Electronic Supplementary Information for Dalton Transactions

Transition metal-substituted Dawson anions of the type $[\alpha_2\text{-}P_2W_{17}O_{61}M]^{n-}$ ($M = Co^{2+}$, Ni^{2+}, Zn^{2+}, Pd^{2+}, Cr^{3+}, Mn^{3+}, Fe^{3+} and Ir^{4+}) as chemo- and regio-selective oxygen transfer catalysts for H_2O_2 in the epoxidation of allylic alcohols under biphasic reaction conditions

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SUPPLEMENTARY DATA

Table S1. Analytical Data for $[^nBu_4N]_6[P_2W_{18}O_{62}]$, $[^nBu_4N]_9[P_2W_{17}O_{61}M(Br)]$ (where $M^{n+} = Co^{2+}$, Ni^{2+}, Cu^{2+} and Zn^{2+}), $[^nBu_4N]_7[HP_2W_{17}O_{61}M(Br)]$ (where $M^{n+} = Cr^{3+}$, Mn^{3+} and Fe^{3+}) and $[K/(^nBu_4N)]_{10-n}[P_2W_{17}O_{61}M(H_2O)]$ (where $M^{n+} = Pd^{2+}$, Ru^{3+} and Ir^{4+})

Compound [a]	%C [b]	%H [b]	%N [b]	%K [b]	%P [b]	%M [b]	% mass loss [b,c]
$(TBA)_6[P_2W_{18}O_{62}]$	20.83 (19.82)	3.96 (3.74)	1.41 (1.44)	-	0.97 (1.06)	-	27.5 (28.3)
$(TBA)_9[P_2W_{17}O_{61}Co(Br)]$	27.39 (26.67)	5.39 (5.04)	1.88 (1.94)	-	0.86 (0.96	0.85 (0.91)	35.6 (37.2)
$(TBA)_9[P_2W_{17}O_{61}Ni(Br)]$	28.29 (26.67)	5.13 (5.04)	1.82 (1.94)	-	0.93 (0.96)	0.79 (0.91)	36.8 (37.0)
$(TBA)_9[P_2W_{17}O_{61}Cu(Br)]$	25.43 (26.65)	4.80 (5.03)	1.78 (1.94)	-	0.95 (0.95)	0.80 (0.98)	35.7 (36.9)
$(TBA)_9[P_2W_{17}O_{61}Zn(Br)]$	25.36 (26.65)	4.43 (5.03)	1.74 (1.94)	-	0.91 (0.95)	1.01 (1.01)	36.4 (36.9)
$K_{0.5}(TBA)_{7.5}[P_2W_{17}O_{61}Pd(H_2O)]$	21.20 (23.51)	4.09 (4.47)	1.58 (1.71)	0.26 (0.32)	1.11 (1.01)	1.48 (1.74)	31.4 (33.2)
$(TBA)_7[HP_2W_{17}O_{61}Cr(Br)]$	22.26 (22.44)	4.37 (4.25)	1.51 (1.64)	-	0.97 (1.03)	0.74 (0.87)	31.5 (31.8)
$(TBA)_7[HP_2W_{17}O_{61}Mn(Br)]$	22.28 (22.43)	3.97 (4.25)	1.55 (1.64)	-	1.01 (1.03)	0.84 (0.92)	30.5 (31.8)
$(TBA)_7[HP_2W_{17}O_{61}Fe(Br)]$	21.73 (22.43)	4.29 (4.25)	1.46 (1.63)	-	0.99 (1.03)	0.84 (0.93)	?31.8 (31.8)
$K(TBA)_6[P_2W_{17}O_{61}Ru(H_2O)]$	19.16 (19.96)	3.74 (3.80)	1.16 (1.45)	0.52 (0.68)	1.04 (1.07)	- [d]	27.6 (29.6)
$K(TBA)_5[P_2W_{17}O_{61}Ir(H_2O)]$	18.77 (17.08)	3.40 (3.26)	1.25 (1.25)	0.70 (0.70)	- [e]	2.83 (3.42)	25.6 (25.1)

[a] TBA = $[(n\text{-}C_4H_9)_4N]^+$.

[b] Calculated values in parentheses.

[c] Mass loss from 150 to 850°C.

[d] Ru could not be accurately analysed because of volatilization of RuO_4 under the hot acidic oxidizing conditions used to dissolve the sample.

[e] P could not be analysed because of interference from the presence of Ir.

Table S2. IR (1300-600 cm^{-1}) and ^{31}P nmr data (in CH_3CN) for compounds of the type $[^nBu_4N]_6[P_2W_{18}O_{62}]$, $[^nBu_4N]_9[P_2W_{17}O_{61}M(Br)]$ (where M^{n+} = Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}), $[^nBu_4N]_7[HP_2W_{17}O_{61}M(Br)]$ (where M^{n+} = Cr^{3+}, Mn^{3+} and Fe^{3+}) and $[K/^nBu_4N]_{10-n}[P_2W_{17}O_{61}M(H_2O)]$ (where M^{n+} = Pd^{2+}, Ru^{3+} and Ir^{4+})

Compound [a]	IR absorptions (cm^{-1}) [b]	^{31}P nmr (ppm) [c,d]
$(TBA)_6[P_2W_{18}O_{62}]$	1090(s), 1020(m), 986(m), 955(s), 914(s), 815(sh), 790(s,br)	-13.5
$(TBA)_9[P_2W_{17}O_{61}Co(Br)]$	1087(s), 1012(m), 955(sh), 944(s), 914(s), 888(sh), 822(sh), 797(s,br)	-28.1
$(TBA)_9[P_2W_{17}O_{61}Ni(Br)]$	1086(s), 1010(m), 958(sh), 944(s), 908(s), 886(sh), 818(sh), 778(s,br)	-13.2
$(TBA)_9[P_2W_{17}O_{61}Cu(Br)]$	1086(s), 1015(m), 953(sh), 943(s), 917(s), 885(s), 815(sh), 790(s,br)	-13.8
$(TBA)_9[P_2W_{17}O_{61}Zn(Br)]$	1086(s), 1013(m), 955(sh), 944(s), 913(s), 888(s), 820(sh), 795(s,br)	-8.2, -12.7
$K_{0.5}(TBA)_{7.5}[P_2W_{17}O_{61}Pd(H_2O)]$	1090(s), 1015(m), 965(sh), 955(s), 913(s), 899(s), 821(sh), 788(s,br)	-11.8
$(TBA)_7[HP_2W_{17}O_{61}Cr(Br)]$	1094(s), 1016(m), 951(s), 912(s), 893(s), 815(sh), 789(s,br)	-13.1
$(TBA)_7[HP_2W_{17}O_{61}Mn(Br)]$	1089(s), 1013(m), 950(s), 915(s), 890(sh), 825(sh), 786(s,br)	-12.5
$(TBA)_7[HP_2W_{17}O_{61}Fe(Br)]$	1089(s), 1012(m), 958(sh), 948(s), 913(s), 887(sh), 822(sh), 787(s,br)	-13.2
$K(TBA)_6[P_2W_{17}O_{61}Ru(H_2O)]$	1090(s), 1018(m), 966(sh), 955(s), 914(s), 897(sh), 821(sh), 790(s,br)	-11.8
$K(TBA)_5[P_2W_{17}O_{61}Ir(H_2O)]$	1090(s), 1018(m), 966(sh), 955(s), 914(s), 898(sh), 825(sh), 791(s,br)	-11.8

[a] TBA = $[(n\text{-}C_4H_9)_4N]^+$.

[b] s = strong, m = medium, br = broad, sh = shoulder.

[c] CH_3CN solution, referenced to 85% H_3PO_4.

[d] For the Co^{2+}, Ni^{2+}, Cu^{2+}, Pd^{2+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Ru^{3+} and Ir^{4+}-containing compounds only one ^{31}P resonance is observed as the other (the closer of the two phosphorus sites to the paramagnetic, substituted transition metal ion) collapses into the background as a result of fast relaxation.

Table S3. Oxidation of selected allylic alcohols by 30% aqueous H_2O_2 using transition metal-substituted Dawson-type phosphopolyoxotungstate catalysts [M = Pd(II), Zn(II) and Ir(IV)] and the sandwich-type $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ ion in biphasic 1,2-dichloroethane-acetonitrile/water at 30°C [a]

Anion	Substrate (% conversion)			
	3-methyl-2-buten-1-ol	*trans*-crotyl alcohol	geraniol	2-cyclo hexen-1-ol
$[P_2W_{17}O_{61}Pd(H_2O)]^{8-}$	>95	69	82	12 [b]
$[P_2W_{17}O_{61}Zn(Br)]^{9-}$	63	46	-	-
$[P_2W_{17}O_{61}Ir(H_2O)]^{6-}$	82	-	65	-
$[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$	>95	93	>95	-

[a] Reaction conditions: Reactions were carried out in 1:1 v/v 1,2-dichloroethane/acetonitrile (3 mL:3 mL) at 30°C for 6 hours using 10 mmol of allylic alcohol, 10 μmol of catalyst and 10 mmol of H_2O_2.

[b] Reaction product exclusively 2-cyclohexen-1-ol.

Table S4. ^{31}P nmr data on compounds of the type $[^nBu_4N]_6[P_2W_{18}O_{62}]$, $[^nBu_4N]_9[P_2W_{17}O_{61}M(Br)]$ (M^{n+} = Co^{2+}, Ni^{2+}, and Zn^{2+}), $[^nBu_4N]_7[HP_2W_{17}O_{61}M(Br)]$ (M^{n+} = Cr^{3+}, Mn^{3+} and Fe^{3+}) and $[K/^nBu_4N]_{10-n}[P_2W_{17}O_{61}M(H_2O)]$ (M^{n+} = Pd^{2+} and Ir^{4+}) before and after treatment with H_2O_2 for 6 hours at 30 or 35°C [a]

Anion	^{31}P nmr (ppm) (± 0.02 ppm)	
	1,2-DCE/butan-1-ol	1,2-DCE/butan-1-ol/H_2O_2
$[P_2W_{18}O_{62}]^{6-}$ [c]	-12.77	-12.76
$[P_2W_{17}O_{61}Co(Br)]^{9-}$ [b]	-25.24	-24.90
$[P_2W_{17}O_{61}Ni(Br)]^{9-}$ [b]	-13.86	-13.72
$[P_2W_{17}O_{61}Zn(Br)]^{9-}$ [b]	-13.51, -9.24	-13.27, -9.09
$[P_2W_{17}O_{61}Pd(H_2O)]^{8-}$ [b]	-12.78	-12.65
$[HP_2W_{17}O_{61}Cr(Br)]^{7-}$ [c]	-13.28	-13.06
$[HP_2W_{17}O_{61}Mn(Br)]^{7-}$ [c]	-12.49	-12.55
$[HP_2W_{17}O_{61}Fe(Br)]^{7-}$ [c]	-13.06	-13.20
$[P_2W_{17}O_{61}Ir(H_2O)]^{6-}$ [c]	-12.78	-12.61

[a] Reaction conditions: [catalyst] = 0.01 M in 1,2-dichloroethane/butan-1-ol (1,2-DCE = 1,2-dichlorobutane), with [butan-1-ol]:[catalyst] = 500:1 and (no. moles H_2O_2):(no. moles of catalyst) = 500:1.

[b] 30°C.

[c] 35°C.