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Di(hydroperoxy)adamantane Adducts: Synthesis, Characterization and Application as Oxidizers for the Direct Esterification of Aldehydes

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X-Ray Crystallography

1. A solution of **1** in a 1:1 mixture of hexanes:dichloromethane was concentrated by slow evaporation. A colorless plate with very well-defined faces from a representative sample of crystals of the same habit was collected and data were obtained as outlined in Table **S1**. The X-ray radiation employed was generated from a Cu-Iμs X-ray tube (K_α = 1.5418 Å with a potential of 50 kV and a current of 1.0 mA). 45 data frames were taken at widths of 1.0°. These reflections were used to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (20 sets) was initiated using omega and phi scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program *APEX3*.[S1] The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program *SADABS* [S2] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data were used to determine the space group. A solution was obtained readily using *XT/XS* in *APEX3*.[S1,S3] A molecule of water was found hydrated. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms.[S4] All non-hydrogen atoms were refined with anisotropic thermal parameters.

Absence of additional symmetry and voids were confirmed using *PLATON (ADDSYM)*.[S5] The structure was refined (weighted least squares refinement on F^2) to convergence.[S3,S6] *Olex2* and *Mercury* were employed for the final data presentation and structure plots.[S6,S7]

2. A solution of **2** in a 2:3 mixture of hexanes:dichloromethane was concentrated by slow evaporation. A colorless block with very well-defined faces from a representative sample of crystals of the same habit was

collected and data were obtained as outlined in Table **S1**, and the structure was solved as in **1**.

The X-ray radiation employed was generated from a Mo-X-ray sealed tube (K_α = 0.71073 Å with a potential of 40 kV and a current of 40.0 mA). 60 data frames were taken at widths of 1.0°. These reflections were used in the auto-indexing procedure to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (4 sets) was initiated using omega scans.

Unusual thermal ellipsoids and the residual electron density peaks near [C23-C31, O2-O5] indicated disorder of the group, and were modeled between two positions with an occupancy ratio of 0.57:0.43. Appropriate restraints and constraints were added to keep the bond distances, angles and thermal ellipsoids meaningful.

3. A solution of **3** in a 2:3 mixture of hexanes:dichloromethane was concentrated by slow evaporation. A colorless block with very well-defined faces from a representative sample of crystals of the same habit was collected and data were obtained as outlined in Table **S2**, and the structure was solved as in **1**. The X-ray radiation employed was generated from a Mo-X-ray sealed tube (K_α = 0.71073 Å). 45 data frames were taken at widths of 1.0°. These reflections were used in the auto-indexing procedure to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (13 sets) was initiated using omega and phi scans.

Unusual thermal ellipsoids and the residual electron density peaks near [C23-C31, O2-O5] indicated disorder and were modeled between two positions with an occupancy ratio of 0.89:0.11. Appropriate restraints and constraints were added to keep the bond distances, angles and thermal ellipsoids meaningful. In the thermal ellipsoids plot, only the major component of the disorder is shown.

4. A solution of **4** in a 2:3 mixture of hexanes:dichloromethane was concentrated by slow evaporation. A yellow block with very well-defined faces from a representative sample of crystals of the same habit was collected and data were obtained as outlined in Table **S2**, and the structure was solved as in **1**. The X-ray radiation employed was generated from a Mo-X-ray sealed tube (K_α = 0.71073 Å). 45 data frames were taken at widths of 1.0°. These reflections were used to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (4 sets) was initiated using omega scans.

Unusual thermal ellipsoids and the residual electron density peaks near [C19-C28, O2-O5] indicated disorder and were modeled between two positions with an occupancy ratio of 0.60:0.40. Appropriate restraints and constraints were added to keep the bond distances, angles, and thermal ellipsoids meaningful. In the thermal ellipsoids plot, only the major component of the disorder is shown.

5. A solution of **8** in a 2:3 mixture of hexanes:dichloromethane was concentrated by slow evaporation. A colorless block with very well-defined faces from a representative sample of crystals of the same habit was collected and data were obtained as outlined in Table **S2**, and the structure was solved as in **1**. The X-ray radiation employed was generated from a Mo-X-ray sealed tube ($K_\alpha = 0.71073$ Å with a potential of 40 kV and a current of 40 mA). 60 data frames were taken at widths of 1.0°. These reflections were used to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (10 sets) was initiated using omega and phi scans.

Two molecules of dichloromethane were found solvated. While both were found disordered, we were able to model the disorder successfully for one. The second dichloromethane was partially occupied and disordered and could not be modeled successfully. The latter was MASKed using OLEX2, which gave 70 e$^-$ per unit cell (lower than expected number of electrons for CH_2Cl_2: $42 \times 2 = 84$).
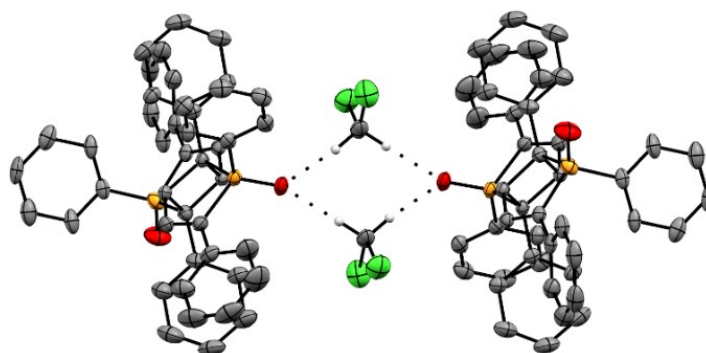

Figure S1. Single crystal X-ray structure of the phosphole oxide dimer DCM adduct **8** including the bridging CH_2Cl_2 molecules.[58]

Table S1. Crystallographic data for **1** and **2**.

	1	2
Deposition #	CCDC 1980801	CCDC 1980802
empirical formula	$C_{10}H_{18}O_5$	$C_{31}H_{37}O_5P$
formula weight	218.24	520.57
temperature [K]	110.0	110.0
diffractometer	Bruker Venture	Bruker APEX 3
wavelength [Å]	1.54178	0.71073
crystal system	orthorhombic	orthorhombic
space group	*Pbca*	*Pbca*
unit cell dimensions:		
a [Å]	10.5546(9)	21.0842(16)
b [Å]	8.3898(7)	11.7871(9)
c [Å]	23.5993(19)	21.7655(17)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
V [Å^3]	2089.7(3)	5409.2(7)
Z	8	8
ρ_{calc} [Mg/m^3]	1.387	1.278
μ [mm^{-1}]	0.931	0.141
F(000)	944	2224
crystal size [mm^3]	0.162 × 0.158 × 0.032	0.481 × 0.208 × 0.067
Θ limit [°]	3.746 to 62.465	1.871 to 25.000
index range (h, k, l)	−12, 12; −9, 9; −26, 27	−25, 25; −14, 14; −25, 25
reflections collected	30771	57147
independent reflections	1676	4759
R(int)	0.0308	0.0467
completeness to Θ	99.9 %	100.0 %
max. and min. transmission	0.5220 and 0.4283	0.7456 and 0.6923
data/restraints/parameters	1676 / 0 / 136	4759 / 807 / 446
goodness-of-fit on F^2	1.083	1.063
R indices (final) [$I > 2\sigma(I)$]		
R_1	0.0380	0.0341
wR_2	0.1007	0.0862
R indices (all data)		
R_1	0.0403	0.0456
wR_2	0.1042	0.0945
largest diff. peak and hole [eÅ^{-3}]	0.389 and -0.215	0.252 and -0.250

Table S2. Crystallographic data for **3**, **4** and **8**.

	3	4	8
Deposition #	CCDC 1980803	CCDC 1980804	CCDC 2023784
empirical formula	$C_{31}H_{37}O_5P$	$C_{28}H_{48}O_5P$	$C_{45}H_{36}Cl_2O_2P_2$
formula weight	520.57	495.63	741.58
temperature [K]	110.0	110.0	110.0
diffractometer	Bruker Quest	Bruker Quest	Bruker APEX 3
wavelength [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	P-1	P-1
unit cell dimensions:			
a [Å]	16.0424(17)	9.6844(3)	9.0759(5)
b [Å]	11.7362(12)	11.1339(4)	11.4561(7)
c [Å]	14.7397(16)	13.0829(5)	20.3379(12)
α [°]	90	99.3060(10)	86.205(3)
β [°]	106.362(3)	96.0350(10)	86.487(3)
γ [°]	90	90.6870(10)	72.612(3)
V [Å³]	2662.8(5)	1383.78(8)	2011.7(2)
Z	4	2	2
ρ_{calc} [Mg/m³]	1.299	1.190	1.224
μ [mm⁻¹]	0.143	0.134	0.276
F(000)	1112	542	772
crystal size [mm³]	0.245 × 0.159 × 0.146	0.526 × 0.397 × 0.322	0.514 × 0.367 × 0.208
Θ limit [°]	2.182 to 27.606	2.234 to 24.998	4.328 to 24.998
index range (h, k, l)	−20, 20; −15, 15; −19, 19	−11, 11; −13, 13; −15, 15	−10, 10; −13, 13; −24, 24
reflections collected	109510	14566	54613
independent reflections	6163	4842	7046
R(int)	0.0710	0.0199	0.0525
completeness to Θ	100.0 %	99.1 %	99.4
max. and min. transmission	0.5301 and 0.3923	0.4305 and 0.4023	0.7456 and 0.6211
data/restraints/parameters	6163 / 7 / 383	4842 / 821 / 410	7046 / 271 / 495
goodness-of-fit on F²	1.084	1.021	1.029
R indices (final) [$I > 2\sigma(I)$]			
R_1	0.0392	0.0395	0.0411
wR_2	0.0938	0.0993	0.0981
R indices (all data)			
R_1	0.0482	0.0426	0.0528
wR_2	0.0999	0.1015	0.1067
largest diff. peak and hole [eÅ⁻³]	0.310 and -0.414	0.381 and -0.362	0.456 and -0.442

References

[S1] Bruker (2015), *APEX3*, Bruker AXS Inc., Madison, Wisconsin, USA.

[S2] Bruker (2001), *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA.

[S3] G. M. Sheldrick (2008), *XT, XS* Acta Cryst. A**64**, 112-122. G. M. Sheldrick (2015), Acta Cryst. A**71**, 3-8. G. M. Sheldrick (2015), Acta Cryst. C**71**, 3-8. BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

[S4] The refinement was stabilized (zero shift) before the H atoms were added to the OOH groups. The latter H atoms were placed in one of the following ways: (a) If residual electron densities accounting for the corresponding H atoms were found, they were assigned as H atoms, and then were set riding on the parent O atoms. (b) If the H atoms could not be located from residual electron densities, they were placed geometrically with respect to the O atoms they were hydrogen-bonded to, and then were set riding on the parent O atoms. The last step was carried out after all remaining atoms were stabilized, confirming there were no major shifts in those atoms after the addition of the hydrogen atoms in question.

[S5] A. L. Spek (2009), *PLATON*, Acta Cryst. D**65**, 148-155.

[S6] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. J. Puschmann (2009), *OLEX2*, Appl. Cryst., **42**, 339-341.

[S7] R. Taylor, C. F. Macrae (2001), *Mercury*, Acta Cryst., B**57**, 815-827.

Direct Oxidative Esterification

Table S3. Direct oxidative esterification of 1 equivalent of nonyl aldehyde using the Ahn adduct $Ph_3PO \cdot (HOO)_2CMe_2$ (**9**) as oxygen source and $AlCl_3$ as the catalyst. All reactions have been performed in 1 mL of methanol and at room temperature under a nitrogen atmosphere.

Entry #	Aldehyde 1 eq (mmol/mg)	Adduct (mmol/mg)	Catalyst (mmol/mg)	Time (min)	Main Product	Conversion (%)	Ester in Product (%)
1	0.267/38.0	0.159/61.3 **(0.596 eq)**	0.067/9.0 **(0.25 eq)**	10	Ester	71.7	80
2	0.302/43.0	0.171/65.9 **(0.566 eq)**	0.0757/10.1 **(0.25 eq)**	45	Ester	99.6	100
3	0.260/37.0	0.155/59.8 **(0.596 eq)**	0	45	Acid	11.6	0
4	0.232/33.0	0	0.060/8.0 **(0.26 eq)**	45	Acid	12.6	32
5	0.274/39.0	0	0	45	Acid	3.9	0
6	0.274/39.0	0.162/62.6	0.594/58.4*	45	Acid	100	13

* Catalyst used in entry 6 is 12 M HCl. 0.594 mmol corresponds to the amount of the HCl in the solution.

Table S4. Direct oxidative esterification of 1 equivalent of nonyl aldehyde using the Ahn adduct $Ph_3PO \cdot (HOO)_2CMe_2$ (**9**) as oxygen source and $AlCl_3$ as the catalyst. All reactions have been performed in 1 mL of methanol and at room temperature under a nitrogen atmosphere. The reaction time was 45 minutes for all entries.

Entry #	Aldehyde 1 eq (mmol/mg)	Adduct[†] (mmol/mg)	Active oxygen[‡] (mmol)	Catalyst (mmol/mg)	Conversion (%)	Ester in Product (%)
1	0.288/41.0	0.3489/134.8 **(1.211 eq)**	0.5931 **(2.059 eq)**	0.0772/10.3 **(0.268 eq)**	97.4	100
2	0.302/43.0	0.171/65.9 **(0.566 eq)**	0.291 **(0.964 eq)**	0.0757/10.1 **(0.251 eq)**	99.6	100
3	0.345/49.0	0.136/52.7 **(0.394 eq)**	0.231 **(0.670 eq)**	0.0877/11.7 **(0.254 eq)**	83.8	100
4	0.295/42.0	0.0807/31.2 **(0.274 eq)**	0.137 **(0.464 eq)**	0.0757/10.1 **(0.257 eq)**	58.7	100

[†]Adduct used for the reaction has 85% oxidative power.

[‡]Active oxygen(mmol) = adduct(mmol)·0.85·2; hereby 0.85 is the oxidative power and 2 is the number of active oxygen atoms per adduct.

Table S5. Direct oxidative esterification of 1 equivalent each of benzaldehyde (**10**) using the Ahn adduct $Ph_3PO\cdot(HOO)_2CMe_2$ (**9**) as oxygen source and $AlCl_3$ as the catalyst. All reactions have been performed in 1 mL of methanol and at room temperature under a nitrogen atmosphere.

Entry #	Aldehyde 1 eq (mmol/mg)	Adduct (mmol/mg)	Catalyst (mmol/mg)	Time	Main Product	Conversion (%)	Ester in Product (%)
1	0.297/31.5	0.174/67.0 (0.586 eq)	0.0780/10.4 (0.262 eq)	45 min	Ester	32.1*	100
2	0.411/43.6	0.4329/167.1 (1.053 eq)	0.188/25.0 (0.457 eq)	5 h	Ester	85.6	100
3	0.411/43.6	0.4329/167.1 (1.053 eq)	0.188/25.0 (0.457 eq)	8 h	Ester	79.2*	100
4	0.642/68.0	0.3883/149.9 (0.604 eq)	0.159/21.2 (0.248 eq)	1 h	Ester	40.5	87
5	0.642/68.0	0.3883/149.9 (0.604 eq)	0.159/21.2 (0.248 eq)	6 h	Ester	79.2	95.5
6	0.642/68.0	0.3883/149.9 (0.604 eq)	0.159/21.2 (0.248 eq)	11 h	Ester	74.4	94.4

*The reaction mixtures of entries 1 and 3 were extracted with hexane prior to analysis, which might be the reason why their conversion values are slightly lower.

Table S6. Direct oxidative esterification of 1 equivalent each of *p*-methylbenzaldehyde (**11**), *p*-bromobenzaldehyde (**12**), and *o*-hydroxybenzaldehyde (**13**) using the Ahn adduct $Ph_3PO\cdot(HOO)_2CMe_2$ (**9**) as oxygen source and $AlCl_3$ as the catalyst. All reactions have been performed in 1 mL of methanol and at room temperature under a nitrogen atmosphere.

Alde-hyde	Aldehyde 1 eq (mmol/mg)	Adduct (mmol/mg)	Catalyst (mmol/mg)	Time	Main Product	Conversion (%)	Ester in Product (%)
11	0.567/68.0	0.351/135.6 (0.619 eq)	0.150/20.0 (0.265 eq)	45 min	Ester	37.2	93.4
11	0.567/68.0	0.351/135.6 (0.619 eq)	0.150/20.0 (0.265 eq)	5 h	Ester	70.0	88.1
12	0.112/20.8	0.0754/29.1 (0.673 eq)	0.029/3.8 (0.255 eq)	5 h	Ester	82.1	100
13	0.205/25.0	0.132/51.0 (0.645 eq)	0.050/6.6 (0.242 eq)	5 h	Ester	45.6	100