$_3$), 8.38 (s, CH$_2$CH$_3$).

NMR (δ, C_6D_6), ^{31}P 31.42 (s); ^{1}H 11.95 (s, 2H, OO*H*), 7.62-7.56 (m, 6H, H_o), 7.03-6.98 (m, 3H, H_p), 6.96-6.91 (m, 6H, H_m), 2.09 (q, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 2H, CH_2CH$_3$), 1.65 (s, 3H, CCH_3), 1.11 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 3H, CH$_2$CH_3); ^{13}C 132.32 (d, $^{2}J(^{31}P\text{-}^{13}C)$ = 10.4 Hz, C_o), 132.11 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 104.0 Hz, C_i), 132.10 (d, $^{4}J(^{31}P\text{-}^{13}C)$ = 3.2 Hz, C_p), 128.72 (d, $^{3}J(^{31}P\text{-}^{13}C)$ = 12.3 Hz, C_m), 111.70 (s, CH$_3$*C*), 26.94 (s, *C*H$_2$CH$_3$), 18.16 (s, CCH$_3$), 8.78 (s, CH$_2$CH$_3$). IR: v(PO) = 1118.7 cm^{-1}. mp (decomp.) 54 °C.

$Cy_3PO{\cdot}(HOO)_2CMeEt$ (**4**): $[Cy_3PO{\cdot}H_2O_2]_2$ (300 mg, 0.91 mmol) was placed in a round bottom flask and dissolved in 30 mL of butanone (0.33 mol). After addition of aqueous H_2O_2 (0.5 mL, 5 mmol) the solution was stirred overnight. Excess butanone was removed under vacuum until a precipitate appeared. Subsequently, 50 mL of EtOH was added to the flask, and the azeotropic mixture of EtOH and H_2O was removed in vacuo at ambient temperature to give white crystals of **4** (345 mg, 0.82 mmol, 90% yield).

NMR (δ, $CDCl_3$), ^{31}P 58.77 (s); ^{1}H 11.47 (s, 2H, OO*H*), 1.97-1.80 (m, 15H, PC*H*CH$_{eq}$C*H*$_{eq}$), 1.73 (q, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 2H, CH_2CH$_3$), 1.76-1.72 (m, 3H, PCH(CH$_2$)$_2$C*H*$_{eq}$), 1.48-1.39 (m, 6H, PCHC*H*$_{ax}$), 1.38 (s, 3H, CCH_3), 1.29-1.23 (m, 9H, PCHCH$_2$C*H*$_{ax}$C*H*$_{ax}$), 0.97 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 3H, CH$_2$CH_3); ^{13}C 111.26 (s, CH$_3$*C*), 34.72 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 60.5 Hz, P*C*), 26.72 (d, $^{3}J(^{31}P\text{-}^{13}C)$ = 12.1 Hz, PCHCH$_2$*C*H$_2$), 26.02 (s, *C*H$_2$CH$_3$), 25.96 (d, $^{2}J(^{31}P\text{-}^{13}C)$ = 2.8 Hz, PCH*C*H$_2$), 25.91 (d, $^{4}J(^{31}P\text{-}^{13}C)$ = 1.4 Hz, PCH(CH$_2$)$_2$*C*H$_2$), 17.41 (s, *C*CH$_3$), 8.36 (s, CH$_2$*C*H$_3$). IR: v(PO) = 1124.4 cm^{-1}. mp (decomp.) 108 °C.

$Cy_3PO{\cdot}(HOO)_2CEt_2$ (**5**): $[Cy_3PO{\cdot}H_2O_2]_2$ (330 mg, 1 mmol) was placed in a round bottom flask and combined with 3-pentanone (0.4 mL, 2 mmol) and aqueous H_2O_2 (0.2 mL, 2 mmol). The mixture was stirred for 1 h, then left to crystallize. $Cy_3PO{\cdot}(HOO)_2CEt_2$ (**5**) was obtained in the form of white, rod-shaped crystals (425 mg, 97% yield).

NMR (δ, $CDCl_3$), ^{31}P 58.35 (s); ^{1}H 10.82 (br. s, 2H, OO*H*), 1.96-1.81 (m, 15H, PC*H*$_{ax}$C*H*$_{eq}$C*H*$_{eq}$), 1.76-1.71 (m, 3H, PCH(CH$_2$)$_2$C*H*$_{eq}$), 1.81 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.4 Hz, 4H, CCH_2), 1.68 (q, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 4H, CCH_2), 1.47-1.37 (m, 8H, PCHCH_{ax}, CCH$_2$CH$_2$CH_2), 1.30-1.22 (m, 9H, PCHCH$_2$C*H*$_{ax}$C*H*$_{ax}$), 0.94 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 6H, CCH$_2$CH_3); ^{13}C 113.76 (s, *C*CH$_3$), 34.64 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 60.5 Hz, P*C*), 26.68 (d, $^{3}J(^{31}P\text{-}^{13}C)$ = 11.6 Hz, PCHCH$_2$*C*H$_2$), 25.93 (d, $^{2}J(^{31}P\text{-}^{13}C)$ = 3.3 Hz, PCH*C*H$_2$), 25.87 (d, $^{4}J(^{31}P\text{-}^{13}C)$ = 0.9 Hz, PCH(CH$_2$)$_2$*C*H$_2$), 21.64 (s, *C*H$_2$CH$_3$), 7.91 (s, CH$_2$*C*H$_3$). IR: v(PO) = 1126.4 cm^{-1}. mp (decomp.) 138 °C.

$Cy_3PO{\cdot}(HOO)_2C(CH_2)_5$ (**6**): 0.3 mL of H_2SO_4 (5 mmol) and 13.5 mL of aqueous H_2O_2 (0.135 mol) were combined with THF (25 mL) in a round bottom flask. Cyclohexanone (1.00 mL, 9.7 mmol) was added dropwise over a period of 15 min, while stirring vigorously. After stirring for 5 h, 10 mL of CH_2Cl_2 was added, and $NaHCO_3$ was used to neutralize the mixture to pH 7. Then the organic layer was collected, washed with H_2O (4 times 3 mL), dried with $MgSO_4$, and filtered. All solvents were removed from the filtrate in vacuo to leave pure $(HOO)_2C(CH_2)_5$ behind. The ^{1}H and ^{13}C NMR spectra of $(HOO)_2C(CH_2)_5$ matched those reported in the literature.[22] $[Cy_3PO{\cdot}H_2O_2]_2$ (297 mg, 0.9 mmol) was dissolved in 1 mL of toluene and added to the flask. The mixture was stirred for 2 h and subsequently concentrated in vacuo to about 3 mL at ambient temperature. $Cy_3PO{\cdot}(HOO)_2C(CH_2)_5$ (**6**) was obtained in the form of clear, hexagonal crystals (235 mg, 0.53 mmol, 59% yield).

NMR (δ, $CDCl_3$), ^{31}P 58.01 (s); ^{1}H 10.66 (br. s, 2H, OO*H*), 1.97-1.79 (m, 15H, PC*H*$_{ax}$C*H*$_{eq}$C*H*$_{eq}$), 1.81 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.4 Hz, 4H, CCH_2), 1.75-1.71 (m, 3H, PCH(CH$_2$)$_2$C*H*$_{eq}$), 1.58 (quin, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.4 Hz, 4H, CCH$_2$CH_2), 1.47-1.37 (m, 8H, PCHCH_{ax}, CCH$_2$CH$_2$CH_2), 1.31-1.22 (m, 9H, PCHCH$_2$C*H*$_{ax}$C*H*$_{ax}$); ^{13}C 109.52 (s, *C*CH$_3$), 34.67 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 60.5 Hz, P*C*), 29.68 (s, *C*CH$_2$), 26.69 (d, $^{3}J(^{31}P\text{-}^{13}C)$ = 12.1 Hz, PCHCH$_2$*C*H$_2$), 25.94 (d, $^{2}J(^{31}P\text{-}^{13}C)$ = 3.3 Hz, PCH*C*H$_2$), 25.89 (d, $^{4}J(^{31}P\text{-}^{13}C)$ = 0.9 Hz, PCH(CH$_2$)$_2$*C*H$_2$), 25.55 (s, CCH$_2$CH$_2$CH$_2$), 22.53 (s, CCH$_2$CH$_2$). IR: v(PO) = 1103.3 cm^{-1}. mp (decomp.) 144-150 °C.

$Cy_3PO{\cdot}(HOO)_2CMePh$ (**7**): $[Cy_3PO{\cdot}H_2O_2]_2$ (425 mg, 1.30 mmol) was dissolved in 3 mL of acetophenone (25.7 mmol) in a round bottom flask. After aqueous H_2O_2 (1.3 mL, 130 mmol) was added the mixture was stirred for 4 h. The solution was concentrated in vacuo to about 3 mL and allowed to crystallize. $Cy_3PO{\cdot}(HOO)_2CMePh$ (**7**) was obtained in the form of colorless crystals (327 mg, 54%).

NMR (δ, $CDCl_3$), ^{31}P 58.31 (s); ^{1}H 11.89 (br. s, 2H, OO*H*), 7.59-7.56 (m, 2H, H_o), 7.38-7.33 (m, 2H, H_m), 7.31-7.27 (m, 1H, H_p), 1.94-1.80 (m, 15H, PC*H*$_{ax}$C*H*$_{eq}$C*H*$_{eq}$), 1.75-1.71 (m, 3H, PCH(CH$_2$)$_2$C*H*$_{eq}$), 1.66 (s, 3H, CH_3), 1.47-1.37 (m, 6H, PCHC*H*$_{ax}$), 1.30-1.20 (m, 9H, PCHCH$_2$C*H*$_{ax}$C*H*$_{ax}$); ^{13}C 140.09 (s, C_i), 127.98 (s, C_o), 127.82 (s, C_p), 125.94 (s, C_m), 110.18, (S, *C*CH$_3$), 34.68 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 60.5 Hz, P*C*), 26.70 (d, $^{3}J(^{31}P\text{-}^{13}C)$ = 12.1 Hz, PCHCH$_2$*C*H$_2$), 25.95 (d, $^{2}J(^{31}P\text{-}^{13}C)$ = 3.3 Hz, PCH*C*H$_2$), 25.89 (d, $^{4}J(^{31}P\text{-}^{13}C)$ = 1.4 Hz, PCH(CH$_2$)$_2$*C*H$_2$), 23.40 (C*C*H$_3$). IR: v(PO) = 1122.6 cm^{-1}. mp (decomp.) 100 °C.

$(Ph_2P(O)CH_2CH_2P(O)Ph_2){\cdot}((HOO)_2CEt_2)_2$ (**8**): $Ph_2P(O)CH_2CH_2P(O)Ph_2$ (20 mg, 0.05 mmol) was dissolved in 0.3 mL of pentanone (2.8 mmol) in a round bottom flask. Subsequently, aqueous H_2O_2 (0.1 mL, 1 mmol) was added, the solution was stirred for 1 h and then left to crystallize via slow evaporation of the solvent. Adduct **8** crystallized in the form of colorless, needle-like crystals (22 mg, 78% yield).

NMR (δ, $CDCl_3$), ^{31}P 39.42 (s); ^{1}H 10.81 (virtual doublet, $J(^{31}P\text{-}^{1}H$ = 82.2 Hz, 2H, OO*H*), 7.81-7.75 (m, 8H, H_o), 7.58-7.53 (m, 4H, H_p), 7.51-7.46 (m, 8H, H_m), 2.66 (d, $^{3}J(^{31}P\text{-}^{1}H)$ = 2.7 Hz, 2H, PCH_2), 1.75 (q, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 8H, CH_2CH$_3$), 1.00 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 12H, CH$_2$CH_3); ^{13}C 132.74 (s, C_p), 130.67 (virtual quintet, $J(^{31}P\text{-}^{13}C)$ = 5.1 Hz, C_o), 129.61 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 102.8 Hz, C_i), 129.23 (virtual quintet, $J(^{31}P\text{-}^{13}C)$ = 6.1 Hz, C_m), 114.13 (s, *C*CH$_3$), 21.81 (s, CH$_2$CH$_3$), 21.05 (virtual triplet, $J(^{31}P\text{-}^{13}C)$ = 33.0 Hz, PCH$_2$), 7.99 (s, CH$_3$). IR: v(PO) = 1149.6 cm^{-1}. mp (decomp.) 104-110 °C.

$Ph_2P(O)CH_2P(O)Ph_2{\cdot}(HOO)_2CMe_2$ (**9**): $Ph_2PCH_2PPh_2$ (384 mg, 1 mmol) was dissolved in 60 mL of CH_2Cl_2 in a round bottom flask. Then aqueous H_2O_2 (0.5 mL, 5 mmol) was added, and the solution was stirred for 1 h. The organic layer was collected in a separation funnel, and the solvent was removed in vacuo. The resulting white residue of $Ph_2P(O)CH_2P(O)Ph_2$ was dissolved in 5 mL of acetone, and after the addition of 0.5 mL of aqueous H_2O_2, the product was allowed to crystallize. Adduct **9** was obtained as white, needle-like crystals (364 mg, 76% yield).

NMR (δ, $CDCl_3$), ^{31}P 30.33 (s); ^{1}H 11.01 (br. s, 2H, OO*H*), 7.72-7.66 (m, 8H, H_o), 7.47-7.42 (m, 4H, H_p), 7.38-7.33 (m, 8H, H_m), 3.62 (t, $^{3}J(^{31}P\text{-}^{1}H)$ = 14.7 Hz, 2H, PCH_2), 1.48 (s, 6H, CCH_3); ^{13}C 132.21 (s, C_p), 131.07 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 107.0 Hz, C_i), 130.86 (virtual quintet, $J(^{31}P\text{-}^{13}C)$ = 5.1 Hz, C_o), 128.64 (virtual quintet, $J(^{31}P\text{-}^{13}C)$ = 6.1 Hz, C_m), 109.21 (s, *C*CH$_3$), 33.40 (t, $^{1}J(^{31}P\text{-}^{13}C)$ = 59.1 Hz, PCH$_2$)20.63 (s, CCH$_3$).

NMR (δ, $(CD_3)_2CO$), ^{31}P 26.63 (s); ^{1}H 10.49 (br. s, OO*H*), 7.87-7.81 (ddd, $^{3}J(^{31}P\text{-}^{1}H)$ = 12.2 Hz, $^{3}J(^{1}H\text{-}^{1}H)$ = 8.3 Hz, $^{4}J(^{1}H\text{-}^{1}H)$ = 1.2 Hz, H_o), 7.52-7.47 (dt, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.3 Hz, $^{4}J(^{1}H\text{-}^{1}H)$ = 1.2 Hz, H_p), 7.43-7.38 (dt, $^{3}J(^{1}H\text{-}^{1}H)$ = 8.3 Hz, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.3 Hz, H_m), 3.99 (t, $^{2}J(^{31}P\text{-}^{1}H)$ = 13.9 Hz, CH_2), 1.36 (s, CH_3); ^{13}C 133.46 (d, $^{1}J(^{31}P\text{-}^{13}C)$ = 106.2 Hz, C_i), 131.74 (s, C_p), 130.89 (virtual quintet, $J(^{31}P\text{-}^{13}C)$ = 29.3 Hz, C_o), 128.38 (virtual quintet, $J(^{31}P\text{-}^{13}C)$ = 30.5 Hz, C_m), 108.34 (s, CH$_3$*C*), 33.11 (t, $^{1}J(^{31}P\text{-}^{13}C)$ = 60.9 Hz, PCH$_2$), 20.25 (s, *C*H$_3$). IR: v(PO) = 1163.1 cm^{-1}. mp (decomp.) 120 °C.

Representative procedure for the oxidation of tetrahydrothiophene (THT) to the sulfoxide: 17.6 mg (0.2 mmol) of THT and 0.1 mmol of the respective adduct were weighed into a 5 mm NMR tube and dissolved in 0.5 mL of C_6D_6 inside a glove box. The tube was then sealed with a glass stopper[48] lubricated with silicone grease. ^{1}H and ^{13}C NMR spectra of the sample were recorded at room temperature every 30 min until the oxidation was complete. In between the measurements, the sample was kept in an oil bath with the desired reaction temperature. Stirring versus shaking the NMR tube did not change the pace of the reaction.

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[30] CCDC 1449060 contains the supplementary crystallographic data of $Ph_3PO{\cdot}(HOO)_2CMeEt$ (**3**) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_rdquest/cif., $(C_{18}H_{15}O_1P_1){\cdot}(C_4H_{10}O_4)$ unit cell parameters: *a* 13.212(3), *b* 10.652(2), *c* 15.084(3), *P*c.

[31] CCDC 1449059 contains the supplementary crystallographic data of $Cy_3PO{\cdot}(HOO)_2CMeEt$ (**4**) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_rdquest/cif., $(C_{18}H_{33}O_1P_1){\cdot}(C_4H_{10}O_4)$ unit cell parameters: *a* 10.9525(6), *b* 18.6740(10), *c* 11.5031(6), $P2_1/c$.

[32] Data sets of two polymorphs of **5** with orthorhombic **(a)** and columnar **(b)** crystals have been obtained:
(a) CCDC 1451015 contains the supplementary crystallographic data of $Cy_3PO{\cdot}(HOO)_2CEt_2$ (**5**) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_rdquest/cif., $(C_{18}H_{33}O_1P_1){\cdot}(C_5H_{12}O_4)$ unit cell parameters: *a* 11.0007(5), *b* 18.5990(8), *c* 11.8282(6), $P2_1/c$.
(b) CCDC 1451754 contains the supplementary crystallographic data of $Cy_3PO{\cdot}(HOO)_2CEt_2$ (**5**) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_rdquest/cif., $(C_{18}H_{33}O_1P_1){\cdot}(C_5H_{12}O_4)$ unit cell parameters: *a* 9.6292(4), *b* 11.1735(5), *c* 12.0349(6), *P*-1.

[33] CCDC 1451014 contains the supplementary crystallographic data of $Cy_3PO{\cdot}(HOO)_2C(CH_2)_5$ (**6**) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_rdquest/cif., $(C_{18}H_{33}O_1P_1){\cdot}(C_6H_{12}O_4)$ unit cell parameters: *a* 10.8742(4), *b* 18.6293(6), *c* 11.9591(4), $P2_1/c$.

[34] CCDC 1449062 contains the supplementary crystallographic data of $Cy_3PO{\cdot}(HOO)_2CMePh$ (**7**) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_rdquest/cif., $(C_{18}H_{33}O_1P_1){\cdot}(C_8H_{10}O_4)$ unit cell parameters: *a* 19.2260(9), *b* 10.9723(5), *c* 25.2474(15), C_2/c.

[35] CCDC 1449063 contains the supplementary crystallographic data of $(Ph_2P(O)CH_2CH_2P(O)Ph_2){\cdot}((HOO)_2CEt_2)_2$ (**8**) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_rdquest/cif., $(C_{26}H_{24}O_2P_2){\cdot}(C_5H_{12}O_4)_2$ unit cell parameters: *a* 8.7944(19), *b* 12.076(3), *c* 17.271(4), $P2_1/n$.

[36] CCDC 1449058 contains the supplementary crystallographic data of $Ph_2P(O)CH_2P(O)Ph_2{\cdot}(HOO)_2CMe_2$ (**9**) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_rdquest/cif., $(C_{25}H_{22}O_2P_2){\cdot}(C_3H_8O_4)$ unit cell parameters: *a* 23.6612(14), *b* 11.1060(6), *c* 21.4016(12), Pb_cn.

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