

Supporting Information

**Hydrogen Peroxide and Dihydroperoxy Propane Adducts of  
Phosphine Oxides as Stoichiometric and Soluble Oxidizing Agents**

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## Supplementary Material

### Experimental Procedures

The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of liquids were recorded at 499.70, 125.66, and 202.28 MHz on a 500 MHz Varian spectrometer. The  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded with  $^1\text{H}$  decoupling if not stated otherwise. Neat  $\text{Ph}_2\text{PCL}$  ( $\delta(^{31}\text{P}) = +81.92$  ppm) in a capillary centered in the 5 mm NMR tubes was used for referencing the  $^{31}\text{P}$  chemical shifts of dissolved compounds. For referencing the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts, if not mentioned otherwise, the residual proton signals and the carbon signals of the solvents  $\text{C}_6\text{D}_6$  ( $\delta(^1\text{H}) = 7.16$  ppm,  $\delta(^{13}\text{C}) = 128.00$  ppm),  $\text{CDCl}_3$  ( $\delta(^1\text{H}) = 7.26$  ppm,  $\delta(^{13}\text{C}) = 77.00$  ppm) and acetone- $d_6$  ( $\delta(^1\text{H}) = 2.09$  ppm,  $\delta(^{13}\text{C}) = 30.60$  ppm), have been used. All signal assignments were based on comparisons with analogous phosphine oxides.<sup>[10]</sup> The  $^{31}\text{P}$  solid-state NMR spectra were measured with a Bruker Avance 400 widebore NMR spectrometer equipped with a 4 mm multinuclear MAS probehead and  $\text{ZrO}_2$  rotors. For the  $^{31}\text{P}$  CP measurements  $^1\text{H}$  high-power decoupling was applied with a contact pulse duration of 5 ms.  $\text{NH}_4\text{H}_2\text{PO}_4$  was used to establish the Hartmann-Hahn matching condition and as the external chemical shift standard ( $\delta(^{31}\text{P}) = +0.81$  ppm). The recycle delay was 3 s for all CP spectra. 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 and a purified  $\text{N}_2$  atmosphere, if not stated otherwise. Reagents purchased from Sigma Aldrich or VWR were used without further purification. Aqueous  $\text{H}_2\text{O}_2$  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.).

Representative procedure to determine the oxidative power of hydrogen peroxide and dihydroperoxy propane adducts of phosphine oxides: 6 mg of **3** (0.015 mmol) and 16 mg of  $\text{PPh}_3$  (0.061 mmol) are dissolved in 0.35 mL of  $\text{CDCl}_3$  in an NMR tube under air ( $\text{PPh}_3$  is not oxidized by oxygen from the air under these conditions). The oxidation is monitored via  $^{31}\text{P}$  NMR spectroscopy and is complete within 20 min. The integral ratio between the signals of  $\text{OPPh}_3$  and the remaining  $\text{PPh}_3$  is used to calculate the oxidative power of **3**. For this particular reaction, 51% of the initial  $\text{PPh}_3$  (0.031 mmol) is oxidized, which amounts to 2 molar equivalents of active oxygen per mole of **3**. After adduct **3** was stored as a powder at  $-20$  °C for 10 days no loss of oxidative power was found when an aliquot of this batch was investigated as described.

Hydrogen peroxide adduct of tributylphosphine oxide [ $\text{Bu}_3\text{PO}\cdot\text{H}_2\text{O}_2$ ]<sub>2</sub> (**1**):  $\text{Bu}_3\text{P}$  (20 mg, 0.099 mmol) is weighed into a Schlenk flask inside a glove box. The flask is then sealed, brought outside, and acetone (40 mL) is added under a nitrogen flow. Once the phosphine is dissolved,  $\text{H}_2\text{O}_2$  (1.0 mL, 10 mmol) is added and the reaction mixture is stirred for 1 h. 100 mL of EtOH is then added to the flask, and the azeotropic mixture of EtOH and  $\text{H}_2\text{O}$  is removed *in vacuo* at ambient temperature. The resulting viscous sample is washed with toluene. The [ $\text{Bu}_3\text{PO}\cdot\text{H}_2\text{O}_2$ ]<sub>2</sub> adduct is obtained as white rhombic crystals (19 mg, 0.075 mmol, 76% yield).

NMR ( $\delta$ ,  $\text{CDCl}_3$ ),  $^{31}\text{P}$  43.16 (s);  $^1\text{H}$  9.10 (br. s,  $\text{H}_2\text{O}_2$ ), 1.41 (d,  $^3J(^{31}\text{P}-^1\text{H}) = 12.5$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  39.17 (d,  $^1J(^{31}\text{P}-^{13}\text{C}) = 49.6$  Hz, PC), 29.00 ( $\text{CH}_3$ ).

NMR ( $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ),  $^{31}\text{P}$  65.61 (s); 1.34 (d,  $^3J(^{31}\text{P}-^1\text{H}) = 12.0$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  40.35 (d,  $^1J(^{31}\text{P}-^{13}\text{C}) = 51.1$  Hz, PC), 30.08 (s,  $\text{CH}_3$ ). mp 122-135 °C.

Hydrogen peroxide adduct of triphenylphosphine oxide, [ $\text{Ph}_3\text{PO}\cdot\text{H}_2\text{O}_2$ ]<sub>2</sub>· $\text{H}_2\text{O}_2$  (**2**):

$\text{Ph}_3\text{P}$  (150 mg, 0.572 mmol) is weighed into a Schlenk flask flushed with nitrogen.  $\text{CH}_2\text{Cl}_2$  (150 mL) is added under a nitrogen flow. Once the phosphine is completely dissolved,  $\text{H}_2\text{O}_2$  (1.0 mL, 10 mmol) is added and the reaction mixture is stirred for 30 min. The organic layer is collected via separation funnel, and the solvent is removed *in vacuo*. The resulting white precipitate is dissolved in acetone (60 mL), and after the addition of  $\text{H}_2\text{O}_2$  (0.1 mL, 1 mmol), the sample is allowed to crystallize. [ $\text{Ph}_3\text{PO}\cdot\text{H}_2\text{O}_2$ ]<sub>2</sub>· $\text{H}_2\text{O}_2$  is obtained as colorless needles (286 mg, 0.434 mmol, 76% yield).

NMR ( $\delta$ ,  $\text{CDCl}_3$ ),  $^{31}\text{P}$  32.84 (s);  $^1\text{H}$  11.24 (br. s,  $\text{H}_2\text{O}_2$ ), 8.93 (br. s,  $\text{H}_2\text{O}_2$ ), 7.67-7.62 (m, 6H,  $H_o$ ), 7.58-7.55 (m, 3H,  $H_p$ ), 7.49-7.45 (m, 6H,  $H_m$ );  $^{13}\text{C}$  132.43 (s,  $C_p$ ), 132.04 (d,  $^2J(^{31}\text{P}-^{13}\text{C}) = 10.2$  Hz,  $C_o$ ), 130.71 (d,  $^1J(^{31}\text{P}-^{13}\text{C}) = 108.8$  Hz,  $C_i$ ), 128.69 (d,  $^3J(^{31}\text{P}-^{13}\text{C}) = 12.1$  Hz,  $C_m$ ).

Dihydroperoxy propane adduct  $\text{Cy}_3\text{PO}\cdot(\text{HOO})_2\text{CMe}_2$  (**3**):

$\text{Cy}_3\text{P}$  (100 mg, 0.357 mmol) is weighed into a Schlenk flask inside a glove box. The flask is then sealed, brought outside, and acetone (60 mL) is added under a nitrogen flow. Once the phosphine is completely dissolved,  $\text{H}_2\text{O}_2$  (0.5 mL, 5.1 mmol) is added and the reaction mixture is stirred for 1 h. 100 mL of EtOH is then added to the flask, and the azeotropic mixture of EtOH and  $\text{H}_2\text{O}$  is removed *in vacuo* at ambient temperature.  $(\text{Cy}_3\text{PO})\cdot(\text{HOO})_2\text{CMe}_2$  is obtained as colorless hexagonal crystals (126 mg, 0.311 mmol, 87% yield).

NMR ( $\delta$ ,  $\text{CDCl}_3$ ),  $^{31}\text{P}$  55.59 (s);  $^1\text{H}$  1.97-1.80 (m, 15H,  $\text{PCH}_{\text{ax}}\text{CH}_{\text{eq}}\text{CH}_{\text{eq}}$ ), 1.77-1.70 (s, 3H,  $\text{PCH}(\text{CH}_2)_2\text{CH}_{\text{eq}}$ ), 1.49-1.36 (s, 12H,  $\text{PCHCH}_{\text{ax}}$ ,  $\text{CH}_3$ ), 1.36-1.21 (m, 9H,  $\text{PCHCH}_2\text{CH}_{\text{ax}}\text{CH}_{\text{ax}}$ );  $^{13}\text{C}$  108.91 (s,  $\text{CH}_3\text{C}$ ), 34.79 (d,  $^1J(^{31}\text{P}-^{13}\text{C}) = 60.9$  Hz, PC), 26.74 (d,  $^3J(^{31}\text{P}-^{13}\text{C}) = 12.7$  Hz,  $\text{PCHCH}_2\text{CH}_2$ ), 25.98 (d,  $^2J(^{31}\text{P}-^{13}\text{C}) = 3.6$  Hz,  $\text{PCHCH}_2$ ), 25.92 (d,  $^4J(^{31}\text{P}-^{13}\text{C}) = 1.8$  Hz,  $\text{PCH}(\text{CH}_2)_2\text{CH}_2$ ), 20.63 (s,  $\text{CH}_3$ ).

NMR ( $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ),  $^{31}\text{P}$  56.44 (s);  $^1\text{H}$  11.45 (br. s, OOH), 2.02-1.89 (m, 9H,  $\text{PCH}_{\text{ax}}\text{CH}_{\text{eq}}$ ), 1.86-1.76 (m, 6H,  $\text{PCHCH}_2\text{CH}_{\text{eq}}$ ), 1.74-1.66 (m, 3H,  $\text{PCH}(\text{CH}_2)_2\text{CH}_{\text{eq}}$ ), 1.52-1.38 (m, 6H,  $\text{PCHCH}_{\text{ax}}$ ), 1.37-1.19 (m, 9H,  $\text{PCHCH}_2\text{CH}_{\text{ax}}\text{CH}_{\text{ax}}$ ), 1.30 (s,  $\text{CH}_3$ );  $^{13}\text{C}$  108.61 (s,  $\text{CH}_3\text{C}$ ), 35.53 (d,  $^1J(^{31}\text{P}-^{13}\text{C}) = 61.0$  Hz, PC), 27.36 (d,  $^3J(^{31}\text{P}-^{13}\text{C}) = 12.1$  Hz,  $\text{PCHCH}_2\text{CH}_2$ ), 26.74 (s,  $\text{PCH}(\text{CH}_2)_2\text{CH}_2$ ), 26.73 (d,  $^2J(^{31}\text{P}-^{13}\text{C}) = 2.8$  Hz,  $\text{PCHCH}_2$ ).

Dihydroperoxy propane adduct  $\text{Ph}_3\text{PO}\cdot(\text{HOO})_2\text{CMe}_2$  (**4**):

$\text{Ph}_3\text{P}$  (200 mg, 0.762 mmol) is weighed into a Schlenk flask flushed with nitrogen. Acetone (100 mL) is added under a nitrogen flow. Once the phosphine is completely dissolved,  $\text{H}_2\text{O}_2$  (1.0 mL, 10 mmol) is added and the reaction mixture is stirred for 3 h. The sample is concentrated *in vacuo* to 5 mL, then allowed to crystallize.  $(\text{Ph}_3\text{PO})\cdot(\text{HOO})_2\text{CMe}_2$  is obtained as colorless rectangular crystals (243 mg, 0.629 mmol, 82.5% yield).

NMR ( $\delta$ , CDCl<sub>3</sub>), <sup>31</sup>P 34.74 (s); <sup>1</sup>H 11.29-10.90 (br. s, OOH), 7.68-7.61 (m, 6H, H<sub>o</sub>), 7.60-7.55 (m, 3H, H<sub>p</sub>), 7.51-7.46 (m, 6H, H<sub>m</sub>), 1.47 (m, 6H, CH<sub>3</sub>); <sup>13</sup>C 132.57 (s, C<sub>p</sub>), 132.10 (d, <sup>2</sup>J(<sup>31</sup>P-<sup>13</sup>C) = 10.7 Hz, C<sub>o</sub>), 130.56 (d, <sup>1</sup>J(<sup>31</sup>P-<sup>13</sup>C) = 106.1 Hz, C<sub>i</sub>), 128.77 (d, <sup>3</sup>J(<sup>31</sup>P-<sup>13</sup>C) = 12.6 Hz, C<sub>m</sub>), 109.28 (s, CH<sub>3</sub>C), 20.64 (s, CH<sub>3</sub>).

NMR ( $\delta$ , (CD<sub>3</sub>)<sub>2</sub>CO), <sup>31</sup>P 31.21 (s); <sup>1</sup>H 10.97 (br. s, OOH), 7.76-7.68 (m, 6H, H<sub>o</sub>), 7.67-7.62 (m, 3H, H<sub>p</sub>), 7.60-7.53 (m, 6H, H<sub>m</sub>), 1.35 (s, CH<sub>3</sub>).



Figure S1. Representative single crystals of Ph<sub>3</sub>PO·(HO)<sub>2</sub>CMe<sub>2</sub> (4). The given scale is in cm units.

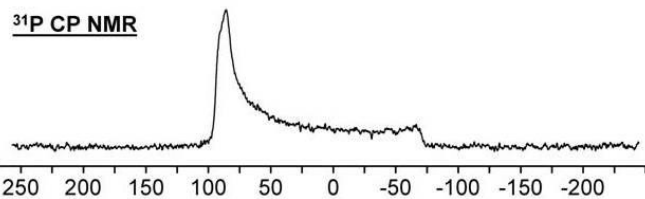


Figure S3. <sup>31</sup>P CP NMR spectrum of polycrystalline 4. The CSA, defined as the span of the signal  $\delta_{11}$ - $\delta_{33}$ , is 166.3 ppm.  $\delta_{11}$  = 95.4,  $\delta_{22}$  = 85.0,  $\delta_{33}$  = -70.9,  $\delta_{\text{iso}}$  = 36.5 ppm.

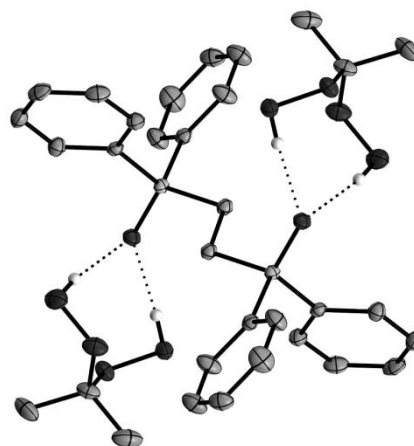


Figure S4. Single-crystal X-ray structure of [CH<sub>2</sub>Ph<sub>2</sub>PO·(HO)<sub>2</sub>CMe<sub>2</sub>]<sub>2</sub> (5).<sup>[24,28]</sup>

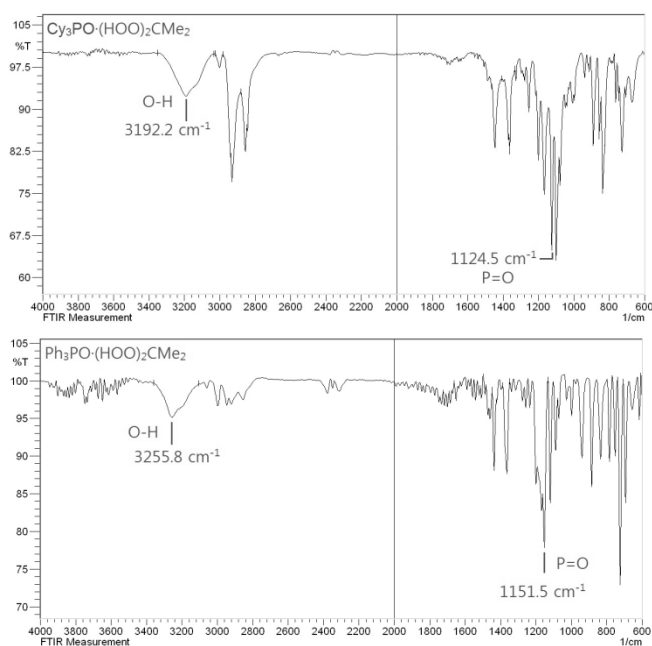


Figure S2. IR spectra of neat 3 (top) and 4 (bottom).

Table S1. Solubilities of the dihydroperoxy propane adducts 3 and 4 in representative solvents.

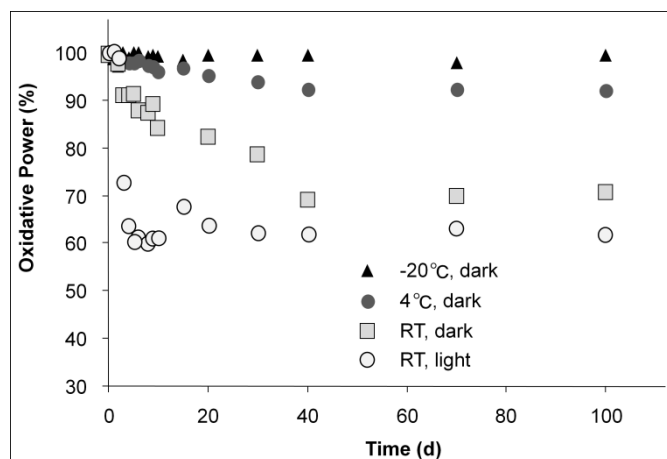
Solvent	Solubilities [mg/mL] of R <sub>3</sub> PO·(HO) <sub>2</sub> CMe <sub>2</sub>	
	R = Cy (3)	R = Ph (4)
H <sub>2</sub> O	0	0
MeOH	256	120
EtOH	210	190
Acetone	352	113
EtOAc	237	179
CHCl <sub>3</sub>	766	576
THF	249	133
CH <sub>2</sub> Cl <sub>2</sub>	194	333
Et <sub>2</sub> O	230	81
Toluene	400	173
Benzene	405	117
Hexane	8	3

Table S2. Melting points and decomposition temperature ranges [°C] of the

phosphine oxides and their corresponding adducts.

R	m.p. of R <sub>3</sub> PO	Decomp. temp. of (R <sub>3</sub> PO) <sub>x</sub> ·(H <sub>2</sub> O <sub>2</sub> ) <sub>y</sub>	Decomp. temp. of R <sub>3</sub> PO·(HOO) <sub>2</sub> CMe <sub>2</sub>
Cy	155-157 <sup>[a]</sup>	120-134 <sup>[a]</sup>	70-104
Ph	156.5-158 <sup>[a]</sup>	143-185	75-85

[a] values taken from reference [10].



**Figure S5.** Oxidative power of Ph<sub>3</sub>PO·(HOO)<sub>2</sub>CMe<sub>2</sub> (**4**) stored at a) room temperature, b) room temperature in the absence of light, c) 3.5 °C in the absence of light, and d) -19.6 °C in the dark. 100% equals to 2 moles of active oxygen atoms per mole of **1**.