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Supporting Information

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Bis(μ-hydroxo) Bridged Di-vanadium-catalyzed Selective Epoxidation of Alkenes with Hydrogen Peroxide

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Full Experimental Section

Instruments

IR spectra were measured on Jasco FT/IR-460 Plus using KBr disks. *In-situ* IR spectra were measured on a Mettler Toledo React IR 4000 spectrometer. NMR spectra were recorded at 298 K on JEOL JNM-EX-270 (^{29}Si, 53.45 MHz; ^{183}W, 11.20 MHz; ^{51}V, 70.90 MHz) spectrometer. Chemical shifts (δ) were reported in ppm downfield from external $SiMe_4$ (solvent, $CDCl_3$), Na_2WO_4 (solvent, D_2O) and $VOCl_3$ (neat) for ^{29}Si, ^{183}W and ^{51}V spectra, respectively. UV-vis spectra were recorded on a Perkin Elmer Lambda 12 spectrometer. GC analyses were performed on Shimadzu GC-14B with a flame ionization detector equipped with TC-WAX capillary (internal diameter = 0.25 mm, length = 30 m) or SE-30 packed column. Mass spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). CSI-MS spectra were recorded on JMS-T100LC. Typical measurements are as follows: Olifice voltage (–95 V), sample flow (0.05 mL·min^{-1}), solvent (1,2-$C_2H_4Cl_2$), concentration (0.14 mM), spray temp. (253 K), ion source temp. (room temp.).

Syntheses and characterization of polyoxometalates.

[(*n*-C_4H_9)$_4$N]$_4$[γ-1,2-$H_2SiV_2W_{10}O_{40}$]·H_2O (tetrabutylammonium salt of I). Aqueous solution of [γ-1,2-$H_2SiV_2W_{10}O_{40}$]$^{4-}$ was prepared according to ref. [36], and the anion was isolated as the tetra-*n*-butylammonium salt. K_8[γ-$SiW_{10}O_{36}$]·12H_2O[37] (8 g, 2.7 mmol) was quickly dissolved in 1 M HCl (28 mL). $NaVO_3$ (0.5 M, 11 mL, 5.5 mmol) was added, and the

mixture was gently stirred for 5 min. The solution was filtered off followed by the addition of $[(n\text{-}C_4H_9)_4N]Br$ (8 g, 25 mmol) in a single step. The resulting yellow precipitate was collected by the filtration and then washed with an excess amount of water (300 mL). The crude product was purified twice with the precipitation method (addition of 1 L of H_2O into acetonitrile solution of TBA-**1** (50 mL)). Analytically pure TBA-**1** was obtained as a pale yellow powder. Yield: 7.43 g (76%). Anal. calcd for $[(C_4H_9)_4N]_4[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]\cdot H_2O$: C, 21.4; H, 4.15; N, 1.56; Si, 0.78; V, 2.83; W, 51.1; H_2O, 0.50. Found: C, 21.4; H, 3.91; N, 1.59; Si, 0.79; V, 2.88; W, 51.2; H_2O, 0.50. ^{51}V NMR (CD_3CN): An intense line at –563.6 ppm ($\Delta\nu_{1/2}$ = 133 Hz) attributed to two equivalent vanadium atoms was observed. ^{183}W NMR (CD_3CN): δ, –82.2 ppm ($\Delta\nu_{1/2}$ = 9.6 Hz), –95.6 ppm ($\Delta\nu_{1/2}$ = 2.5 Hz) and –129.7 ppm ($\Delta\nu_{1/2}$ = 2.9 Hz) with an integrated intensity ratio of 2: 1: 2. ^{29}Si NMR (CD_3CN): δ, –84.0 ppm ($\Delta\nu_{1/2}$ = 2.0 Hz). UV-vis spectrum (in CH_3CN) showed shoulder bands at 240 nm (ε = 36000 $M^{-1}cm^{-1}$), 285 nm (ε = 24000 $M^{-1}cm^{-1}$) and 350 nm (ε = 5900 $M^{-1}cm^{-1}$), characteristic of the γ-Keggin structure.[38,39] IR spectrum (KBr, cm^{-1}): 1151, 1106, 1057, 1004, 995, 966, 915, 904, 875, 840, 790, 691, 550, 519, 482, 457, 405.

$[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{12}O_{40}]$. The tetra-*n*-butylammonium salt of $[\gamma\text{-}SiW_{12}O_{40}]^{4-}$ was synthesized according to the published method.[41] The crude product was purified by recrystallization from acetonitrile/water (6/1 *v*/*v*). The IR spectrum showed the bands at 1006, 971, 910, 872, 839, 796, 768sh, 703sh, 553, 538, 522, 488, 461 and 414 cm^{-1}. Anal. calcd for $[(C_4H_9)_4N]_4SiW_{12}O_{40}$: C, 20.0; H, 3.78; N, 1.46. Found: C, 19.9; H, 3.61; N, 1.39.

$[(n\text{-}C_4H_9)_4N]_{4.5}H_{0.5}[\alpha\text{-}SiVW_{11}O_{40}]\cdot 0.5H_2O$. The potassium salt of $[\alpha\text{-}SiV^{IV}W_{11}O_{40}]^{6-}$ was synthesized by the modification of the method reported in ref. [42] as follows: $K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 13H_2O$[37] (35 g, 11 mmol) was suspended in 35 mL of warm water (~ 333 K). A slightly excess amount of $VOSO_4\cdot nH_2O$ (3.5 g, *ca*. 13 mmol) in water (5 mL) was added dropwise into the solution. Then KCl (5 g) was added. The resulting clear purple solution was cooled to 273 K and a black precipitate was formed. After 15 min, the precipitate was collected, and recrystallized from water. Yield: 27.8 g (81%). The potassium salt of [α-

$SiVW_{11}O_{40}]^{5-}$ was synthesized as follows: The potassium salt of $[\alpha\text{-}SiV^{IV}W_{11}O_{40}]^{6-}$ (6 g, 1.9 mmol) was dissolved in warm water (~ 313 K, 10 mL). Bromine water was added to the solution until the color changed from purple to yellow. Then KCl (0.3 g) was added, and the clear solution was cooled to 273 K. Yellow needlelike crystals were formed, collected, and dried in air. Yield: 4.4 g (73%). ^{51}V NMR (D_2O): δ, –548.5 ppm ($\Delta\nu_{1/2}$ = 44 Hz). The tetra-*n*-butylammonium salt of $[\alpha\text{-}SiVW_{11}O_{40}]^{5-}$ was synthesized as a yellow precipitate by adding $[(n\text{-}C_4H_9)_4N]Br$ (1 g, 3.1 mmol) to the aqueous solution of the potassium salt of $[\alpha\text{-}SiVW_{11}O_{40}]^{5-}$ (1 g, 0.32 mmol). The product was purified by the reprecipitation from acetonitrile (15 mL) / water (300 mL) to remove excess tetra-*n*-butylammonium bromide, and dried in vacuo. Analytically pure $[(n\text{-}C_4H_9)_4N]_{4.5}H_{0.5}[\alpha\text{-}SiVW_{11}O_{40}]\cdot 0.5H_2O$ was obtained as a yellow powder. Yield: 0.95 g (78%). Anal. calcd for $[(C_4H_9)_4N]_{4.5}H_{0.5}SiVW_{11}O_{40}\cdot 0.5H_2O$: C, 22.5; H, 4.29; N, 1.64; Si, 0.73; V, 1.33; W, 52.6; H_2O, 0.23. Found: C, 22.2; H, 4.08; N, 1.65; H_2O, 0.23. ^{51}V NMR (CD_3CN containing 1.7% water): δ, –561.4 ppm ($\Delta\nu_{1/2}$ = 211 Hz). UV-vis spectrum: λ_{min} = 236 nm (ε = 33000 $M^{-1}cm^{-1}$), λ_{max} = 260 nm (ε = 42000 $M^{-1}cm^{-1}$), λ_{sh} = 360 nm (ε = 3000 $M^{-1}cm^{-1}$). IR spectrum (KBr, cm^{-1}): 1152, 1106, 1008, 962, 910, 878, 794, 534.

$[(n\text{-}C_4H_9)_4N]_{4.5}H_{2.5}[$a-1,2,3-$SiV_3W_9O_{40}]$. The potassium salt of $[\alpha\text{-}1,2,3\text{-}SiV_3W_9O_{40}]^{7-}$ was synthesized by the modification of the method in ref. [43]. $NaVO_3$ (0.95 g, 7.8 mmol) was dissolved in hot water (15 mL). After cooling, $Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$[37] (7.25 g, 2.6 mmol) was added. Then 6 M HCl (9.3 mL) was added dropwise and the solution was stirred for 45 min. The resulting red clear solution was adjusted to pH = 6~7 with K_2CO_3. Finally, KCl (4 g) was added and an orange precipitate was formed. The precipitate was collected and recrystallized from water. Yield: 5.5 g (72%). ^{51}V NMR (D_2O): δ, –534.7 ppm ($\Delta\nu_{1/2}$ = 290 Hz). The tetra-*n*-butylammonium salt was synthesized as a red precipitate by adding $[(n\text{-}C_4H_9)_4N]Br$ (4 g, 12 mmol) to aqueous 1 M HCl solution (50 mL) of the potassium salt (4 g, 1.3 mmol). The product was purified by the reprecipitation from acetonitrile (15 mL) / water (300 mL), and dried in vacuo. Analytically pure $[(n\text{-}C_4H_9)_4N]_{4.5}H_{2.5}[\alpha\text{-}1,2,3\text{-}SiV_3W_9O_{40}]$ was

obtained as a red powder. Yield: 2.1 g (45%). Anal. calcd for $[(C_4H_9)_4N]_{4.5}H_{2.5}SiV_3W_9O_{40}$: C, 24.2; H, 4.62; N, 1.77; Si, 0.79; V, 4.28; W, 46.4. Found: C, 23.2; H, 4.41; N, 1.86; Si, 0.75; V, 4.20; W, 46.8. ^{51}V NMR (CD_3CN containing 1.7% water): δ, –574.6 ppm ($\Delta\nu_{1/2}$ = 710 Hz). UV-vis spectrum (CH_3CN): λ_{sh} = 253 nm (ε = 39000 $M^{-1}cm^{-1}$), λ_{sh} = 380 nm (ε = 3600 $M^{-1}cm^{-1}$). IR spectrum (KBr, cm^{-1}): 1152, 1106, 1060, 1024, 1004, 992, 964, 906, 802, 766sh, 736sh, 546.

$[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$. The potassium salt of silicodecatungstate, $K_8[\gamma\text{-}SiW_{10}O_{36}]?12H_2O$[37] (6 g, 2 mmol), was dissolved in 60 mL of H_2O. The pH of this aqueous solution was adjusted to 2 with HNO_3. After stirring the solution for 15 min at ambient temperature, an excess amount of $[(n\text{-}C_4H_9)_4N]Br$ (6.46 g, 20 mmol) was added in a single step. The resulting white precipitate of $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ was collected by the filtration and then washed with an excess amount of H_2O. After the dryness, the crude product was purified twice with the precipitation method (addition of 1 L of H_2O into an CH_3CN solution of $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (15 mL)). Analytically pure $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ was obtained as a white powder.[31] Yield 3.4 g (54 %). Anal. calcd for $C_{64}H_{150}N_4O_{37}SiW_{10}$ ($[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]\cdot H_2O$): C, 22.38; H, 4.40; N, 1.63; Si, 0.82; W, 53.53. Found: C, 22.09; H, 4.19; N, 1.64; Si, 0.80; W, 53.24. ^{29}Si NMR (CD_3CN/DMSO, 2/1 *v/v*): δ –83.38 ppm. ^{183}W NMR (CD_3CN/DMSO, 2/1 *v/v*): δ, –95.2 ppm ($\Delta\nu_{1/2}$ = 3.3 Hz), –98.8 ppm ($\Delta\nu_{1/2}$ = 3.3 Hz), –118.0 ppm ($\Delta\nu_{1/2}$ = 4.0 Hz), –119.1 ppm ($\Delta\nu_{1/2}$ = 4.0 Hz), –195.5 ppm ($\Delta\nu_{1/2}$ = 4.3 Hz) with an integrated intensity ratio of 1: 1: 1: 1: 1. UV-vis (in CH_3CN): 275 nm (ε = 22000 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): 999, 958, 920, 902, 877, 784, 745, 691, 565, 544.

$[(n\text{-}C_6H_{13})_4N]_3[\{W(=O)(O_2)_2\}_4(m\text{-}PO_4)]$. 1.39 g (50% yield) of this compound was synthesized according to the literature procedure in ref. [44]. Anal. calcd for $C_{72}H_{156}N_3O_{24}PW_4$ ($[(n\text{-}C_6H_{13})_4N]_3\cdot[\{W(=O)(O_2)_2\}_4(m\text{-}PO_4)]$): C, 39.05; H, 7.10; N, 1.90; P, 1.40; W, 33.22. Found: C, 38.82; H, 6.97; N, 1.81; P, 1.36; W, 33.28. IR (KBr, cm^{-1}): 1093, 1055, 977, 913, 853, 843, 765, 728, 648, 591, 572, 548, 524, 443.

[(*n*-$C_{12}H_{25}$)$(CH_3)_3N]_2$[{W(=O)$(O_2)_2$}$_2$(*m*-O)]. The method[45] for the preparation of the tetra-*n*-butylammonium derivative of [{W(=O)$(O_2)_2$}$_2$(*m*-O)]$^{2-}$ was modified (i.e., $[(CH_3)_4N]^+$ was replaced by [(*n*-$C_{12}H_{25}$)$(CH_3)_3N]^+$). Desired dodecyltrimethylammonium derivative was obtained with a 50% yield (1.3 g). Anal. calcd for $C_{30}H_{68}N_2O_{11}W_2$ ([(*n*-$C_{12}H_{25}$)$(CH_3)_3N]_2$[{W(=O)$(O_2)_2$}$_2$(*m*-O)]): C, 34.35; H, 7.00; N, 2.70; W, 35.48. Found: C, 35.53; H, 6.92; N, 2.66; W, 35.43. IR (KBr, cm^{-1}): 963, 936, 911, 838, 770, 720, 603, 569, 531.

Catalytic reactions

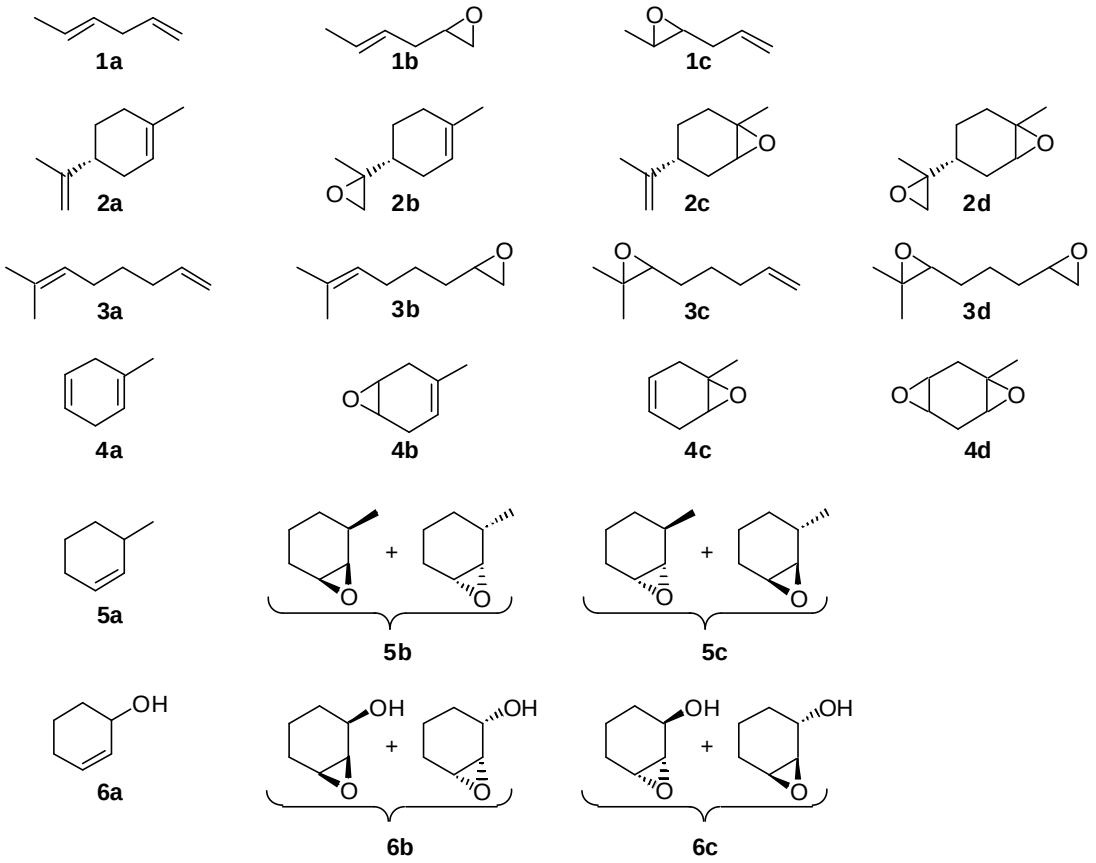
The epoxidation of gaseous substrates (propylene and 1-butene) was carried out with Teflon coated autoclave. For the other substrates, glass tube reactor was used. The epoxidation was carried out as follows: Catalyst (1.67 mM); CH_3CN/*t*BuOH (1.5/1.5 mL); H_2O_2 (30% aq., 33.3 mM), and substrates (propylene, 6 atm; 1-butene, 1 atm; others, 33.3 mM) were charged in the reaction vessel. The reaction was carried out at 293 ± 0.2 K. The reaction solution was periodically sampled and analyzed by GC in combination with mass spectroscopy. The products were identified by the comparison of mass and NMR spectra with those of authentic samples. The carbon balance in each experiment was in the range of 95–100%. Remaining H_2O_2 after the reaction was analyzed by the $Ce^{4+/3+}$ titration.[40] After the reaction, the catalyst was recovered by the evaporation to dryness followed by washing with *t*BuOH and *n*-hexane.

The isolated yield of 1,2-epoxyoctane was determined as follows. CH_3CN/*t*BuOH (75 mL each) solution of reaction mixture (catalyst, 0.25 mmol; 1-octene, 5 mmol; H_2O_2, 5 mmol) was stirred at 293 K. After 24 h, the reaction mixture was reduced to ca. 75 mL by the evaporation. *n*-Pentane (50 mL) and water (200 mL) were added to this concentrated solution. The organic products solved in the water phase were extracted with *n*-pentane (30 mL × 3). Combined organic phase was washed with water (100 mL × 3) and then dried over $MgSO_4$. The drying reagent was filtered off, and the solvent was evaporated to give colorless

liquid of 1,2-epoxyoctane (0.554 g, 86% yield). ^{13}C NMR ($CDCl_3$): δ, 13.91, 22.46, 22.84, 29.01, 31.67, 32.41, 46.93, 52.22 ppm.

Characterization of dienes, 3-substituted cyclohexenes, and their derivatives

The data (GC retention time, mass, and NMR) of all dienes and 3-substituted cyclohexenes used in this study and their corresponding epoxides were listed below.



1a. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), final column temperature (493 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (2.4 min). MS (70 eV, EI): *m*/*z* (%): 82 (46) [M^+], 81 (11) [M^+–H], 79 (12), 67 (100), 65 (13), 54 (16), 53 (15). ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ 1.64–1.66 (m, 3H, methyl), 2.70–2.75 (m, 2H, allyl H), 4.70–5.06 (m, 2H), 5.39–5.54 (m, 2H), 5.76–5.90 (m, 1H). ^{13}C {^{1}H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 18.0, 37.3, 115.0, 126.6, 129.7, 138.3.

1b. GC (SE-30 packed column, 2 m, GL Science Inc.): carrier gas (N_2, 100 kPa), initial column temperature (343 K), final column temperature (493 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (2.8 min). MS (70 eV, EI): *m*/*z* (%): 97 (7) [M^+–H], 83 (50), 80 (28), 79 (13), 69 (25), 68 (30), 67 (71), 57 (15), 55 (100). ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 18.7, 36.5, 47.2, 52.6, 126.8, 128.9.

1c. GC (SE-30 packed column, 2 m, GL Science Inc.): carrier gas (N_2, 100 kPa), initial column temperature (343 K), final column temperature (493 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (1.9 min). MS (70 V, EI): *m*/*z* (%): 97 (6) [M^+–H], 83 (36), 69 (39), 57 (21), 55 (51), 54 (82), 53 (40), 45 (13), 43 (35), 42 (26), 41 (71), 39 (100) ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 17.7, 36.8, 54.5, 58.9, 117.3, 134.8.

2a. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (393 K), final column temperature (513 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (2.2 min). MS (70 eV, EI): *m*/*z* (%): 136 (33) [M^+], 121 (28), 107 (26), 94 (36), 93 (82), 92 (30), 91 (22), 81 (12), 80 (15), 79 (37), 77 (19), 68 (100), 67 (70). ^1H NMR (270 MHz, CD_3CN, 298 K, TMS): δ 1.42–4.50 (m, 1H), 1.63 (s, 3H, methyl), 1.72 (s, 3H, methyl) 1.74–2.10 (m, 6H), 4.70–4.72 (m, 2H), 5.38–5.40 (m, 1H). ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 20.9, 23.6, 28.8, 31.2, 31.6, 41.9, 108.8, 121.3, 134.3, 151.1.

2b. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (393 K), final column temperature (513 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (4.0 and 4.1 min). MS (70 eV, EI): *m*/*z* (%): 152 (3) [M^+], 138 (12), 137 (26), 134 (22), 122 (11), 121 (100), 119 (30).

2c. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (393 K), final column temperature (513 K), progress rate

(10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (3.3 and 3.4 min). MS (70 eV, EI): *m*/*z* (%): 152 (4) [M^+], 137 (45), 123 (20), 119 (19), 110 (13), 109 (51), 108 (26), 107 (10), 95 (22), 94 (16), 93 (45), 91 (18), 84 (11), 83 (11), 82 (29), 81 (35), 79 (41), 71 (26), 69 (12), 68 (16), 67 (70), 55 (21), 53 (16), 44 (14), 43 (100). ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ 1.23, 1.25 (s, 3H, methyl), 1.29–1.34 (m, 1H), 1.66, 1.68 (s, 3H, methyl), 1.57–2.10 (m, 6H), 2.94–3.01 (m, 1H, epoxy H), 4.68–4.74 (m, 2H). ^{13}C {^{1}H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 20.5, 21.2, 23.2, 24.4, 25.3, 26.8, 29.4, 30.8, 31.3, 31.5, 37.3, 41.3, 57.6, 57.8, 59.5, 60.7, 109.2, 109.4, 150.1, 150.5.

2d. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (393 K), final column temperature (513 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (7.4–7.7 min).

3a. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (323 K), initial time (5 min), final column temperature (513 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (1.5 min). MS (70 eV, EI): *m*/*z* (%): 124 (23) [M^+], 109 (15), 83 (12), 82 (81), 81 (54). ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ 1.39 (q, 2H, methylene), 1.58 (s, 3H, methyl), 1.66 (s, 3H, methyl), 1.91–2.07 (m, 4H, allyl H), 4.71–5.01 (m, 2H), 5.02–5.14 (m, 1H), 5.75–5.90 (m, 1H). ^{13}C {^{1}H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 17.6, 25.8, 28.1, 29.9, 34.0, 114.7, 125.2, 132.2, 139.9.

3b. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (323 K), initial time (5 min), final column temperature (493 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (5.9 min). MS (70 eV, EI): *m*/*z* (%): 140 (0.4) [M^+], 125 (1), 109 (2), 107 (3), 97 (1), 96 (1), 95 (10), 93 (3), 91 (3), 83 (9), 82 (100). ^{13}C {^{1}H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 17.8, 25.9, 28.5, 29.9, 32.8, 47.3, 52.7, 125.3, 132.2.

3c. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (323 K), initial time (5 min), final column temperature (493 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (3.5 min). MS (70 eV, EI): *m*/*z* (%): 140 (0.1) [M^+], 125 (3), 97 (2), 86 (3), 85 (8), 83 (3), 82 (17), 81 (14). ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 19.0, 25.1, 26.6, 29.1, 34.2, 58.6, 64.6, 114.7, 139.6.

3c. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), initial time (2 min), final column temperature (443 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (10.4 and 10.5 min).

4a. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), final column temperature (493 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (2.4 min). MS (70 eV, EI): *m*/*z* (%): 94 (69) [M^+], 93 (12) [M^+–H], 91 (36), 79 (100), 77 (59). ^1H NMR (270 MHz, CD_3CN, 298 K, TMS): δ 1.64 (s, 3H, methyl), 2.51–2.68 (m, 4H, allyl H), 5.36–5.39 (m, 1H), 5.68–5.69 (m, 2H). ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 23.5, 27.4, 31.1, 119.3, 124.9, 125.0, 132.0.

4b. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), final column temperature (493 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (5.6 min). MS (70 eV, EI): *m*/*z* (%): 110 (100) [M^+], 109 (14) [M^+–H], 95 (80), 92 (11), 91 (27), 82 (21), 81 (97), 80 (11), 79 (91), 77 (36). ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 23.6, 26.1, 30.4, 50.9, 51.9, 116.4, 129.3.

4c. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), final column temperature (493 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (4.5

min). MS (70 eV, EI): *m*/*z* (%): 110 [M^+] (4), 109 [M^+–H] (1), 95 (7), 91 (6), 79 (13), 67 (13), 43 (100).

4c. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (333 K), final column temperature (443 K), progress rate (10 K/min), injection temperature (523 K), detection temperature (523 K), retention time (9.8 min).

5a. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), initial time (2 min), final column temperature (443 K), progress rate (10 K/min), injection temperature (453 K), detection temperature (523 K), retention time (1.7 min). ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 22.2, 22.3, 25.9, 31.0, 32.2, 127.2, 134.4.

5b. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), initial time (2 min), final column temperature (443 K), progress rate (10 K/min), injection temperature (453 K), detection temperature (523 K), retention time (3.8 min). MS (70 eV, EI): *m*/*z* (%): 112 (4) [M^+], 97 (100), 83 (35), 79 (23), 71 (17), 69 (28), 68 (78), 67 (55). ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 19.4, 21.3, 24.7, 28.2, 31.1, 54.0, 57.8.

5c. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), initial time (2 min), final column temperature (443 K), progress rate (10 K/min), injection temperature (453 K), detection temperature (523 K), retention time (4.0 min). MS (70 eV, EI): *m*/*z* (%): 112 (4) [M^+], 97 (100), 83 (35), 79 (22), 71 (20), 69 (29), 68 (79), 67 (56). ^{13}C {^1H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 18.2, 19.9, 25.8, 30.2 (2C), 53.5, 58.0.

6a. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), initial time (2 min), final column temperature (443 K), progress rate (10 K/min), injection temperature (453 K), detection temperature (523

K), retention time (7.5 min). ^{13}C {^{1}H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 20.0, 25.6, 32.7, 65.7, 129.8, 131.7.

6b. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), initial time (2 min), final column temperature (443 K), progress rate (10 K/min), injection temperature (453 K), detection temperature (523 K), retention time (11.4 min). MS (70 eV, EI): *m*/*z* (%): 96 (4) [M^+–H_2O], 95 (5), 83 (2), 81 (5), 73 (2), 71 (13), 70 (100), 69 (14), 68 (13), 67 (13).

6c. GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (343 K), initial time (2 min), final column temperature (443 K), progress rate (10 K/min), injection temperature (453 K), detection temperature (523 K), retention time (13.2 min). MS (70 eV, EI): *m*/*z* (%): 96 (2) [M^+–H_2O], 95 (3), 86 (2), 83 (2), 81 (2), 73 (2), 71 (15), 70 (100), 69 (13), 68 (8), 67 (12). ^{13}C {^{1}H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ 15.9, 25.5, 30.7, 53.9, 57.5, 66.3.

X-ray crystallography

The crystals were mounted on a glass fiber for indexing and intensity data collection on a Rigaku Saturn CCD area detector (for tetramethylammonium salt of **I**, TMA-**I**) or a Rigaku Mercury CCD area detector (for 18-crown-6-potassium salt of **II**, CEK-**II**) with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). The structures were solved by direct methods[46] (for TMA-**I**) or heavy-atom Patterson methods[47] (for CEK-**II**) and expanded using Fourier techniques.[48] The crystal parameters were summarized in Table S9. All calculations were performed using the CrystalStructure crystallographic software package.[49]

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[49] CrystalStructure 3.5.1, Rigaku/MSC, **2002**.

Table S1: Comparison of R_{cis}/R_{trans} values for the competitive epoxidation of *cis*- and *trans*-alkenes.

system	alkenes	R_{cis}/R_{trans}	ref.
I/H_2O_2	*cis*-2-octene / *trans*-2-octene	**3×10^2**	**this work**
[γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$/H_2O_2	*cis*-2-octene / *trans*-2-octene	11.5	[a]
$H_3PW_{12}O_{40}/H_2O_2$	*cis*-2-octene / *trans*-2-octene	3.7	[b]
$Na_2WO_4 \cdot 2H_2O/NH_2CH_2PO_3H_2/H_2O_2$	*cis*-3-octene / *trans*-3-octene	7.3	[c]
m-CPBA	*cis*-2-octene / *trans*-2-octene	1.2	[d]
dimethyldioxirane	*cis*-3-hexene / *trans*-3-hexene	8.3	[e]

[a] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, 300, 964. [b] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 3587. [c] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella, R. Noyori, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 905. [d] S. Ueno, K. Yamaguchi, K. Yoshida, K. Ebitani, K. Kaneda, *Chem. Commun.* **1998**, 295. [e] A. L. Baumstark, P. C. Vasquez, *J. Org. Chem.* **1988**, *53*, 3437.

***Table S2*:** Comparison of diastereoselectivity for the epoxidation of 3-methyl-1-cyclohexene.

system	yield based on alkene [%]	yield based on oxidant [%]	diastereoselectivity (*syn*: *anti*)	ref.
I/H_2O_2	**91**	**91**	**5 : 95**	**this work**
Ti-β/H_2O_2	47	43	8 : 92	[a]
Ti-MCM-41/TBHP	71	65	42 : 58	[a]
Ti-ITQ-2/TBHP	68	62	39 : 61	[a]
CH_3ReO_3/UHP	31	31	49 : 51	[b]
dimethyldioxirane	~100	100	47 : 53	[b]

[a] W. Adam, A. Corma, H. García, O. Weichold, *J. Catal.* **2000**, *196*, 339. [b] W. Adam, C. M. Mitchell, C. R. Saha-Möller, *Eur. J. Org. Chem.* **1999**, 785.

***Table S3*:** Comparison of diastereoselectivity for the epoxidation of 2-cyclohexen-1-ol.

system	yield based on alkene [%]	yield based on oxidant [%]	diastereoselectivity (*syn*: *anti*)	ref.
I/H_2O_2	**87**	**87**	**12 : 88**	**this work**
Peracid	n.r.	n.r.	92 : 8	[a]
$Mo(CO)_6$/TBHP	90	82	98 : 2	[a]
$VO(acac)_2$/TBHP	n.r.	n.r.	98 : 2	[a]
acetone/OXONE	69	35	36 : 64	[b]
dimethyldioxirane	75	75	34 : 66	[c]
1/OXONE	>85	>85	14 : 86	[d]
CH_3ReO_3/UHP	n.r.	n.r.	36 : 64	[e]
Mn(TDCPP)Cl/H_2O_2	59	12	20 : 80	[f]
TS-1/H_2O_2	67	80	90 : 10	[g]
Mn-tmtacn/H_2O_2	63	32	30 : 70	[h]
$Na_2WO_4/NH_2CH_2PO_3H_2/H_2O_2$	n.r.	n.r.	90 : 10	[i]
MS-4A/TBHP	38	19	97 : 3	[j]

[a] K. B. Sharpless, R. C. Michaelson, *J. Am. Chem. Soc.* **1973**, *95*, 6136. [b] M. Kurihara, S. Ito, N. Tsutsumi, N. Miyata, *Tetrahedron Lett.* **1994**, *35*, 1577. [c] R. W. Murray, M. Singh, B. L. Williams, H. M. Moncrieff, *J. Org. Chem.* **1996**, *61*, 1830. [d] D. Yang, G.-S. Jiao, Y.-C. Yip, M.-K. Wong, *J. Org. Chem.* **1999**, *64*, 1635. [e] W. Adam, C. M. Mitchell, C. R. Saha-Möller, *Eur. J. Org. Chem.* **1999**, 785. [f] W.-K. Chan, P. Liu, W.-Y. Yu, M.-K. Wong, C.-M. Che, *Org. Lett.* **2004**, *6*, 1597. [g] R. Kumer, G. C. G. Pais, B. Pandey, P. Kumar, *J. Chem. Soc., Chem. Commun.* **1995**, 1315. [h] D. E. De Vos, B. F. Sels, M. Reynaers, Y. V. Subba Rao, P. A. Jacobs, *Tetrahedron Lett.* **1998**, 3221. [i] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella, R. Noyori, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 905. [j] R. Antonioletti, F. Bonadies, L. Locati, A. Scettri, *Tetrahedron Lett.* **1992**, *33*, 3205.

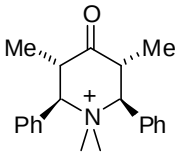

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Table S4: Comparison of regioselectivity for the epoxidation of *trans*-1,4-hexadiene.

system	[terminal epoxide]/ [total epoxide]	ref.
I/H_2O_2	**0.99**	**this work**
[γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$/H_2O_2	0.61	[a]
[$PO_4(WO(O_2)_2)_4$]$^{3-}$/H_2O_2	0.17	[a]
[{$W(=O)(O_2)_2$}$_2$(*m*-O)]$^{2-}$/H_2O_2	0.28	[a]
$Mo(CO)_6$/CHP	0.14	[b]
m-CPBA	0.02	[c]
Mn(TPP)(OAc)/NaOCl/4'-(imidazol-1-yl)acetophenone	0.02	[c]
Mn(TTMPP)(OAc)/NaOCl/4'-(imidazol-1-yl)acetophenone	0.04	[c]
Mn(TTPPP)(OAc)/NaOCl/4'-(imidazol-1-yl)acetophenone	0.35	[c]
[MnT(3',5'-G2Ph)P]$^+$/PhIO	0.03	[d, e]
[MnT(3',5'-G1Ph)P]$^+$/PhIO	0.03	[d, e]
[MnT(2',4',6'-OMePh)P]$^+$/PhIO	0.03	[d, e]
[MnT(2',4',6'G1AP)P]$^+$/PhIO	0.12	[d, e]

[a] K. Kamata, Y. Nakagawa, K. Yamaguchi, N. Mizuno, *J. Catal.* **2004**, *224*, 224. [b] M. N. Sheng, J. G. Zajacek, *J. Org. Chem.* **1970**, *35*, 1839. [c] K. S. Suslick, B. R. Cook, *J. Chem. Soc., Chem. Commun.* **1987**, 200. [d] P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, *J. Am. Chem. Soc.* **1996**, *118*, 5708. [e] P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, *J. Mol. Catal. A* **1996**, *113*, 109.

Table S5: Comparison of regioselectivity for the epoxidation of *R*-(+)-limonene.

system	[terminal epoxide]/ [total epoxide]	ref.
I/H_2O_2	**0.99**	**this work**
[γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$/H_2O_2	0.38	[a]
[$PO_4(WO(O_2)_2)_4$]$^{3-}$/H_2O_2	0.04	[a]
[{$W(=O)(O_2)_2$}$_2$(*m*-O)]$^{2-}$/H_2O_2	0.08	[a]
[PO_4{$WO(O_2)_2$}$_4$]$^{3-}$	<0.03	[b]
[HPO_4{$WO(O_2)_2$}$_2$]$^{2-}$	<0.01	[c]
[Ph_3PCH_2Ph]$_2$[W_2O_{11}]	<0.01	[d]
[PO_4{$WO(O_2)_2$}$_4$]$^{3-}$-amberlite	0.03	[e]
[$WZnMn_2(ZnW_9O_{34})_2$]$^{12-}$	0.50	[f]

$[(Mn(H_2O)_3)_2(WO_2)_2(BiW_9O_{33})_2]^{10-}$	<0.01	[g]
$[(Mn(H_2O))_3(SbW_9O_{33})_2]^{12-}$	<0.01	[g]
$[(Mn(H_2O)_3)_2(Mn(H_2O)_2)_2(TeW_9O_{33})_2]^{8-}$	<0.01	[g]
$[PZnMo_2W_9O_{39}]^{5-}$	<0.01	[h]
benzonitrile/$KHCO_3$	0.37	[i]
m-CPBA	<0.01	[i]
MTO	<0.01	[j]
MTO	0.34	[k]
Ti-β	0.55	[l]
dicyclohexylcarboimide/$KHCO_3$	0.18-0.40	[m, n]
Mn-dmtacn-SiO_2	0.17	[o]
Fe(TDCPN$_5$P)Cl	0.27	[p]
Mn-tmtacn /CH_3COOH	0-0.67	[q]
Mn(TTPPP)(OAc)/NaOCl (TTPPP = tetrakis(2,4,6-triphenylphenyl)porphyrinato)	0.62	[r]
Fe(TTPPP)Cl/PhIO	0.75	[s]
MnCl(2,7,12,17-tetramethyl-3,8,13,18-tetra[2,6-bis(4-phenyl)-4-fluorophenyl]porphyrin)/DMAP/NaOCl	0.66	[t]

[a] K. Kamata, Y. Nakagawa, K. Yamaguchi, N. Mizuno, *J. Catal*. **2004**, *224*, 224. [b] S. Sakaguchi, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* **1996**, *61*, 5307. [c] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.-M. Brégeault, *Inorg. Chem.* **1994**, *33*, 871. [d] J. Prandi, H. B. Kagan, H. Mimoun, *Tetrahedron Lett.* **1986**, *27*, 2617. [e] A. L. Villa, B. F. Sels, D. E. De Vos, P. A. Jacobs, *J. Org. Chem.* **1999**, *64*, 7267. [f] R. Neumann, D. Juwiler, *Tetrahedron* **1996**, *52*, 8781. [g] M. Bösing, A. Nöh, I. Loose, B. Krebs, *J. Am. Chem. Soc.* **1998**, *120*, 7252. [h] S. Tangestaninejad, B. Yadollahi, *Chem. Lett.* **1998**, 511. [i] R. G. Carlson, N. S. Behn, C. Cowles, *J. Org. Chem.* **1971**, *36*, 3832. [j] T. R. Boehlow, C. D. Spilling, *Tetrahedron Lett.* **1996**, *37*, 2717. [k] A. M. Al-Ajlouni, J. H. Espenson, *J. Org. Chem.* **1996**, *61*, 3969. [l] J. C. van der Waal, M. S. Rigutto, H. van Bekkum, *Appl. Catal. A* **1998**, *167*, 331. [m] G. Majetich, R. Hicks, *Synlett* **1996**, 649. [n] G. Majetich, R. Hicks, G. Sun, P. McGill, *J. Org. Chem.* **1998**, *63*, 2564. [o] B. F. Sels, A. L. Villa, D. Hoegaerts, D. E. De Vos, P. A. Jacobs, *Top. Catal*. **2000**, *13*, 223. [p] J. F. Bartoli, K. L. Barch, M. Palacio, P. Battioni, D. Mansuy, *Chem. Commun.* **2001**, 1718. [q] D. Mandelli, K. B. Voitiski, U. Schuchardt, G. B. Shul'pin, *Chem. Nat. Compd.* **2002**, *38*, 243. [r] K. S. Suslick, B. R. Cook, *J. Chem. Soc., Chem. Commun.* **1987**, 200. [s] K. H. Ahn, J. T. Groves, *Bull. Korean Chem. Soc.* **1994**, *15*, 957. [t] T. Lai, S. K. Lee, L. Yeung, H. Liu, I. D. Williams, C. K. Chang, *Chem. Commun.* **2003**, 620.

Table S6: Comparison of regioselectivity for the epoxidation of 7-methyl-1,6-octadiene.

system	[terminal epoxide]/ [total epoxide]	ref.
I/H_2O_2	**0.93**	**this work**
$[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}/H_2O_2$	0.17	[a]
$[PO_4(WO(O_2)_2)_4]^{3-}/H_2O_2$	0.02	[a]
$[\{W(=O)(O_2)_2\}_2(m\text{-}O)]^{2-}/H_2O_2$	0.03	[a]
Al_2O_3/H_2O_2	<0.01	[b]
$CF_3CH_2OH/H_2O_2/Na_2HPO_4$	<0.01	[c]
$(CF_3)_2CO/C_2F_5OH/H_2O_2/Na_2HPO_4$	<0.01	[d]

[a] K. Kamata, Y. Nakagawa, K. Yamaguchi, N. Mizuno, *J. Catal*. **2004**, *224*, 224. [b] M. C. A. van Vliet, D. Mandelli, I. W. C. E. Arends, U. Schuchardt, R. A. Sheldon, *Green Chem.* **2001**, *3*, 243. [c] M. C. A. van Vliet,

I. W. C. E. Arends, R. A. Sheldon, *Synlett* **2001**, 248. [d] M. C. A. van Vliet, I. W. C. E. Arends, R. A. Sheldon, *Synlett* **2001**, 1305.

Table S7: Comparison of regioselectivity for the epoxidation of 1-methyl-1,4-cyclohexadiene.

system	[4,5 epoxide]/ [total epoxide]	ref.
I/H_2O_2	**0.88**	**this work**
[γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$/H_2O_2	0.89	[a]
[$PO_4(WO(O_2)_2)_4$]$^{3-}$/H_2O_2	0.04	[a]
[{$W(=O)(O_2)_2$}$_2$(*m*-O)]$^{2-}$/H_2O_2	0.02	[a]
m-CPBA	0.08	[b]
Mn(TPP)(OAc)/NAOCl/4'-(imidazol-1-yl)acetophenone	0.53	[b]
Mn(TTMPP)(OAc)/NaOCl/4'-(imidazol-1-yl)acetophenone	0.70	[b]
Mn(TTPPP)(OAc)/NaOCl/4'-(imidazol-1-yl)acetophenone	0.95	[b]
[MnT(3',5'-G2Ph)P]$^+$/PhIO	0.55	[c, d]
[MnT(3',5'-G1Ph)P]$^+$/PhIO	0.52	[c, d]
[MnT(2',4',6'-OMePh)P]$^+$/PhIO	0.71	[c, d]
[MnT(2',4',6'G1AP)P]$^+$/PhIO	0.74	[c, d]
[$PW_{11}CoO_{39}$]$^{5-}$/isobutyraldehyde/O_2 (1 atm)	0.69	[e]
m-CPBA	0.07	[f]
MnCl(2,7,12,17-tetramethyl-3,8,13,18-tetra[2,6-bis(4-phenyl) -4-fluorophenyl]porphyrin)/NaOCl	0.11	[f]
MnCl(2,7,12,17-tetramethyl-3,8,13,18-tetra[2,6-bis(4-phenyl) -4-fluorophenyl]porphyrin)/DMAP/NaOCl	0.33	[f]

[a] K. Kamata, Y. Nakagawa, K. Yamaguchi, N. Mizuno, *J. Catal*. **2004**, *224*, 224. [b] K. S. Suslick, B. R. Cook, *J. Chem. Soc., Chem. Commun.* **1987**, 200. [c] P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, J. Am. Chem. Soc. **1996**, *118*, 5708. [d] P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, *J. Mol. Catal. A* **1996**, *113*, 109. [e] N. Mizuno, M. Tateishi, T. Hirose, M. Iwamoto, *Chem. Lett.* **1993**, 1985. [f] T. S. Lai, S. K. S. Lee, L. L. Yeung, H. Y. Liu, I. D. Williams, C. K. Chang, *Chem. Commun.* **2003**, 620.

Table S8: Initial and relative rates for the epoxidation of a series of C_8-olefins with H_2O_2 catalyzed by **I**.[a]

olefin	R_0 (μM·min^{-1})	relative rate[b]
2-methyl-1-heptene	420	1.1
1-octene	384	1.0
cis-2-octene	334	0.87
2-methyl-1-heptene	10	0.03
trans-2-octene	<1.4	<0.01

[a] Reaction conditions: Alkene (33.3 mM), **I** (tetrabutylammonium salt, 1.67 mM), H_2O_2 (30% aq., 33.3 mM), CH_3CN/*t*BuOH (1.5/1.5 mL), 293 K. R_0 values were determined from the reaction profiles at low conversion (=10%) of hydrogen peroxide. [b] The R_0 value obtained with 1-octene was taken as unity.

***Table S9*:** Crystallographic data for TMA-**I** and CEK-**II**.

	TMA-**I**	CEK-**II**
Formula	$[N(CH_3)_4]_4[H_2SiV_2W_{10}O_{40}]\cdot 3H_2O$	$[K(C_{12}H_{24}O_6)]_4[HSiV_2W_{10}O_{39}(OCH_3)]\cdot 1.5CH_3CN$
Fw	2959.07	3814.06
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (#14)	P-1 (#2)
a (Å)	11.7992(7)	15.107(7)
b (Å)	37.804(2)	17.440(8)
c (Å)	12.7372(8)	21.742(12)
α (deg)	90	81.44(2)
β (deg)	110.308(3)	84.21(2)
γ (deg)	90	67.64(2)
V (Å^3)	5328.4(6)	5232.6(43)
Z	4	2
T (K)	113	183
Wavelength (Å)	0.71070	0.71070
D_{calc} (g cm^{-1})	3.688	2.421
Abs coeff (cm^{-1})	219.76	113.67
No. of reflections measured	Total: 118316 Unique: 12403 (R_{int} = 0.039)	Total: 67858 Unique: 21485 (R_{int} = 0.061)
No. of observations used	10946	10511
R^a	0.022	0.064
$R_w{}^a$	0.025	0.072

Table S10: Epoxidation of terminal alkenes with H_2O_2 catalyzed by various polyoxometalates.

polyoxometalate	alkene	solvent	H_2O_2/alkene	temp. (K)	yield (%)	ref.
I	1-butene	CH_3CN/*t*BuOH	**1/1**	293	91	**this**
I	1-hexene	CH_3CN/*t*BuOH	**1/1**	293	92	**work**
I	1-octene	CH_3CN/*t*BuOH	**1/1**	293	93	
$[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$	1-butene	CH_3CN	0.2/1	305	88	[a]
$[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$	1-octene	CH_3CN	0.2/1	305	90	[a]
$H_3PW_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	53	[b]
$H_3PMo_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	6	[b]
$H_4SiW_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1	[b]
$H_3PMo_6W_6O_{40}$	1-octene	$CHCl_3$	1.5/1	333	16	[b]
$PW_{12}O_{40}^{3-}/SiO_2$	1-octene	without solvent	2/1	363	49	[c]
$H_5BW_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1, <1†	[d]
$H_4SiW_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1, <1†	[d]
$H_3PMo_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1, 5†	[d]
$H_3PW_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1, 52†	[d]
$H_6P_2W_{18}O_{62}$	1-octene	$CHCl_3$	1.5/1	333	<1, <1†	[d]
$K_4W_{10}O_{32}$	1-octene	$CHCl_3$	1.5/1	333	<1, 6†	[d]
$(NH_4)_{10}H_2W_{12}O_{42}$	1-octene	$CHCl_3$	1.5/1	333	44, 35†	[d]
$(NH_4)_6Mo_7O_{24}$	1-octene	$CHCl_3$	1.5/1	333	11, 7†	[d]
H_2WO_4	1-octene	$CHCl_3$	1.5/1	333	50, 50†	[d]
Na_2WO_4/H_3PO_4	1-octene	$CHCl_3$	1.5/1	333	13, 17†	[d]
$K_7[PW_{11}O_{39}]$	1-octene	benzene	2.2/1	344	6	[e]
$K_7[PW_{11}O_{39}]$	1-nonene	benzene	2.2/1	344	7	[e]
$K_7[PW_{11}O_{39}]$	1-dodecene	benzene	2.2/1	344	5	[e]
$H_3PW_{12}O_{40}$	1-octene	benzene	2.2/1	344	11	[e]
$H_3PW_{12}O_{40}$	1-nonene	benzene	2.2/1	344	11	[e]
$H_3PW_{12}O_{40}$	1-dodecene	benzene	2.2/1	344	12	[e]
$H_3PW_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	51	[f]
$H_4SiW_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$H_3PMo_{12}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	1	[f]
$Na_7PW_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	42	[f]
$K_5PTiW_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_4PVW_{11}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_5PMn^{II}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_5PFe^{II}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_5PCo^{II}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]

Table S10: (continued)

$K_5PZn^{II}OW_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	6	[f]
$K_7PTi_2W_{10}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$H_5PV_2Mo_{10}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_8SiW_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_6SiTiW_{11}O_{40}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_6SiMn^{II}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_6SiFe^{II}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_6SiCo^{II}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_7BMn^{II}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_7BCo^{II}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$K_6BCo^{III}W_{11}O_{39}$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$[(CH_3)_4N]_4[(C_6H_5Si)_2OSiW_{11}O_{39}]$	1-octene	$CHCl_3$	1.5/1	333	<1	[f]
$[WZnPt^{II}_2(ZnW_9O_{34})_2]^{12-}$	1-octene	$ClCH_2CH_2Cl$	2.9/1	298	2	[g]
$[WZnPd^{II}_2(ZnW_9O_{34})_2]^{12-}$	1-octene	$ClCH_2CH_2Cl$	2.9/1	298	2	[g]
$[WZnRh^{III}_2(ZnW_9O_{34})_2]^{10-}$	1-octene	$ClCH_2CH_2Cl$	2.9/1	298	2	[g]
$[WZnRu^{III}_2(ZnW_9O_{34})_2]^{10-}$	1-octene	$ClCH_2CH_2Cl$	2.9/1	298	<1	[g]
$[Fe^{III}_4(H_2O)_2(PW_9O_{34})_2]^{6-}$	1-hexene	CH_3CN	0.25/1	298	<1	[h]
$[Fe^{III}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$	1-hexene	CH_3CN	0.25/1	r.t.	11	[i]
$[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$	1-octene	$ClCH_2CH_2Cl$	2/1	343	5	[j]
$[\gamma\text{-}SiW_{10}\{Fe^{III}(OH_2)\}_2O_{38}]^{6-}$	1-octene	CH_3CN	0.2/1	305	45	[k]
$[Ni^{II}(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$	1-octene	$ClCH_2CH_2Cl$	3/1	343	15	[l]
$[PZnMo_2W_9O_{39}]^{5-}$	1-octene	$CHCl_3$	10/1	343	2	[m]
$[\alpha\beta\beta\alpha\text{-}(Mn^{II}OH_2)_2Mn^{II}_2(As_2W_{15}O_{56})_2]^{16-}$	1-hexene	$ClCH_2CH_2Cl$	0.7/1	r.t.	2	[n]
$[\alpha\beta\beta\alpha\text{-}(Mn^{II}OH_2)_2Mn^{II}_2(P_2W_{15}O_{56})_2]^{16-}$	1-hexene	$ClCH_2CH_2Cl$	0.7/1	r.t.	1	[n]
$[((Mn^{II}OH_2)Mn^{II}_2PW_9O_{34})_2(PW_6O_{26})]^{17-}$	1-hexene	$ClCH_2CH_2Cl$	0.7/1	298	<1	[o]
$K_{11}[Y\{PW_{11}O_{39}\}_2]$	1-octene	benzene	2.2/1	344	7	[e]
$K_{11}[Y\{PW_{11}O_{39}\}_2]$	1-nonene	benzene	2.2/1	344	8	[e]
$K_{11}[Y\{PW_{11}O_{39}\}_2]$	1-dodecene	benzene	2.2/1	344	7	[e]
$K_{11}[La\{PW_{11}O_{39}\}_2]$	1-octene	benzene	2.2/1	344	6	[e]
$K_{11}[La\{PW_{11}O_{39}\}_2]$	1-nonene	benzene	2.2/1	344	8	[e]
$K_{11}[La\{PW_{11}O_{39}\}_2]$	1-dodecene	benzene	2.2/1	344	7	[e]
$K_{11}[Ce^{III}\{PW_{11}O_{39}\}_2]$	1-octene	benzene	2.2/	344	2	[e]
$K_{11}[Ce^{III}\{PW_{11}O_{39}\}_2]$	1-nonene	benzene	2.2/1	344	2	[e]
$K_{11}[Ce^{III}\{PW_{11}O_{39}\}_2]$	1-dodecene	benzene	2.2/1	344	2	[e]
$K_{10}[Ce^{IV}\{PW_{11}O_{39}\}_2]$	1-octene	benzene	2.2/1	344	2	[e]

Table S10: (continued)

$K_{10}[Ce^{IV}\{PW_{11}O_{39}\}_2]$	1-nonene	benzene	2.2/1	344	2	[e]
$K_{10}[Ce^{IV}\{PW_{11}O_{39}\}_2]$	1-dodecene	benzene	2.2/1	344	1	[e]
$K_{11}[Pr\{PW_{11}O_{39}\}_2]$	1-octene	benzene	2.2/1	344	7	[e]
$K_{11}[Pr\{PW_{11}O_{39}\}_2]$	1-nonene	benzene	2.2/1	344	8	[e]
$K_{11}[Pr\{PW_{11}O_{39}\}_2]$	1-dodecene	benzene	2.2/1	344	8	[e]
$K_{11}[Sm\{PW_{11}O_{39}\}_2]$	1-octene	benzene	2.2/1	344	9	[e]
$K_{11}[Sm\{PW_{11}O_{39}\}_2]$	1-nonene	benzene	2.2/1	344	8	[e]
$K_{11}[Sm\{PW_{11}O_{39}\}_2]$	1-dodecene	benzene	2.2/1	344	5	[e]
$K_{11}[Tb\{PW_{11}O_{39}\}_2]$	1-octene	benzene	2.2/1	344	6	[e]
$K_{11}[Tb\{PW_{11}O_{39}\}_2]$	1-nonene	benzene	2.2/1	344	7	[e]
$K_{11}[Tb\{PW_{11}O_{39}\}_2]$	1-dodecene	benzene	2.2/1	344	7	[e]
$K_{11}[Yb\{PW_{11}O_{39}\}_2]$	1-octene	benzene	2.2/1	344	6	[e]
$K_{11}[Yb\{PW_{11}O_{39}\}_2]$	1-nonene	benzene	2.2/1	344	7	[e]
$K_{11}[Yb\{PW_{11}O_{39}\}_2]$	1-dodecene	benzene	2.2/1	344	7	[e]
$[HoW_{10}O_{36}]^{9-}$	1-octene	$CHCl_3$	1.5/1	333	<1	[p]
$H_3PO_4/Na_2WO_4{\cdot}2H_2O$	1-octene	$ClCH_2CH_2Cl$	0.6/1	343	82	[q]
$H_3PO_4/Na_2WO_4{\cdot}2H_2O$	1-dodecene	$ClCH_2CH_2Cl$	0.6/1	343	87	[q]
$NH_2CH_2PO_3H_2/Na_2WO_4{\cdot}2H_2O$	1-octene	without solvent	1.5/1	383	57	[r]
$NH_2CH_2PO_3H_2/Na_2WO_4{\cdot}2H_2O$	1-octene	toluene	1.5/1	383	63	[r]
$NH_2CH_2PO_3H_2/Na_2WO_4{\cdot}2H_2O$	1-nonene	without solvent	1.5/1	383	57	[r]
$NH_2CH_2PO_3H_2/Na_2WO_4{\cdot}2H_2O$	1-nonene	toluene	1.5/1	383	63	[r]
$NH_2CH_2PO_3H_2/Na_2WO_4{\cdot}2H_2O$	1-decene	toluene	1.5/1	383	61	[r]
$NH_2CH_2PO_3H_2/Na_2WO_4{\cdot}2H_2O$	1-undecene	without solvent	1.5/1	383	61	[r]
$NH_2CH_2PO_3H_2/Na_2WO_4{\cdot}2H_2O$	1-undecene	toluene	1.5/1	383	66	[r]
$NH_2CH_2PO_3H_2/Na_2WO_4{\cdot}2H_2O$	1-dodecene	without solvent	1.5/1	383	58	[r]
$[PO_4(WO_3)_4]^{3-}$	propylene	xylene/tributylphosphate	0.4/1	338	85[‡]	[s]
$[PO_4(WO_3)_4]^{3-}$	1-hexene	toluene/tributylphosphate	0.33/1	308	90	[s]
$[PO_4(WO_3)_4]^{3-}$	1-hexene	trimethylbenzene/trioctylphosphate	0.33/1	318	95[†]	[t]
$[PO_4(WO_3)_4]^{3-}$	1-octene	trimethylbenzene/trioctylphosphate	0.33/1	318	79[†]	[t]
$[PO_4(WO_3)_4]^{3-}$	1-dodecene	trimethylbenzene/trioctylphosphate	0.33/1	318	73[†]	[t]
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-pentene	benzene	1.7/1	348	32	[u]
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-hexene	benzene	1.7/1	348	27	[u]
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-heptene	benzene	1.7/1	348	19	[u]
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-octene	benzene	1.7/1	348	35	[u]
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-nonene	benzene	1.7/1	348	53	[u]

Table S10: (continued)

$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-decene	benzene	1.7/1	348	51	[u]
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-undecene	benzene	1.7/1	348	49	[u]
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-dodecene	benzene	1.7/1	348	55	[u]
$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	1-pentene	benzene	1.7/1	348	43	[u]
$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	1-hexene	benzene	1.7/1	348	38	[u]
$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	1-heptene	benzene	1.7/1	348	32	[u]
$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	1-octene	benzene	1.7/1	348	27	[u]
$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	1-nonene	benzene	1.7/1	348	54	[u]
$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	1-decene	benzene	1.7/1	348	55	[u]
$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	1-undecene	benzene	1.7/1	348	57	[u]
$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	1-dodecene	benzene	1.7/1	348	57	[u]
$[PO_4\{MoO(O_2)_2\}_4]^{3-}$	1-pentene	benzene	1.7/1	348	1	[u]
$[PO_4\{MoO(O_2)_2\}_4]^{3-}$	1-hexene	benzene	1.7/1	348	2	[u]
$[PO_4\{MoO(O_2)_2\}_4]^{3-}$	1-heptene	benzene	1.7/1	348	2	[u]
$[PO_4\{MoO(O_2)_2\}_4]^{3-}$	1-octene	benzene	1.7/1	348	1	[u]
$[PO_4\{MoO(O_2)_2\}_4]^{3-}$	1-nonene	benzene	1.7/1	348	1	[u]
$[PO_4\{MoO(O_2)_2\}_4]^{3-}$	1-decene	benzene	1.7/1	348	1	[u]
$[PO_4\{MoO(O_2)_2\}_4]^{3-}$	1-undecene	benzene	1.7/1	348	2	[u]
$[PO_4\{MoO(O_2)_2\}_4]^{3-}$	1-dodecene	benzene	1.7/1	348	3	[u]
$[AsO_4\{MoO(O_2)_2\}_4]^{3-}$	1-pentene	benzene	1.7/1	348	3	[u]
$[AsO_4\{MoO(O_2)_2\}_4]^{3-}$	1-hexene	benzene	1.7/1	348	5	[u]
$[AsO_4\{MoO(O_2)_2\}_4]^{3-}$	1-heptene	benzene	1.7/1	348	3	[u]
$[AsO_4\{MoO(O_2)_2\}_4]^{3-}$	1-octene	benzene	1.7/1	348	3	[u]
$[AsO_4\{MoO(O_2)_2\}_4]^{3-}$	1-nonene	benzene	1.7/1	348	5	[u]
$[AsO_4\{MoO(O_2)_2\}_4]^{3-}$	1-decene	benzene	1.7/1	348	3	[u]
$[AsO_4\{MoO(O_2)_2\}_4]^{3-}$	1-undecene	benzene	1.7/1	348	6	[u]
$[AsO_4\{MoO(O_2)_2\}_4]^{3-}$	1-dodecene	benzene	1.7/1	348	9	[u]
$[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$	1-hexene	benzene	5.3/1	348	7	[v]
$[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$	1-heptene	benzene	5.3/1	348	11	[v]
$[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$	1-octene	benzene	5.3/1	348	11	[v]
$[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$	1-nonene	benzene	5.3/1	348	10	[v]
$[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$	1-decene	benzene	5.3/1	348	11	[v]
$[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$	1-undecene	benzene	5.3/1	348	10	[v]
$[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$	1-dodecene	benzene	5.3/1	348	10	[v]
$[W_4O_6(O_2)_6(OH)_2(H_2O)_2]^{2-}$	1-hexene	benzene	5.3/1	348	<1	[v]

Table S10: (continued)

$[W_4O_6(O_2)_6(OH)_2(H_2O)_2]^{2-}$	1-octene	benzene	5.3/1	348	1	[v]
$[W_4O_6(O_2)_6(OH)_2(H_2O)_2]^{2-}$	1-decene	benzene	5.3/1	348	1	[v]
$[W_4O_6(O_2)_6(OH)_2(H_2O)_2]^{2-}$	1-dodecene	benzene	5.3/1	348	1	[v]
$[W_2O_3(O_2)_4]^{2-}$	1-hexene	benzene	5.3/1	343	2	[w]
$[W_2O_3(O_2)_4]^{2-}$	1-heptene	benzene	5.3/1	343	2	[w]
$[W_2O_3(O_2)_4]^{2-}$	1-octene	benzene	5.3/1	343	3	[w]
$[W_2O_3(O_2)_4]^{2-}$	1-nonene	benzene	5.3/1	343	5	[w]
$[W_2O_3(O_2)_4]^{2-}$	1-decene	benzene	5.3/1	343	4	[w]
$[W_2O_3(O_2)_4]^{2-}$	1-undecene	benzene	5.3/1	343	4	[w]
$[W_2O_3(O_2)_4]^{2-}$	1-dodecene	benzene	5.3/1	343	5	[w]
$[(Ph_2PO_2)\{WO(O_2)_2\}]^{2-}$	1-heptene	benzene	2.9/1	348	2	[x]
$[(Ph_2PO_2)\{WO(O_2)_2\}]^{2-}$	1-octene	benzene	2.9/1	348	7	[x]
$[(Ph_2PO_2)\{WO(O_2)_2\}]^{2-}$	1-nonene	benzene	2.9/1	348	9	[x]
$[(Ph_2PO_2)\{WO(O_2)_2\}]^{2-}$	1-decene	benzene	2.9/1	348	10	[x]
$[(Ph_2PO_2)\{WO(O_2)_2\}]^{2-}$	1-undecene	benzene	2.9/1	348	10	[x]
$[(Ph_2PO_2)\{WO(O_2)_2\}]^{2-}$	1-dodecene	benzene	2.9/1	348	11	[x]
$[PO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-octene	benzene	2.9/1	348	11	[e]
$[PO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-nonene	benzene	2.9/1	348	18	[e]
$[PO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-decene	benzene	2.9/1	348	20	[e]
$[PO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-undecene	benzene	2.9/1	348	18	[e]
$[PO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-dodecene	benzene	2.9/1	348	18	[e]
$[AsO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-octene	benzene	2.9/1	348	10	[e]
$[AsO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-nonene	benzene	2.9/1	348	19	[e]
$[AsO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-decene	benzene	2.9/1	348	21	[e]
$[AsO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-undecene	benzene	2.9/1	348	20	[e]
$[AsO_4\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	1-dodecene	benzene	2.9/1	348	20	[e]
$[PO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-octene	benzene	2.9/1	348	11	[e]
$[PO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-nonene	benzene	2.9/1	348	23	[e]
$[PO_3(OH)\{WO(O_2)_2\}_2]^{2}$	1-decene	benzene	2.9/1	348	19	[e]
$[PO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-undecene	benzene	2.9/1	348	16	[e]
$[PO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-dodecene	benzene	2.9/1	348	19	[e]
$[AsO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-octene	benzene	2.9/1	348	11	[e]
$[AsO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-nonene	benzene	2.9/1	348	10	[e]
$[AsO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-decene	benzene	2.9/1	348	17	[e]
$[AsO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-undecene	benzene	2.9/1	348	16	[e]

Table S10: (continued)

$[AsO_3(OH)\{WO(O_2)_2\}_2]^{2-}$	1-dodecene	benzene	2.9/1	348	14	[e]
$[(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2(OH_2)]^{3-}$	1-decene	benzene	3.1/1	343	19	[y]
$[(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2(OH_2)]^{3-}$	1-undecene	benzene	3.1/1	343	16	[y]
$[(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2(OH_2)]^{3-}$	1-decene	benzene	3.1/1	343	12	[y]
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	1-octene	$ClCH_2CH_2Cl$	0.6/1	343	89	[z]

Yields were calculated on the basis of initial oxidant. H_2O_2/alkene = molar ratio of H_2O_2 and alkene in each system. Yield (%) = epoxide (mol) / H_2O_2 used (mol) × 100. †Pretreated with hydrogen peroxide before addition of olefins. †Yields were calculated based on 2-ethylanthraquinone.

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Table S11. Comparison of δ(^{51}V, ^{95}Mo or ^{183}W) values between the oxometal, peroxometal and hydroperoxometal complexes

Oxo compound	δ [ppm]	Peroxo/hydroperoxo compound	δ [ppm]	$\delta_{peroxo} - \delta_{oxo}$ [ppm]	Peroxo to metal CT λ_{max} [nm] (ε)	Ref.
Vanadium-Oxo	*^{51}V*	*-Peroxo*				
$VO(OH)_2(O_2)^-$	-602	$V(OH)_2(O_2)_2^-$	-686	-84	n.r.	[a]
$VO_2(OH)(O_2)^-$	-625	$VO(OH)(O_2)_2^-$	-765	-140	n.r.	[a]
$VO_2(ox)_2^{3-}$	-529	$VO(O_2)(ox)_2^{3-}$	-590	-61	440 (308)	[b,c]
VO_2(bpg)	-494	$VO(O_2)$(bpg)	-543	-49	422 (270)	[d,e]
$VO_2(ada)^-$	-506	$VO(O_2)(ada)^-$	-551	-45	427 (420)	[d,e]
$VO_2(nta)^{2-}$	-504.3	$VO(O_2)(nta)^{2-}$	-544	-40	428 (350)	[d,f]
$VO_2(dipic)^-$	-533	$VO(O_2)(dipic)^-$	-595	-62	432 (456)	[b,g,h]
$VO_2(heida)^{2-}$	-512.5	$VO(O_2)(Hheida)^-$	-565	-42	429 (330)	[e,i]
VO(acac){$PhN(CH_2CH_2O)_2$}	-472.1	$V(O_2)$(acac){$PhN(CH_2CH_2O)_2$}	-534	-62	n.r.	[j]
Molybdenum-Oxo	*^{95}Mo*	*-Peroxo*				
MoO_4^{2-}	0	$MoO_3(O_2)^{2-}$	-110	-110	n.r.	[k]
$MoO_3(O_2)^{2-}$	-110	$MoO_2(O_2)_2^{2-}$	-215	-105	n.r.	[k]
$MoO_2(O_2)_2^{2-}$	-215	$MoO(O_2)_3^{2-}$	-435	-220	n.r.	[k]
$MoO(O_2)_3^{2-}$	-435	$Mo(O_2)_4^{2-}$	-496	-61	450 (440)	[k]
$MoO_3(dipic)^{2-}$	+58	$MoO(O_2)$(dipic)	-128	-186	364 (878)	[l]
$MoO_3(nta)^-$	+67	$MoO(O_2)(nta)^-$	-23	-90	n.r.	[l]
$MoO_3(ox)^{2-}$	+5.1	$MoO(O_2)_2(ox)^{2-}$	-228.3	-233	n.r.	[m]
		-Hydroperoxo				
$H_xMoO_2(O_2)_2^{(2-x)-}$ ($0 \le x \le 1$)	-215 ~ -230	$[MoO(O_2)_2(OOH)]_2^{2-}$	-200	**+15 ~ +30**	n.r.	[k]
Tungsten-Oxo	*^{183}W*	*-Peroxo*				
WO_4^{2-}	0	$WO_3(O_2)^{2-}$	-567	-567	n.r.	[n]
$WO_3(O_2)^{2-}$	-567	$WO_2(O_2)_2^{2-}$	-676	-109	n.r.	[n]
$WO_2(O_2)_2^{2-}$	-676	$W(O_2)_4^{2-}$	-1247	-571	325 (420)	[n]
Cp*WO_2Me	-642	Cp*$WO(O_2)$Me	-1078	-436	n.r.	[o]

Abbreviations: ox = oxalate; Hbpg = N,N-bis(2-pyridylmethyl)glycine; H_2ada = N-(2-amidomethyl)-iminodiacetic acid; H_3nta = nitrilotriacetic acid; dipic = dipicolinato; H_3heida = 2-hydroxyethyliminodiacetic acid.

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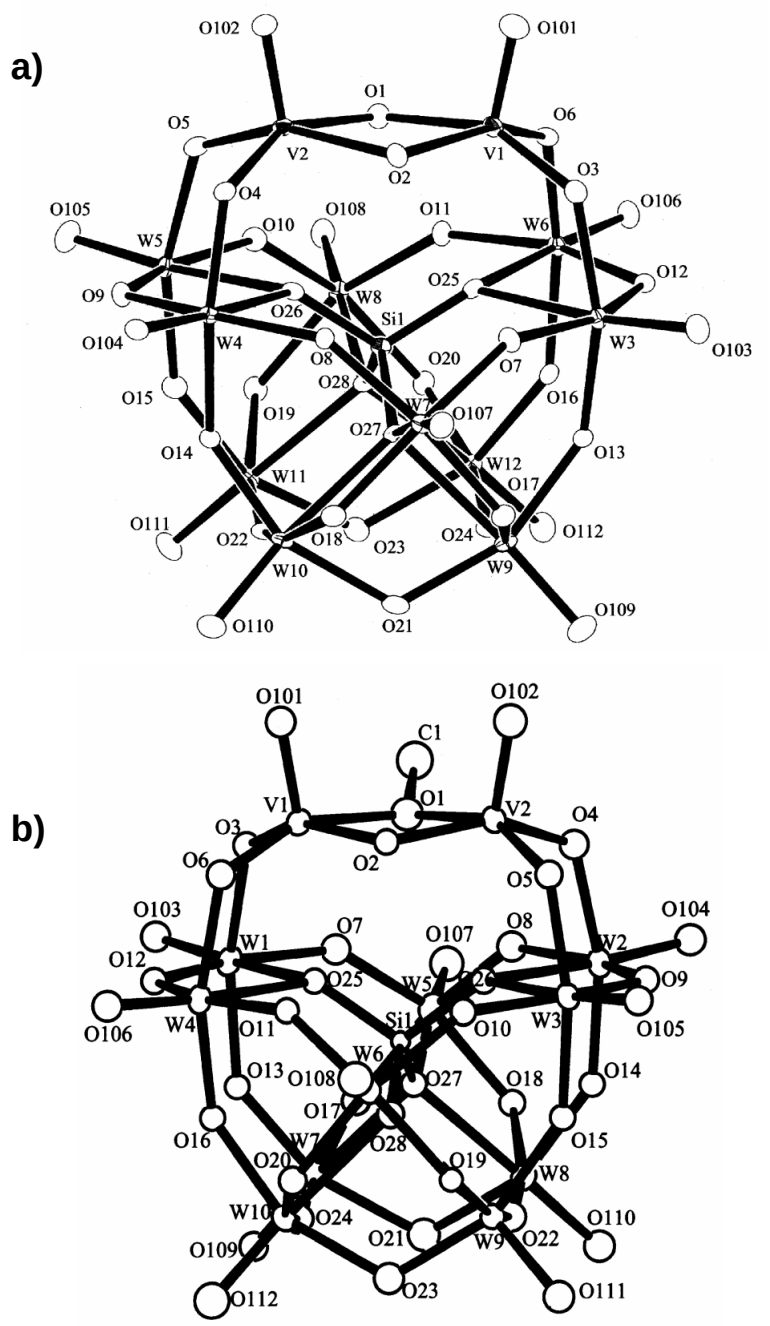

***Figure S1*:** Molecular structure of the anion part of (a) TMA-**I** and (b) CEK-**II**.

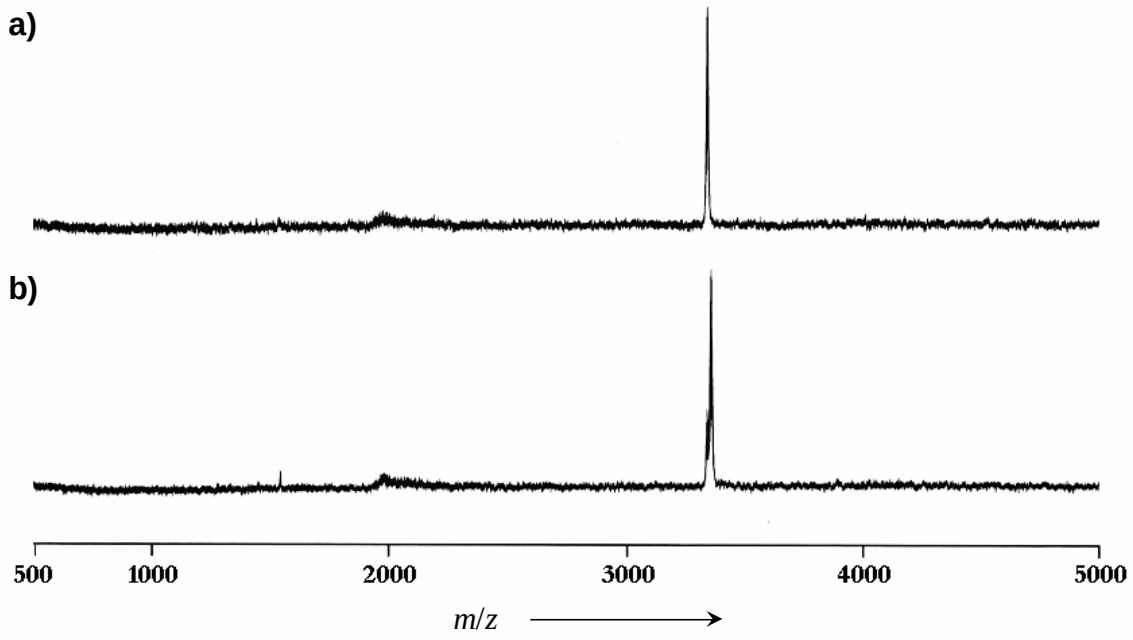

Figure S2. Cold-spray ionization mass (CSI-MS, anion mode, *m*/*z* 500–5000) spectra of (a) TBA-**I** (0.14 mM) in 1,2-$C_2H_4Cl_2$ and (b) TBA-**I** (0.14 mM) in 1,2-$C_2H_4Cl_2$ treated with 350 equiv. H_2O_2 (96% aqueous solution) with respect to TBA-**I** (253 K, 2 h).

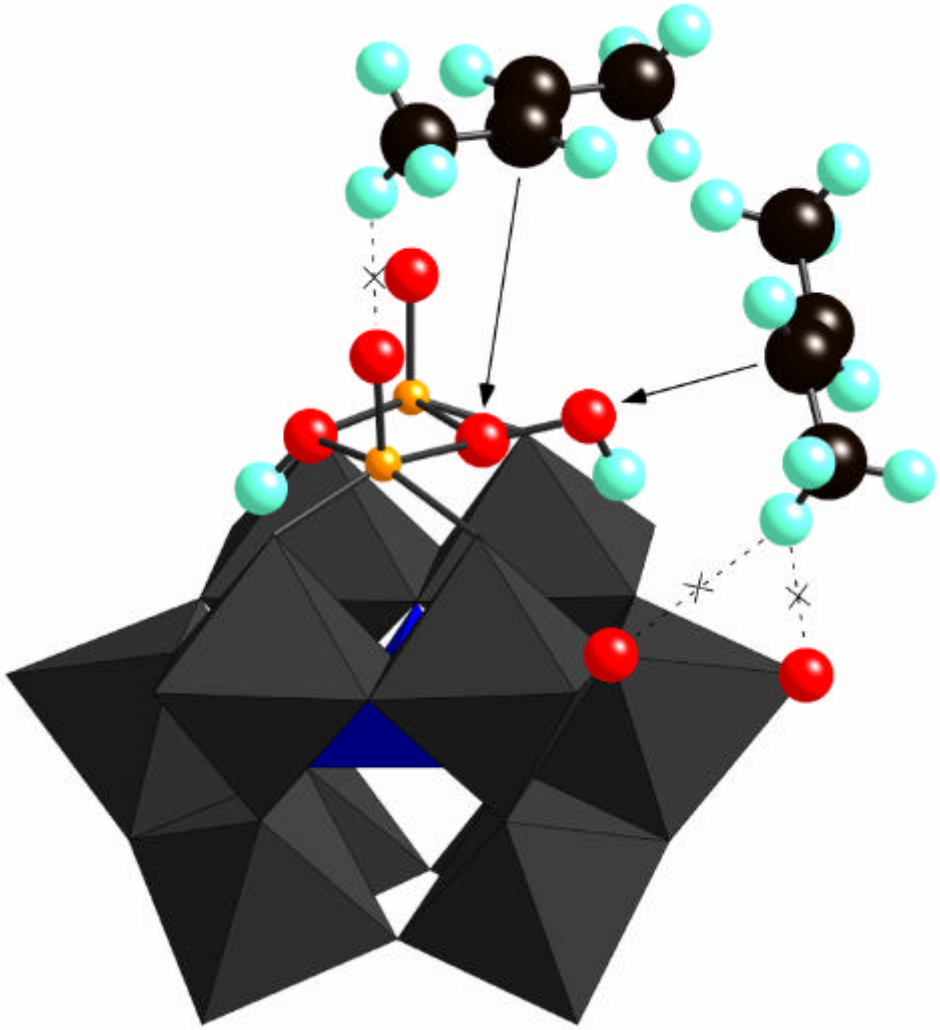

Figure S3. Schematic representation of the approach of *trans*-2-butene to the {VO-(μ-OH)(μ-OOH)-VO} site in [γ-1,2-$SiV_2W_{10}O_{38}(OH)(OOH)]^{4-}$. The structure of [γ-1,2-$SiV_2W_{10}O_{38}(OH)(OOH)]^{4-}$ was calculated with DFT using Gaussian03 program package. Theory: B3LYP; basis sets: 6-31++G** (H and O), 6-31G* (Si), and LanL2DZ (V and W).