

Electronic Supplementary Information (ESI)

Unconventional ionic ring-deconstruction pathways of a three-membered heterocycle

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Table of contents

Experimental data.	S2
Additional NMR data on the formation of complex 2.	S6
X-Ray crystallographic analysis	S7
Computational details.	S9
Calculated structures: Cartesian coordinates and energies for all computed species	S11
References	S14

Experimental data

Preparative methods

All reactions and manipulations were carried out under an atmosphere of dry argon, using Schlenk and vacuum line techniques. Argon was cleaned over a BTS catalyst; the drying of the Ar gas occurred via silica gel and P₂O₅. Solvents were dried according to standard procedures using sodium or sodium/benzophenone and stored in brown glasses over sodium wire, and under inert gas atmosphere.

Analytical methods

Melting point measurements were determined with a Büchi (530) capillary apparatus.

Elemental analysis were performed using an Elementar VarioEL analytical gas chromatograph.

Mass spectrometry: Electron ionization (70eV) mass spectra were recorded on a MAT 90 or on a MAT 95XL Finnigan spectrometer.

NMR spectra were recorded on a Bruker Avance DMX 300 spectrometer (¹H: 300.1 MHz, ¹³C: 75.0 MHz and ³¹P: 121.5 MHz,) or a Bruker Avance III HD Ascend 500MHz Prodigy (¹H: 500.1 MHz, ¹³C: 125.8 MHz and ³¹P: 202.5 MHz) using CDCl₃ as solvent; shifts are given relative to external tetramethylsilane (¹H, ¹³C,) and 85% H₃PO₄ (³¹P).

IR spectra were recorded with a SMART iTR Nicolet 380 FT IR spectrometer; only selected peaks are given.

Procedure for the spectroscopic characterization of complex 2. Oxaphosphirane tungsten complex **1** (34.3 mg, 0.07 mmol) and potassium *tert*-butoxide (7.8 mg, 0.07 mmol) were dissolved in THF-*d*₈ (0.6 ml) in a YOUNG NMR tube at room temperature, thus yielding a deep red reaction solution which was subsequently measured. An isolation of **2** was not possible due to decomposition of **2** upon removal of all volatiles *in vacuo* (2•10⁻² mbar).

¹H NMR (THF-*d*₈): δ = 1.13 (d, |³J_{P,H}| = 10.8 Hz, 9H, PC(CH₃)₃); 1.18 (s, 9H, POC(CH₃)₃); ¹³C{¹H} NMR (THF-*d*₈): δ = 30.0 (d, |³J_{P,C}| = 19.6 Hz, POC(CH₃)₃); 30.1

(d, $^2J_{P,C}$ = 10.1 Hz, PC(CH₃)₃); 35.2 (d, $^1J_{P,C}$ = 36.0 Hz, PC(CH₃)₃); 71.9 (d, $^2J_{P,C}$ = 10.4 Hz, POC(CH₃)₃); 208.6 (d, $^2J_{P,C}$ = 4.9 Hz, *cis*-CO); 212.2 (d, $^2J_{P,C}$ = 12.0 Hz, *trans*-CO); **³¹P{¹H} NMR** (THF-*d*₈): δ = 198.8 (*s*_{Sat}, $^1J_{W,P}$ = 76.8 Hz).

General procedure for the synthesis of complexes 5, 6. To a solution of oxaphosphirane tungsten complex **1** in THF, solid potassium butoxide (1 equivalent) was added at room temperature and the solution is stirred for two hours. Afterwards, an excess of trapping reagent (0.5 M solution of HCl in diethyl ether or iodomethane, respectively) was added and the resulting solution is stirred for further 30 minutes. Subsequent removal of all volatiles *in vacuo* ($2 \cdot 10^{-2}$ mbar) followed by extraction of the residue with *n*-pentane and removal of all volatiles from the combined extracts *in vacuo* ($2 \cdot 10^{-2}$ mbar) yielded **5** and **6** as a brown or yellow oils, respectively.

5: Yield 87 %; **¹H NMR** (CDCl₃): δ = 1.20 (9H, d, $^3J_{P,H}$ = 16.6 Hz, PC(CH₃)₃), 1.43 (9H, s, POC(CH₃)₃), 7.65 (1H, d, $^1J_{P,H}$ = 308.8 Hz, PH); **¹³C{¹H} NMR** (CDCl₃): δ = 26.3 (d, $^2J_{P,C}$ = 6.3 Hz, PC(CH₃)₃), 29.6 (d, $^3J_{P,C}$ = 4.0 Hz, POC(CH₃)₃), 36.3 (d, $^1J_{P,C}$ = 28.2 Hz, PCC(CH₃)₃), 80.1 (d, $^2J_{P,C}$ = 13.2 Hz, POC(CH₃)₃), 197.4 (d_{sat}, $^1J_{W,C}$ = 125.6 Hz, $^2J_{P,C}$ = 7.8 Hz, *cis*-CO), 199.1 (d, $^2J_{P,C}$ = 25.3 Hz, *trans*-CO); **³¹P{¹H} NMR** (CDCl₃): δ = 104.3 (*s*_{Sat}, $^1J_{W,P}$ = 268.7 Hz); **ms** (EI, ¹⁸⁴W): *m/z* (%): 486.0 (25, [M]⁺), 429.9 (18, [M-C₄H₈]⁺), 401.9 (56, [M-C₄H₈-CO]⁺), 373.9 (29, [M-C₄H₈-2CO]⁺), 346.0 (82, [M-5CO]⁺), 343.9 (86, [M-2 tBu-CO]⁺), 57.1 (100, [tBu]⁺); **IR** (ATR): $\tilde{\nu}$ = 1906 (vs, ν (CO)), 1980 (m, ν (CO)), 2071 (s, ν (CO))cm⁻¹.

6: Yield 57 %; **¹H NMR** (CDCl₃): δ = 0.90 (9H, d, $^3J_{P,H}$ = 15.2 Hz, PC(CH₃)₃), 1.10 (9H, d, $^4J_{P,H}$ = 0.5 Hz, POC(CH₃)₃), 1.45 (3H, d, $^2J_{P,H}$ = 4.2 Hz, PCH₃); **¹³C{¹H} NMR** (CDCl₃): δ = 22.0 (d, $^1J_{P,C}$ = 11.3 Hz, PCH₃), 24.4 (d, $^2J_{P,C}$ = 6.5 Hz, PC(CH₃)₃), 30.9 (d, $^3J_{P,C}$ = 3.2 Hz, POC(CH₃)₃), 37.3 (d, $^1J_{P,C}$ = 31.4 Hz, PCC(CH₃)₃), 80.1 (d, $^2J_{P,C}$ = 12.6 Hz, POC(CH₃)₃), 198.9 (d, $^2J_{P,C}$ = 7.8 Hz, *cis*-CO), 199.6 (d, $^2J_{P,C}$ = 24.2 Hz, *trans*-CO); **³¹P{¹H} NMR** (CDCl₃): δ = 128.6 (*s*_{Sat}, $^1J_{W,P}$ = 270.8 Hz); **ms** (EI, ¹⁸⁴W): *m/z* (%): 500.0 (24, [M]⁺), 443.9 (16, [M-C₄H₈]⁺), 416.0 (40, [M-3CO]⁺), 388.0 (29, [M-4CO]⁺), 386.0 (30, [M-2 tBu]⁺), 360.0 (88, [M-5CO]⁺), 358.0 (96, [M-2 tBu-CO]⁺), 57.1 (100, [tBu]⁺); **IR** (ATR): $\tilde{\nu}$ = 1901 (vs, ν (CO)), 1975 (m,

$\nu(\text{CO})$), 2068 (s, $\nu(\text{CO})$) cm^{-1} ; **elemental analysis** for $\text{C}_{14}\text{H}_{21}\text{O}_6\text{PW}$ Calc (%): C 33.62, H 4.23, found (%): C 33.35, H 4.42.

Procedure for the synthesis of complex 7. To a solution of oxaphosphirane tungsten complex **1** (191 mg, 0.38 mmol) in dichloromethane (5 ml), acetonitrile (0.022 ml, 0.42 mmol) was added and the resulting solution cooled to $-30\text{ }^\circ\text{C}$. At this temperature, triflic acid (0.033 ml, 0.38 mmol) was added and the solution stirred for one hour. Afterwards, trimethylamine (0.1 ml, excess) was added and the solution allowed to warm up to room temperature over a period of 45 minutes. Afterwards, all volatiles were removed *in vacuo* ($2 \cdot 10^{-2}$ mbar) and the residue was extracted with *n*-pentane (5 \cdot 3 ml). Removal of all volatiles from the combined extraction solutions *in vacuo* ($2 \cdot 10^{-2}$ mbar) yielded **2** as a colourless powder. Single crystals of **7** were obtained from a concentrated solution of **2** in *n*-pentane by slow evaporation of the solvent at room temperature.

7: Yield 196 mg (95 %); **m.p.** 83-86 $^\circ\text{C}$; **^1H NMR** (CDCl_3): $\delta = 1.07$ (d, $|^3J_{\text{P,H}}| = 14.8$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$); 1.14 (s, 9H, $\text{PCC}(\text{CH}_3)_3$); 2.07 (s, 3H, PNCHCH_3); 4.53 (d, $|^2J_{\text{P,H}}| = 9.7$ Hz, PCH); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl_3): $\delta = 17.2$ (d, $|^2J_{\text{P,C}}| = 8.6$ Hz, PNCNCH_3); 26.7 (d, $|^2J_{\text{P,C}}| = 6.3$ Hz, $\text{PC}(\text{CH}_3)_3$); 29.4 (d, $|^3J_{\text{P,C}}| = 2.9$ Hz, $\text{PCC}(\text{CH}_3)_3$); 34.4 (d, $|^2J_{\text{P,C}}| = 4.6$ Hz, $\text{PCC}(\text{CH}_3)_3$); 38.4 (d, $|^1J_{\text{P,C}}| = 6.3$ Hz, $\text{PC}(\text{CH}_3)_3$); 102.0 (d, $|^1J_{\text{P,C}}| = 11.5$ Hz, $\text{PCC}(\text{CH}_3)_3$); 169.2 (d, $|^2J_{\text{P,C}}| = 13.8$ Hz, $\text{PNC}(\text{CH}_3)_3$); 197.2 (d, $|^2J_{\text{P,C}}| = 7.5$ Hz, *cis*-CO); 198.7 (d, $|^2J_{\text{P,C}}| = 25.5$ Hz, *trans*-CO); **$^{31}\text{P}\{^1\text{H}\}$ NMR** (CDCl_3): $\delta = 115.6$ (s_{sat} , $|^1J_{\text{W,P}}| = 263.0$ Hz); **ms** (EI, ^{184}W) m/z (%): 539.1 (100, $[\text{M}]^+$); 511.1 (18, $[\text{M}-\text{CO}]^+$); 483.0 (52, $[\text{M}-2\text{CO}]^+$); 482.0 (45, $[\text{M}-\text{C}_4\text{H}_9]^+$); 454.0 (24, $[\text{M}-\text{C}_4\text{H}_9-\text{CO}]^+$); 427.0 (42, $[\text{M}-4\text{CO}]^+$); 398.0 (24, $[\text{M}-\text{C}_4\text{H}_9-3\text{CO}]^+$); 57.1 (83, $[\text{C}_4\text{H}_9]^+$); **IR** (ATR): $\tilde{\nu} = 1911$ (vs, $\nu(\text{CO})$), 1948 (m, $\nu(\text{CO})$), 2071 (s, $\nu(\text{CO})$) cm^{-1} ; **elemental analysis** for $\text{C}_{16}\text{H}_{22}\text{NO}_6\text{PW}$ Calc (%): C 35.64, H 4.11, N 2.60, found (%): C 35.60, H 4.09, N 2.54.

Procedure for the spectroscopic characterization of complex 8. To a solution of oxaphosphirane tungsten complex **1** (56 mg, 0.11 mmol) in dichloromethane- d_2 (0.75 ml), triflic acid (0.011 ml, 0.12 mmol) was added at room temperature and the solution stirred for five minutes. Afterwards, the deep red reaction solution was filtered from the formed red residue into an NMR tube and subsequently measured. An isolation was not possible due to decomposition of **3** upon removal of all volatiles *in vacuo* ($2 \cdot 10^{-2}$ mbar).

¹H NMR (CD₂Cl₂): δ = 1.30 (d, ³J_{P,H} = 18.1 Hz, 9H, PC(CH₃)₃), the proton of the OH-functionality could not be identified. Furthermore, a very broad multiplet (0.6 – 1.0 ppm) was observed, which could be caused by a polymer formed from the liberated 2-methyl-2-butene upon cationic polymerization; **¹³C{¹H} NMR** (CD₂Cl₂): δ = 23.0 (d, ²J_{P,C} = 7.7 Hz, PC(CH₃)₃); 43.0 (d, ¹J_{P,C} = 27.6 Hz, PC(CH₃)₃); 194.4 (d, ²J_{P,C} = 7.7 Hz, *cis*-CO); 195.9 (d, ²J_{P,C} = 39.1 Hz, *trans*-CO). The carbon atom of the triflate substituent could not be unequivocally identified, yet very broad signals were observed at 110 to 120 ppm, which most probably are a quartet due to coupling to the fluorine atoms; **³¹P{¹H} NMR** (CD₂Cl₂): δ = 214.0 (br. s_{sat}, ¹J_{W,P} = 332.7 Hz).

Procedure for the synthesis of complex 9. To a solution of oxaphosphirane tungsten complex **1** (165 mg, 0.33 mmol) in dichloromethane (5 ml), triflic acid (0.032 ml, 0.36 mmol) was added at room temperature and the solution stirred for five minutes. Afterwards, one drop of methanol (excess) was added and the resulting solution stirred for further 30 minutes. Subsequent removal of all volatiles *in vacuo* (2•10⁻² mbar) followed by extraction of the residue with *n*-pentane (3•5 ml) and removal of all volatiles from the combined extracts *in vacuo* (2•10⁻² mbar) yielded **9** as a yellow oil.

9: Yield 111 mg (73 %); **¹H NMR** (CDCl₃): δ = 1.15 (9H, d, ³J_{P,H} = 16.1 Hz, PC(CH₃)₃), 3.70 (3H, d, ³J_{P,H} = 12.1 Hz, POCH₃), 3.84 (1H, d, ²J_{P,H} = 11.6 Hz, POH); **¹³C{¹H} NMR** (CDCl₃): δ = 23.6 (d, ²J_{P,C} = 7.1 Hz, PC(CH₃)₃), 39.5 (d, ¹J_{P,C} = 37.8 Hz, PC(CH₃)₃), 54.2 (d, ²J_{P,C} = 3.9 Hz, POCH₃), 196.5 (d, ²J_{P,C} = 8.4 Hz, *cis*-CO), 198.2 (d, ²J_{P,C} = 28.8 Hz, *trans*-CO); **³¹P{¹H} NMR** (CDCl₃): δ = 171.7 (s_{sat}, ¹J_{W,P} = 298.5 Hz); **ms** (EI, 184W) : m/z (%): 460(30, [M]⁺); 432 (18, [M-CO]⁺); 404 (28, [M-2 CO]⁺); 376 (90, [M-3 CO]⁺); 346 (6, [M-4 CO]⁺); 318 (5, [M-5 CO]⁺); 57 (100, [C₄H₉]⁺); **IR** (ATR): $\tilde{\nu}$ = 1896 (vs, ν(CO)), 1982 (m, ν(CO)), 2071 (s, ν(CO)); 3543 (br s, ν(OH)) cm⁻¹.

Additional NMR spectra of the formation of complex 2

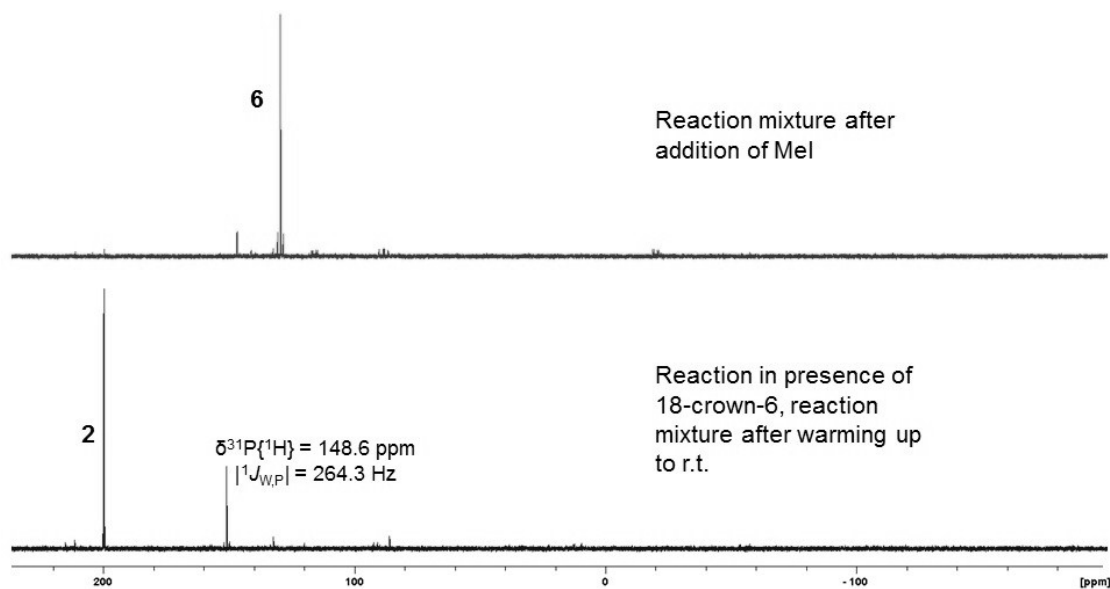


Figure S 1: NMR spectra of the reaction of **1** with KO^tBu in presence of 18-crown-6 at -30 °C; spectra obtained after warming up to ambient temperature (bottom) and after addition of MeI to the reaction mixture at ambient temperature (top).

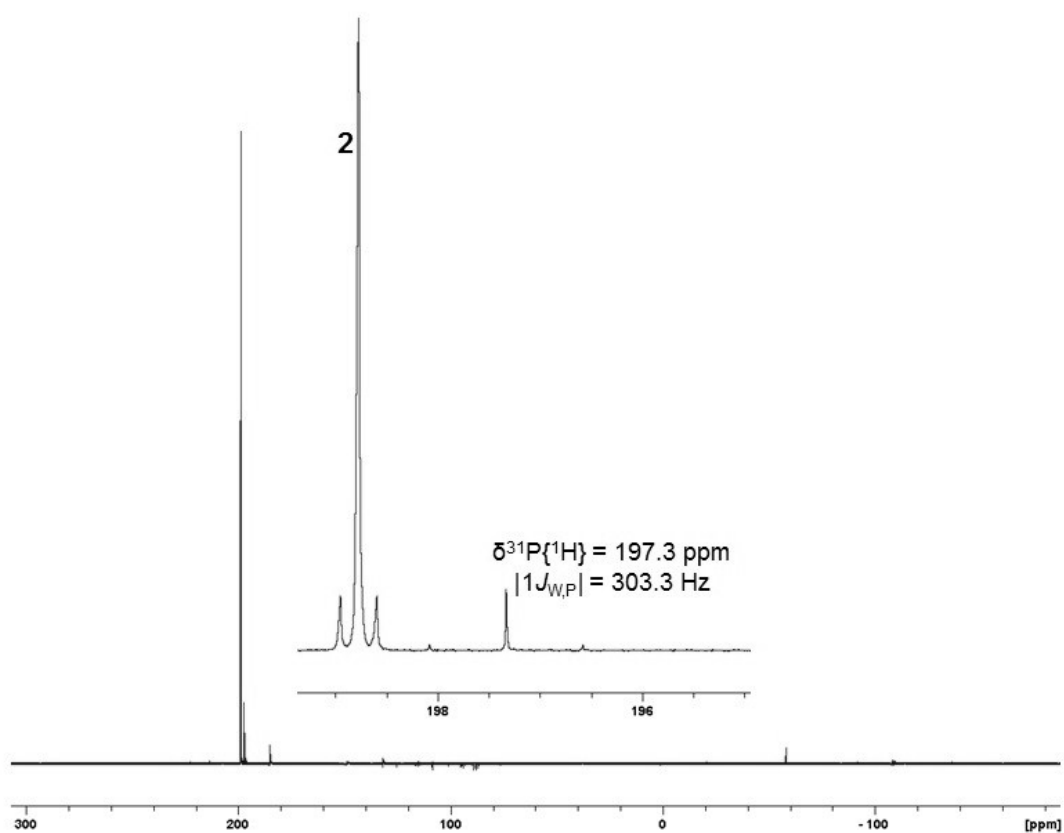
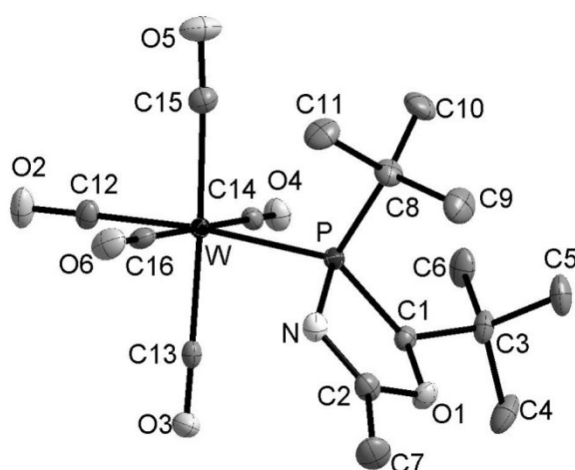


Figure S 2: NMR spectrum of the reaction of **1** with KO^tBu at ambient temperature (in absence of 18-crown-6) and expansion of the main products.

X-Ray crystallographic analysis

Single crystals of **7** were obtained from recrystallizations in *n*-pentane at 8 °C. Crystal structures were recorded on a Bruker X8-KappaApexII diffractometer. The structures were solved by the method of intrinsic phasing as implemented in SHELXT¹ and refined by full-matrix least squares on F² (SHELXL-2014²). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included isotropically using the riding model on the bound atoms. Absorption corrections were carried out semi-empirically from equivalents. Additionally, some calculation of bond lengths and angles were obtained using the Ortep32 program. Crystallographic data for the structure reported in this paper has been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1865572. Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Crystal Habitus	clear colourless plate
Empirical formula	C ₁₆ H ₂₂ NO ₆ PW
Moiety formula	C ₁₆ H ₂₂ N O ₆ P W
Formula weight	539.16
Temperature/K	100
Crystal system	Monoclinic
Space group	P2 ₁ /c
a/Å	9.6668(4)
b/Å	16.0328(6)
c/Å	12.9821(5)
α/°	90
β/°	96.2700(10)

$\gamma/^\circ$	90
Volume/ \AA^3	2000.01(14)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.791
μ/mm^{-1}	5.884
F(000)	1048.0
Crystal size/ mm^3	0.2 • 0.11 • 0.06
Absorption correction	Empirical
Tmin; Tmax	0.4464; 0.7461
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	5.982 to 55.992 $^\circ$
Completeness to theta	0.997
Index ranges	$-8 \leq h \leq 12$, $-21 \leq k \leq 21$, $-17 \leq l \leq 17$
Reflections collected	37519
Independent reflections	4823 [$R_{\text{int}} = 0.0305$, $R_{\text{sigma}} = 0.0173$]
Data/restraints/parameters	4823/2/233
Goodness-of-fit on F^2	1.054
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0125$, $wR_2 = 0.0302$
Final R indexes [all data]	$R_1 = 0.0138$, $wR_2 = 0.0307$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.71/-0.59

Computational details

DFT calculations were performed with the ORCA program.³ All geometry optimizations were run in redundant internal coordinates with tight convergence criteria using the B3LYP functional⁴ together with the def2-TZVP basis set.⁵ For W atoms the [SD(60,MWB)] effective core potential⁶ (ECP) was used. The latest Grimme's semiempirical atom-pair-wise London dispersion correction (DFT-D3) was included in all calculations.⁷ Harmonic frequency calculations verified the nature of ground states having all positive frequencies. From these optimized geometries all reported data were obtained by means of single-point (SP) calculations using the more polarized def2-TZVPP⁸ basis set. Energies were corrected for the zero-point energy (ZPE) term at the optimization level and computed by means of the recently developed near linear scaling domain-based local pair natural orbital (DLPNO) method⁹ to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T)).¹⁰ Solvent effects (tetrahydrofurane) were taken into account via the COSMO solvation model.¹¹

Calculated structures

Cartesian coordinates (in Å) and ZPE (in hartrees) for minima were computed at COSMO_{CH₂Cl₂}/B3LYP-D3/def2-TZVPecp. In addition, electronic energies (in hartrees) are quoted at the COSMO_{CH₂Cl₂}/DLPNO-CCSD(T)/def2-TZVPPecp level.

TfOH: E = -960.969813140528 au
ZPE = 0.03844403 au

S	0.014467	0.016096	1.879741	C	0.004941	0.008734	0.015013
O	1.565478	-0.018875	2.143485	F	0.636033	1.091974	-0.435024
H	1.938716	0.877674	2.226570	F	-1.254672	0.021558	-0.407582
O	-0.541768	1.265736	2.293715	F	0.615616	-1.080071	-0.439341
O	-0.512198	-1.239457	2.299711				

TfO: E = -960.541814996882 au
ZPE = 0.02712147 au

S	-0.000010	-0.000852	0.912675	C	0.000000	-0.000922	-0.948186
O	-0.002062	1.417213	1.235083	F	-1.085364	0.627065	-1.434051
O	-1.225837	-0.710559	1.242061	F	0.000209	-1.252432	-1.439551
O	1.227900	-0.706934	1.242063	F	1.085162	0.627420	-1.434047

1': E = -1284.67504872863 au
ZPE = 0.22222333 au

C	-0.027039	-0.150153	0.069709	C	2.015267	-3.093799	2.255083
O	0.058241	-0.200888	1.539165	O	1.274742	-3.791953	2.774706
P	1.576629	-0.164353	0.850405	C	3.105034	-2.840434	-0.468281
H	-0.335319	0.838741	-0.266987	O	2.978398	-3.398565	-1.459223
C	-0.771341	-1.260787	-0.647352	C	-0.333853	-1.217417	-2.117607
C	2.094162	1.576806	0.937752	H	-0.898236	-1.948784	-2.699042
H	2.580110	1.755949	1.897771	H	-0.509465	-0.231475	-2.553976
H	1.243597	2.247401	0.825523	H	0.728338	-1.448909	-2.215937
H	2.820085	1.766786	0.144866	C	-2.273528	-0.945683	-0.535965
W	3.375694	-1.844854	1.320077	H	-2.504645	0.029002	-0.970897
C	4.881573	-3.123446	1.791268	H	-2.855957	-1.702296	-1.065269
O	5.730698	-3.846077	2.065197	H	-2.591648	-0.939653	0.508476
C	4.723565	-0.591525	0.394073	C	-0.508178	-2.644553	-0.052950
O	5.478350	0.106020	-0.111189	H	0.531575	-2.942621	-0.166633
C	3.699321	-0.824148	3.083808	H	-0.759179	-2.671457	1.006853
O	3.902656	-0.243024	4.048612	H	-1.121927	-3.384580	-0.568961

1' PO-cleavage:

E = -1285.05439942296 au

ZPE = 0.23320065 au

C	0.699133	-0.071371	-0.423777	O	2.690043	1.073570	-3.710280
O	1.903456	-0.379760	-1.088977	C	-0.197488	3.397088	-3.209534
P	0.536002	1.792243	-0.348292	O	-1.042146	3.410782	-3.962046
H	0.728112	-0.398283	0.620725	C	-1.807945	-0.306591	-0.498683
C	-0.490730	-0.773349	-1.125618	H	-2.639918	-0.853650	-0.943023
C	-0.100533	2.137598	1.304811	H	-1.828902	-0.483380	0.578476
H	-0.401549	3.177931	1.399435	H	-1.995727	0.757155	-0.679958
H	0.707845	1.931743	2.014476	C	-0.321485	-2.282569	-0.902499
H	-0.932897	1.476997	1.547181	H	-0.348501	-2.526631	0.161697
W	1.405151	3.352154	-1.837115	H	-1.133570	-2.819539	-1.395570
C	2.345462	4.837398	-3.030485	H	0.622861	-2.636440	-1.315314
O	2.849527	5.645639	-3.638958	C	-0.496182	-0.471438	-2.628358
C	0.524316	4.843199	-0.709749	H	-0.657135	0.589262	-2.826816
O	0.027129	5.658592	-0.090087	H	0.437844	-0.772983	-3.099346
C	3.144222	3.463337	-0.670784	H	-1.311025	-1.018709	-3.103715
O	4.085852	3.524986	-0.043516	H	2.637836	-0.358270	-0.463360
C	2.239871	1.847874	-3.011668				

10:

E = -1285.10563305085 au

ZPE = 0.23446140 au

C	-0.664445	1.682205	-0.374959	O	1.917643	1.925933	-3.907768
O	1.586703	0.158728	-0.645068	C	-0.737805	4.170012	-2.169539
P	0.995864	1.496198	-0.005014	O	-1.692109	4.540412	-2.657636
H	-1.175842	2.282152	0.370833	C	-2.942648	1.486260	-1.367950
C	-1.559005	0.831346	-1.262404	H	-3.618345	0.824454	-1.911252
C	1.375742	1.509933	1.753048	H	-3.366595	1.666682	-0.378505
H	2.447704	1.655349	1.885052	H	-2.902515	2.432951	-1.903262
H	1.073424	0.556990	2.186765	C	-1.701871	-0.515902	-0.507423
H	0.836104	2.326616	2.230778	H	-2.075335	-0.363024	0.506086
W	1.098995	3.620907	-1.302124	H	-2.416778	-1.143474	-1.042667
C	1.872537	5.313273	-2.219355	H	-0.750410	-1.044849	-0.456607
O	2.323846	6.223946	-2.723547	C	-1.003074	0.566452	-2.664043
C	0.554587	4.671588	0.403369	H	-0.947661	1.487709	-3.243551
O	0.255908	5.230331	1.349371	H	-0.017296	0.106314	-2.634692
C	3.045112	3.500419	-0.569330	H	-1.674420	-0.113974	-3.188876
O	4.104451	3.463995	-0.160050	H	2.502767	0.200899	-0.955778
C	1.610092	2.518808	-2.985991				

11·H⁺:

E = -1285.06792557283 au

ZPE = 0.23156120 au

C	-0.531631	-0.681563	0.212249	H	2.176331	1.185876	2.187626
O	2.215101	-0.715832	-0.080056	H	1.343257	-0.346840	2.507351
P	1.122387	0.450618	0.209860	H	0.411287	1.175014	2.387073
H	-1.224870	-0.018075	0.730314	W	1.343119	2.516870	-1.168627
C	-0.882712	-0.816488	-1.167805	C	1.670884	4.206633	-2.275304
C	1.264880	0.614732	2.006397	O	1.863905	5.145381	-2.898217

C	1.763506	3.592607	0.553739	H	-2.174566	0.893478	-1.135417
O	2.003680	4.192378	1.494307	C	-0.259113	-1.980938	0.974298
C	3.359194	2.092120	-1.347313	H	-0.147426	-1.774445	2.034765
O	4.476715	1.876339	-1.444124	H	-1.114925	-2.645899	0.853333
C	0.961823	1.466082	-2.894450	H	0.631928	-2.493195	0.620462
O	0.755584	0.880302	-3.857416	C	-0.285579	-1.873514	-1.986896
C	-0.635334	3.077115	-0.962243	H	-0.399547	-1.699831	-3.052972
O	-1.715877	3.431185	-0.842031	H	0.754975	-2.060088	-1.715135
C	-1.889540	0.056478	-1.763384	H	-0.815746	-2.804195	-1.731591
H	-1.644220	0.357024	-2.781288	H	2.706137	-0.589616	-0.902951
H	-2.776455	-0.594250	-1.863615				

11·HOTf:

E = -2245.64276468593 au

ZPE = 0.25959488 au

C	0.039608	-0.026982	0.071853	H	-0.547011	0.541468	-3.149813
O	2.839153	0.228947	-0.046467	H	-1.801101	-0.383428	-2.373511
P	1.679816	1.308681	-0.008082	H	-1.424563	1.217629	-1.728711
H	-0.732190	0.671723	0.389213	C	0.387382	-1.099817	1.090155
C	-0.065367	-0.384568	-1.284580	H	0.379174	-0.693569	2.097420
C	1.460340	1.843222	1.713238	H	-0.369738	-1.885062	1.043589
H	2.285710	2.522673	1.923878	H	1.357913	-1.553629	0.902836
H	1.488436	1.023931	2.426065	C	0.719423	-1.504543	-1.830914
H	0.516703	2.383239	1.789332	H	0.684463	-1.549428	-2.915618
W	1.936389	3.112995	-1.714893	H	1.753769	-1.452145	-1.478163
C	2.351198	4.624697	-3.015772	H	0.318525	-2.439855	-1.420204
O	2.589156	5.477152	-3.744204	H	3.372995	0.085566	0.810642
C	2.104576	4.461604	-0.154582	O	4.213540	0.004154	2.079612
O	2.213308	5.209430	0.702071	S	5.022937	1.201755	2.390547
C	3.977395	2.728646	-1.586853	O	4.629970	2.374930	1.636141
O	5.097439	2.526587	-1.552582	O	5.262632	1.382944	3.803188
C	1.865727	1.755679	-3.258475	C	6.688392	0.757297	1.696683
O	1.858313	0.992079	-4.113340	F	7.203821	-0.301079	2.337074
C	-0.066550	3.558966	-1.861270	F	7.536077	1.785362	1.832976
O	-1.173715	3.843025	-1.948493	F	6.597278	0.456195	0.394742
C	-0.986834	0.331094	-2.175885				

12·H⁺:

E = -1285.07218638625 au

ZPE = 0.23440763 au

C	-0.239950	-0.657320	0.185526	C	1.581986	3.524342	0.193680
O	1.987122	-1.257770	0.041965	O	1.462244	4.277407	1.041797
P	1.269076	0.409389	0.268229	C	3.813259	1.970406	-0.873179
H	-0.760482	-0.406718	-0.738071	O	4.919858	1.873264	-0.613609
C	0.571119	-1.961430	-0.036812	C	2.010008	0.768966	-2.867946
C	1.696976	0.605364	2.010006	O	2.118314	0.001393	-3.707451
H	2.733885	0.933935	2.077883	C	-0.213826	2.287293	-1.797703
H	1.559032	-0.308583	2.583164	O	-1.325196	2.346877	-2.050360
H	1.059076	1.391191	2.421061	C	0.426655	-2.548573	-1.414060
W	1.797721	2.137932	-1.332974	H	1.159043	-3.338287	-1.585281
C	2.202076	3.691933	-2.638372	H	-0.569791	-2.986930	-1.490904
O	2.422300	4.554305	-3.349458	H	0.515527	-1.788873	-2.190741

C	-1.222376	-0.596343	1.343424	H	1.282921	-3.765683	0.862814
H	-1.671750	0.395894	1.394733	H	0.788835	-2.532217	2.037209
H	-2.027996	-1.314296	1.186354	H	-0.432026	-3.424414	1.123373
H	-0.757290	-0.809254	2.303708	H	2.570980	-1.415585	-0.720185
C	0.561408	-2.976364	1.070631				

12·HOTf:

E = -2245.66480342571 au

ZPE = 0.26199327 au

C	-0.236858	-0.631422	0.129459	H	1.408447	-3.445449	-1.178502
O	1.943924	-1.225276	0.332829	H	-0.313333	-3.092404	-1.386404
P	1.297393	0.318867	0.532026	H	0.899181	-1.954910	-1.996327
H	-0.517655	-0.400929	-0.897837	C	-1.460884	-0.534756	1.018941
C	0.628362	-1.930877	0.141313	H	-1.901658	0.460445	0.943604
C	1.296369	0.608168	2.322250	H	-2.217310	-1.253982	0.698911
H	2.308809	0.861667	2.632159	H	-1.235350	-0.725870	2.066742
H	0.949182	-0.254905	2.886200	C	0.411201	-2.871921	1.305555
H	0.644160	1.460513	2.524382	H	1.170696	-3.654899	1.293282
W	2.210596	2.111086	-0.924862	H	0.463648	-2.356840	2.262656
C	2.968959	3.550533	-2.159580	H	-0.566947	-3.347065	1.221306
O	3.396617	4.354304	-2.857516	H	3.213759	-1.899523	0.569973
C	1.336534	3.535308	0.283174	S	5.067083	-1.638909	1.655287
O	0.844432	4.314807	0.962807	C	6.282486	-1.032986	0.380832
C	3.918566	2.235761	0.238431	O	4.092276	-2.429417	0.759658
O	4.859799	2.352057	0.875852	O	4.430981	-0.473093	2.195481
C	3.029474	0.608104	-2.082833	O	5.793848	-2.538766	2.494055
O	3.452856	-0.249280	-2.710221	F	6.888440	-2.061228	-0.209633
C	0.493500	2.039889	-2.061620	F	7.194778	-0.270295	0.979219
O	-0.466426	1.997163	-2.685283	F	5.646987	-0.313193	-0.545428
C	0.663816	-2.647885	-1.188574				

8':

E = -2049.49064415372 au

ZPE = 0.12343033 au

O	1.971812	-1.236822	-0.238996	C	2.295146	0.633768	-2.820886
P	1.556098	0.223613	0.261764	O	2.785160	-0.095652	-3.550293
C	2.478218	0.504392	1.786218	C	-0.451735	1.184957	-2.017993
H	3.521285	0.679402	1.519458	O	-1.470783	0.753178	-2.301212
H	2.414125	-0.347321	2.463603	H	2.047813	-1.916956	0.451367
H	2.084657	1.395982	2.275294	O	-0.022746	-0.028326	0.946248
W	1.401158	1.937204	-1.481532	S	-0.550295	-1.197861	1.841137
C	1.279666	3.380680	-2.933859	C	-1.828613	-1.883095	0.665891
O	1.212439	4.185312	-3.744901	O	-1.255998	-0.666839	2.960036
C	0.510307	3.192530	-0.106673	O	0.460849	-2.202020	2.011964
O	0.022874	3.877776	0.668757	F	-2.736287	-0.952377	0.397344
C	3.251896	2.646485	-0.906172	F	-1.241387	-2.271137	-0.461998
O	4.275093	3.032107	-0.569441	F	-2.413789	-2.924118	1.249341

Isobutylene:

E = -196.169736053716 au

ZPE = 0.13535372 au

C	-0.005136	-0.001371	0.027833	H	-0.064302	3.068648	0.918584
H	1.082576	0.000908	0.038251	H	1.256023	2.271171	0.047325
C	-0.613932	1.187271	0.026992	H	-0.050931	3.077872	-0.836128
C	-2.103938	1.387584	0.013499	C	-0.628605	-1.363398	0.016002
H	-2.402454	1.967249	-0.865971	H	-0.299581	-1.932570	-0.859178
H	-2.663760	0.454803	0.008040	H	-0.319433	-1.939034	0.894219
H	-2.418861	1.966597	0.887613	H	-1.717033	-1.334221	0.003779
C	0.182887	2.463729	0.039838				

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