

Oxidoperoxidotungsten(VI) Complexes with Secondary Hydroxamic Acids: Synthesis, Structure and Catalytic Uses in Highly Efficient, Selective and Ecologically Benign Oxidation of Olefins, Alcohols, Sulfides and Amines with H₂O₂ as a Terminal Oxidant

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The reaction of a solution of *freshly precipitated* WO₃ in H₂O₂ separately with the secondary hydroxamic acids *N*-benzoyl-*N*-phenylhydroxamic acid (BPHAH), *N*-benzoyl-*N*-*ortho*-tolylhydroxamic acid (BOTHAH), *N*-benzoyl-*N*-*meta*-tolylhydroxamic acid (BMTHAH), *N*-benzoyl-*N*-*para*-tolylhydroxamic acid (BPTH AH) and *N*-cinnamyl-*N*-phenylhydroxamic acid (CPHAH) afforded [WO(O₂)(BPHA)₂] (**1**), [WO(O₂)(BOTH A)₂] (**2**), [WO(O₂)(BMTH A)₂] (**3**), [WO(O₂)(BPTH A)₂] (**4**) and [WO(O₂)(CPHA)₂] (**5**), respectively. Aqueous tungstate solution, on reaction with all these hydroxamic acids, produced [W(O)₂(hydroxamato)₂] (**6**). The complexes show excellent catalytic functions in the oxidation of (a) ole-

fins at room temperature in the presence of NaHCO₃ as promoter, (b) alcohols, sulfides and amines, at reflux, with H₂O₂ as a terminal oxidant, yielding a high turnover number (TON), the highest being for olefin-to-epoxide conversion. An attempt to synthesize peroxide-rich complexes of the type PPh₄[WO(O₂)₂(hydroxamato)] (**7**), for example PPh₄[WO(O₂)₂BMTHA] (**7C**), resulted in the isolation of PPh₄[WO(O₂)₂(C₆H₅COO)] (**8**), which was probably obtained by the hydrolysis of coordinated BMTHA.

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Introduction

Tungsten and molybdenum oxides are potential heterogeneous catalyst in metal-oxide-catalyzed organic oxidation.^[1] Although the oxygen-transfer property of the MO₂²⁺ (M = Mo, W) core is often encountered in biology^[2–4] and several studies on oxygen-transfer modelling with M = Mo are well-known,^[5–8] the corresponding studies with M = W are relatively sparse. However, several metal complexes containing Mo,^[9] W,^[10] Mn,^[11] Fe^[12] and Re^[13] have so far been studied as olefin epoxidation catalysts. Reports of olefin epoxidation with oxido- and oxidoperoxidotungsten complexes as catalyst in the presence of H₂O₂ as terminal oxidant with moderate to high efficiency have appeared in the literature.^[14–17] Recently, we reported the synthesis and structure of oxidoperoxidomolybdenum and -tungsten(VI) complexes with the 8-quinolinol ligand, which coordinates to the MO(O₂)²⁺ and MO(O₂)₂ cores,^[18] and we have also examined the homogeneous catalytic

properties of these complexes in olefin epoxidation^[19,20] with H₂O₂ as oxidant and NaHCO₃ as an additive to obtain an uncommon conversion potential.

Reports of metal complexes in the catalytic oxidation of alcohols^[21] to aldehydes/ketones and carboxylic acids, sulfides to sulfoxides and sulfones,^[22] and amines to nitro, nitroso- and hydroxylamines have appeared in the literature.^[23] Jacobson et al.,^[24] along with many other authors,^[25–27] reported homogeneous oxidation of alcohols to carbonyl compounds with various transition-metal complexes, including those of Mo and W, as catalysts that operated with moderate efficiency. Heteropolytungstate(VI) systems were also used^[28–30] for the catalytic oxidation of alcohols, tertiary amines and sulfides. The Ishii group^[31] studied the oxidation of amines to nitro compounds with peroxidotungstatophosphate as catalyst and H₂O₂ as oxidant. We reported the synthesis and structural characterization of Mo- and W-based catalysts for the highly efficient catalytic oxidation^[18,32] of alcohols, sulfides and amines with H₂O₂ as oxidant.

We had pointed out that, in olefin → epoxide conversion, oxidodiperoxidomolybdenum and -tungsten complexes battle for superior catalytic efficiency. In some cases the W complexes exhibited better catalytic efficiency than those of Mo, while the reverse occurred in other cases. This is con-

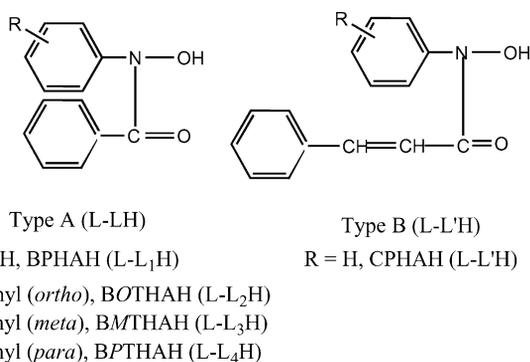
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trary to the earlier concept^[9b] that tungsten complexes are superior to molybdenum complexes when H₂O₂ is used as an oxidant.

In order to study the comparative catalytic potentialities of the peroxido complexes of Mo and W, we report here the synthesis, crystal structure and catalytic activity of a series of oxidoperoxidotungsten(VI) complexes with secondary hydroxamic acids as ligands (L-LH as type A and L-L'H as type B ligands; see Scheme 1) in the epoxidation of olefins at room temperature with NaHCO₃ as cocatalyst and H₂O₂ as terminal oxidant. The three other ligands (L-L₂, L-L₃ and L-L₄) in this work have been derived from the parent BPHAH (L-L₁) ligand by introducing methyl groups in the *o*-, *m*- and *p*-positions respectively. The type B ligand, L-L'H, is chosen in order to create a situation in which some strategic non-hydrogen atoms of the ligand molecule (L-L') will be rigid and hence structurally frozen after complexation, since the benzenoid π system is further coupled with a π residue, namely, the -CH=CH-C=O fragment of the cinnamyl function attached to the metal ion. The isolated complexes have the following compositions:



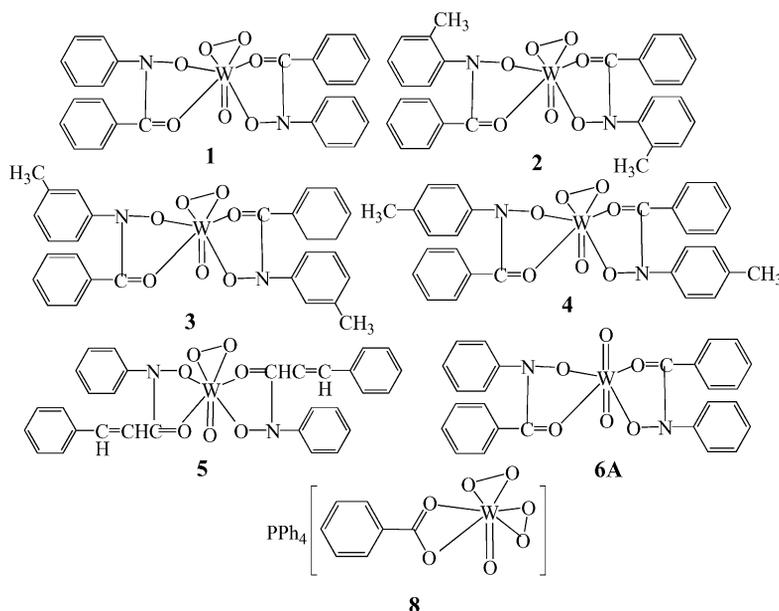
Scheme 1. Structural formulae, the abbreviated notation and the numbering sequence of the ligands.

[WO(O₂)(BPHA)₂] (1), [WO(O₂)(BOTH A)₂] (2), [WO(O₂)(BMTHA)₂] (3), [WO(O₂)(BPTH A)₂] (4), [WO(O₂)(CPHA)₂] (5), [W(O₂)₂(BPHA)₂] (6A) and PPh₄[WO(O₂)₂(C₆H₅COO)] (8). Compounds 1, 2, 3 and 5 have been structurally characterized (see formula drawings in Scheme 2). The specialty of the present series of complexes lies in their selective and very much superior epoxidation of olefins at room temperature with high TOF (TON h⁻¹).

Results and Discussion

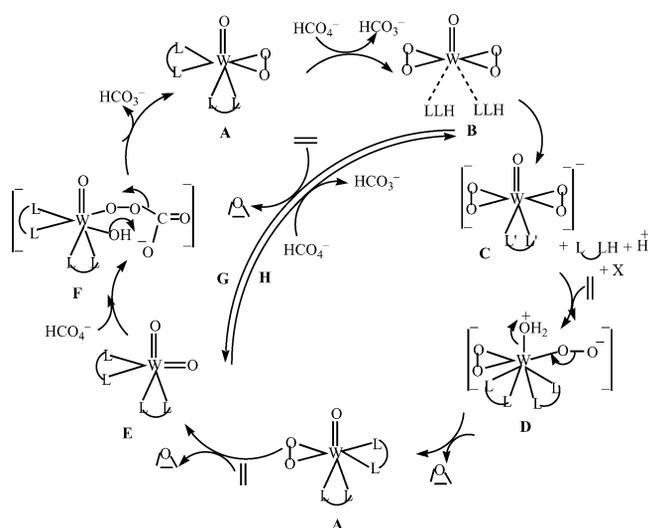
Synthetic Aspects

Complexes 1–4 and 5 can easily be synthesized with high yield by treating a H₂O₂ solution of H₂WO₄ with the appropriate hydroxamic acid. When an excess of H₂O₂ was added to an acetonitrile solution of 3, an anionic diperoxido compound precipitated with a counter cation (PPh₄⁺) added as PPh₄Cl. We expected that the compound would be PPh₄[WO(O₂)₂(hydroxamato)] (7), but actually it was PPh₄[WO(O₂)₂(C₆H₅COO)] (8), as attested by comparison of IR and NMR spectra with those of the analogous Mo complex, which we had structurally characterized earlier.^[35b] Compound 8 is formed by the hydrolysis of 7, an inference drawn from the isolation and structural characterization of PPh₄[WO(O₂)₂(QO)]^[18] whose ease of isolation and crystallization is a result of the compactness of the ligand QO⁻ (8-quinolinolate) relative to that of the hydroxamato ligand. The monooxidomonoperoxido complexes [WO(O₂)(hydroxamato)₂] (1–4 and 5) stoichiometrically oxidize all the olefins, alcohols, sulfides and amines used in this work, themselves being converted into the corresponding dioxido complexes [W(O₂)₂(hydroxamato)₂] (6). All complexes 1–6, however, act as catalyst precursors in the presence of H₂O₂ when the stoichiometrically passive behaviour

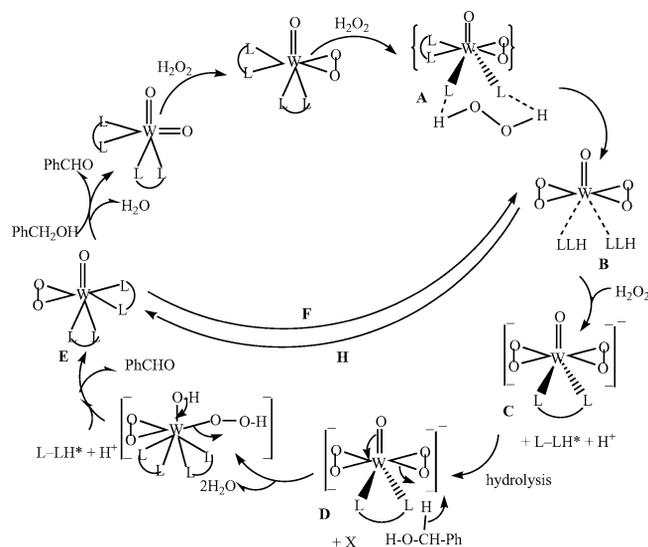


Scheme 2. Molecular formulae of the synthesized complexes.

of **6** is overcome by the in situ generation of the corresponding oxidoperoxido or oxidodiperoxido complexes in the presence of lower or higher amounts of H_2O_2 , respectively. In view of the above discussion, we predicted a course of reaction, which is shown in Scheme 3 and Scheme 4 [for detailed chemical reactions (both stoichiometric and catalytic) see Supporting Information].



Scheme 3. Plausible mechanism of catalytic oxidation of olefins to epoxides with H_2O_2 as an oxidant and NaHCO_3 as cocatalyst. A: catalyst, L-L: hydroxamic acid, B: oxidodiperoxido adduct, C: oxidodiperoxidotungsten complex, L'-L': benzoate, X = $\text{C}_6\text{H}_5\text{NHOH}$, D: intermediate state, E: dioxido complex, F: intermediate state, G: shunt pathway when $[\text{H}_2\text{O}_2]$ in the reaction mixture is in moderate excess, H: shunt pathway when $[\text{H}_2\text{O}_2]$ in the reaction mixture is in large excess.



Scheme 4. Plausible mechanism of catalytic oxidation of benzyl alcohol to benzaldehyde by using H_2O_2 as oxidant. A: intermediate, L-L: hydroxamic acid, B: oxidodiperoxido adduct, C: isolated oxidodiperoxidotungsten complex, D: oxidodiperoxidotungsten complex, L'-L': benzoate, X = $\text{C}_6\text{H}_5\text{NHOH}$, E: catalyst, F: shunt pathway when $[\text{H}_2\text{O}_2]$ in the reaction mixture is sufficient, G: pathway when $[\text{H}_2\text{O}_2]$ in the reaction mixture is insufficient.

Infrared and Electronic Spectroscopy

All compounds are nonelectrolytes and are diamagnetic. The oxidoperoxidometal moieties are characterized by $\nu(\text{W}=\text{O})$ and $\nu(\text{O}-\text{O})$ vibrations (see Supporting Information) at spectral regions appropriate for the respective terminal ligands.^[33] The $\nu(\text{W}=\text{O})$ vibrations of all the complexes (**1–5**) appear around 960 cm^{-1} . The complexes, with the exception of **3**, show $\nu(\text{O}-\text{O})$ bands at 880 cm^{-1} ; complex **3** has this band at 895 cm^{-1} . The $\nu(\text{C}=\text{O})$ vibrations of uncoordinated BPAH, BOTHAH, BMTHAH and BPTAH appear at 1640 , 1640 , 1610 and 1630 cm^{-1} , respectively. The downward shift of these vibrations after complexation occurs to 1550 , 1550 , 1540 and 1550 cm^{-1} , respectively. This indicates that the bonding through the C=O oxygen in the *m*-tolyl system is the weakest. Sterically, the *ortho* complex should have the weakest bond, but perhaps a combination of both steric and electronic (hyperconjugation) effects is responsible for these results. The appearance of several vibrations in the low-wavenumber region suggests that the asymmetric $\nu(\text{O}-\text{O})$ from the WO_2 triangle, $\nu(\text{W}-\text{O})$, where O comes from C=O, and $\nu(\text{W}-\text{O})$, where O is bound to N, occur there (see Experimental Section). The IR spectra of the type B ligand, CPHAH, and its metal complexes deserve special attention. Uncoordinated L-L' (in **5**) shows a sharp and strong band at 1640 cm^{-1} , which remains unchanged upon coordination. L-L' also contains two strong (stronger than the 1640 cm^{-1} band) vibrations at 1590 and 1580 cm^{-1} , indicating that the aliphatic C=C moiety is in conjugation with the aromatic ring as well as with the C=O function, forming a skeleton like $\{\text{Ph}-\text{C}=\text{C}-\text{C}=\text{O}\}$, and it will perhaps be quite correct to assign the 1640-cm^{-1} band in CPHAH to the aliphatic $\nu(\text{C}=\text{C})$ vibration and the latter two bands to the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C}; \text{aromatic})$ vibrations, respectively. In **5**, the $\nu(\text{C}=\text{C})$ vibrations of aliphatic and aromatic groups remain unchanged, but the $\nu(\text{C}=\text{O})$ vibration is redshifted and appears near 1540 cm^{-1} . The position of $\nu(\text{C}=\text{C})$ (aliphatic) vibrations indicates that the aliphatic CH hydrogen atoms are in a *trans* configuration with respect to each other.^[34]

The electronic spectra of the ligands and their metal complexes do not differ *much* in position, profile and intensity. In free hydroxamic acids, three UV bands appear at $\lambda \approx 255\text{ nm}$ ($\pi \rightarrow \pi^*$ of the aromatic ring), one at 270 nm ($\pi \rightarrow \pi^*$ of C=O) and another at 330 nm ($n \rightarrow \pi^*$ of the C=O chromophore). Gaussian analysis indicates that the intensity of the $\pi \rightarrow \pi^*$ band is quite high (ca. $15000\text{ M}^{-1}\text{ cm}^{-1}$) and that of the $n \rightarrow \pi^*$ band is $300\text{ M}^{-1}\text{ cm}^{-1}$, so the molar absorption decreases in the right direction.

Molecular Structure

The crystal data for complexes **1–3** and **5** are given in Table 1, and selected bond lengths for the complexes are listed in Table 2.

Table 1. Crystal data for complexes **1–3** and **5**.

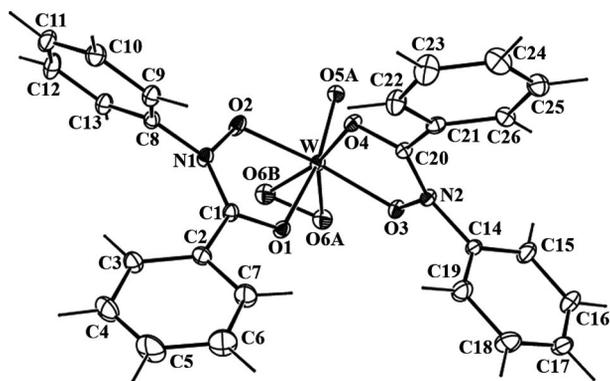
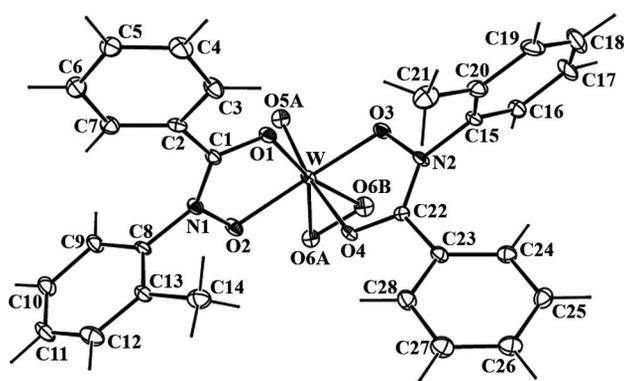
	Complex 1	Complex 2	Complex 3	Complex 5
Empirical formula	C ₂₆ H ₂₀ N ₂ O ₇ W	C ₂₈ H ₂₄ N ₂ O ₇ W	C ₂₈ H ₂₄ N ₂ O ₇ W	C ₆₀ H ₄₈ N ₄ O ₁₄ W ₂
Formula weight	656.29	684.34	684.34	1416.72
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Cell parameters:				
<i>a</i> [Å]	25.311(4)	12.953(4)	10.522(1)	12.928(3)
<i>b</i> [Å]	8.793(1)	15.004(8)	16.686(2)	15.181(4)
<i>c</i> [Å]	22.826(3)	13.902(4)	15.251(2)	15.109(3)
β [°]	102.05(1)	90.35(3)	97.55(1)	109.14(1)
Volume [Å ³]	4968.2(12)	2701.8(18)	2654.7(6)	2801.4(11)
Space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁</i>
<i>Z</i>	8	4	4	2
$\rho_{\text{calcd.}}/\rho_{\text{obs.}}$ [g cm ⁻³]	1.755/1.740	1.682/1.660	1.712/1.730	1.680/1.690
<i>F</i> (000)	2560	1344	1344	1392
μ (Mo- <i>Kα</i>) [mm ⁻¹]	4.698	4.324	4.400	4.173
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal size [mm]	0.46 × 0.34 × 0.25	0.52 × 0.28 × 0.26	0.56 × 0.44 × 0.28	0.48 × 0.38 × 0.24
2 θ range [°]	1.8–25.0	2.0–25.0	1.8–25.0	1.4–26.0
<i>T</i> _{min} , <i>T</i> _{max}	0.168, 0.309	0.167, 0.325	0.136, 0.292	0.197, 0.367
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	4350	4007	4646	10905
Unique reflections	3846	3231	3473	8963
<i>R</i> ₁ , <i>wR</i> ₂	0.0340, 0.082	0.0559, 0.1315	0.041, 0.098	0.0479, 0.0996
Goodness-of-fit (<i>S</i>)	1.059	1.086	1.022	1.058
$\Delta\rho$ [e Å ⁻³], max, min	1.743, -1.072	2.088, -3.265	1.169, -0.973	1.342, -0.438

Table 2. Selected metal–oxygen_(ligand) bond lengths for different complexes.

	1	2	3	5
W–O5A	1.751(7)	1.756(2)	1.691(2)	Molecule 1
W–O6A	1.887(9)	1.864(2)	1.830(2)	Molecule 2
W–O6B	1.870(8)	1.841(2)	1.880(1)	W1–O11(21)
W–O1	2.155(4)	2.132(7)	2.165(5)	W1–O12(22)
W–O2	2.017(4)	2.016(7)	1.997(6)	W1–O13(23)
W–O3	2.001(4)	2.005(7)	2.004(6)	W1–O14(24)
W–O4	2.134(4)	2.134(7)	2.161(5)	W1–O15(25)
				1.732(7)
				1.889(7)
				1.707(2)
				2.175(6)
				2.048(9)
				1.704(7)
				1.823(11)
				1.913(6)
				2.147(6)
				2.001(8)

The molecular views of **1**, **2** and **3** containing the discrete monomeric unit [WO(O₂)(L)₂], L = BPHA for **1**, BOTHA for **2** and BMTHA for **3**, are shown in Figure 1, Figure 2, and Figure 3, respectively. In all complexes, the tungsten atom is bonded to one oxido, one bidentate peroxido and two bidentate BPHA (in **1**), BOTHA (in **2**) or BMTHA (in **3**) ligands. The oxido and peroxido ligands in all three complexes are disordered and have been modelled with

fractional occupancies. The refined occupancy factors for the two disordered oxido and peroxido sites are 0.66(1), 0.34(1) for complex **1**, 0.54(2), 0.46(2) for complex **2** and 0.51(2), 0.49(2) for complex **3**, respectively. The coordination geometry around the tungsten atom in the complexes can be best described as distorted pentagonal bipyramidal; the axial sites of the major fractions are occupied by the oxido (O5) and one phenolato oxygen (O1) atom. Other

Figure 1. Molecular structure of [WO(O₂)(BPHA)₂] (**1**) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.Figure 2. Molecular structure of [WO(O₂)(BOTHA)₂] (**2**) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

phenolato oxygen atoms (O2, O3 and O4) and two peroxido oxygen atoms (O6A and O6B) define the equatorial plane. The W–O_(CO) bond lengths [2.134(4), 2.155(4) Å in **1**, 2.132(7), 2.134(7) Å in **2**, 2.161(5), 2.165(5) Å in **3**] and W–O_(NO) bond lengths [2.001(4), 2.017(4) Å in **1**; 2.005(7), 2.016(7) Å in **2**; 1.947(6), 2.004(6) Å in **3**] in these compounds are comparable to the corresponding values reported for similar structures. The W–O bond lengths involving oxide/peroxide groups [1.751(7)–1.887(9) Å in **1**, 1.756(2)–1.864(2) Å in **2**, 1.691(2)–1.880(1) Å in **3**] appear to have been affected by the disorder.

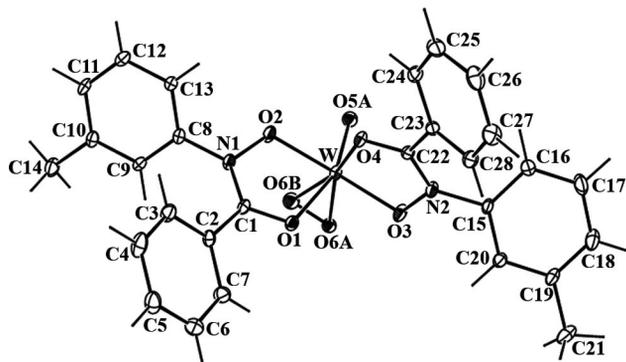


Figure 3. Molecular structure of [WO(O₂)(BMTHA)₂] (**3**) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

The asymmetric unit of complex **5** contains two molecules of [WO(O₂)(CPHA)₂] (Figure 4), which are related by pseudo inversion symmetry about (0.25, 0.50, 0.75). The geometrical parameters of the two molecules (1 and 2) in **5** are comparable and agree well with those reported for other oxidoperoxidotungsten(VI) complexes.^[35] Unlike complexes **1–3**, the structure of **5** is not affected by any disorder. The coordination geometry around the metal centres in **5** can be described as pentagonal bipyramidal. The oxido ligands (O11, O21) and the carbonyl oxygen atoms (O14, O24) occupy the axial sites; the remaining five oxygen atoms (O12,

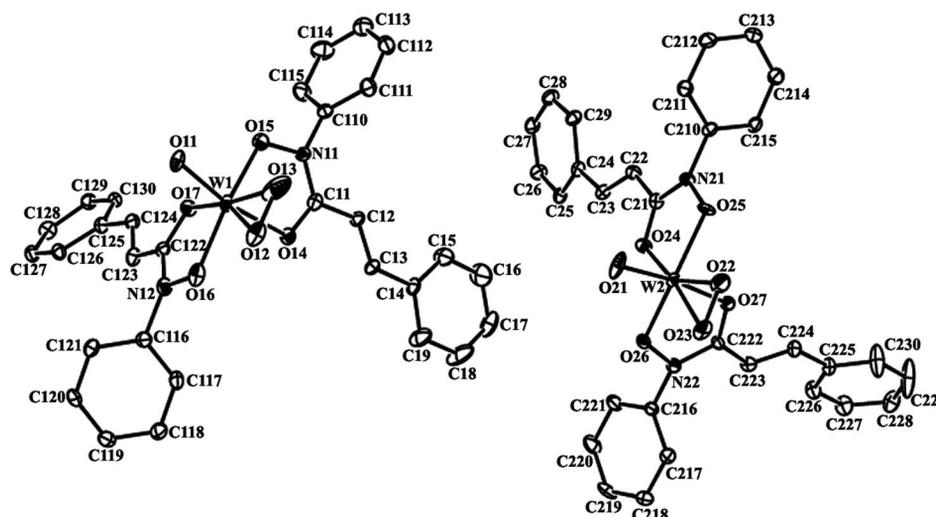


Figure 4. Structures of the two independent molecules, 1 and 2, of [WO(O₂)(CPHA)₂] (**5**) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

O13, O15–O17; O22, O23, O25–O27) define the equatorial planes. In each molecule in **5**, the two WO₂CN rings are almost orthogonal to each other; the dihedral angles between the least-squares planes through the chelate ring atoms in molecule 1 and 2 are 89.2(5) and 88.2(5)°, respectively. As observed in complexes **1–3**, the W–O_(carbonyl) bond lengths [2.121(6)–2.176(6) Å] in **5** are significantly longer than W–O_(hydroxamate) bond lengths [1.964(13)–2.047(9) Å] (Table 2).

The molecular packing in complexes **1–3** and **5** is influenced by intermolecular C–H···O hydrogen bonds, which link the molecules to form an infinite one-dimensional chain.

NMR Spectroscopy

The interesting aspects of the molecular structure in complexes **2**, **4** and **6A** are nicely displayed by ¹H and ¹³C NMR spectra (for complete listings see Experimental Section). There are two signals for each C of C=O in compounds **2**, **4** and **6A**.

Each one of the complexes, **1**, **3**, **4**, **5** and **6A** has only one sharp signal in its ¹⁸³W NMR spectrum in CD₂Cl₂. The chemical shifts observed ($\delta = -313.90, -313.74, -313.77, -315.61$ and 85.78 ppm for complexes **1**, **3**, **4**, **5** and **6A**, respectively, relative to the external reference Na₂WO₄) are characteristic of peroxido (negative values) and oxido (positive value) complexes with a WO⁴⁺ centre. As the peroxide group is a better σ donor than the oxide group, the metal nuclei are more shielded in peroxido complexes relative to those in oxido complexes containing the same ligands.^[36,37] Nakajima et al.^[38] reported that in their mono- and diperoxidotungstate complexes, WO₃(O₂)²⁻ and WO₂(O₂)₂²⁻, the ¹⁸³W signals appeared at -300 and -392 ppm, respectively, as opposed to -314 to -316 ppm observed by us. This slight difference can be attributed to the presence of a higher number of oxide groups and both oxide and peroxide groups, respectively in the complexes

investigated by Nakajima et al. Exhibition of extended conjugation due to the presence of the cinnamyl group makes the W nucleus in complex **5** a little bit more shielded, resulting in its slightly upfield signal relative to other perox-

ido complexes. Ramos et al.^[39] studied a series of tungsten complexes with WO_2^{2+} centres (but no O_2^{2-} groups): ^{183}W NMR signals appeared in the range 41–58 ppm, which is in close agreement with our observations for compound **6A**.

Table 3. Details of the catalytic epoxidation of olefins.

$$\text{Olefin} \xrightarrow[3-4 \text{ equiv. H}_2\text{O}_2, 25 \text{ mol-\% NaHCO}_3, \text{ r.t. (25 }^\circ\text{C), CH}_3\text{CN}]{0.1-0.0067 \text{ mol-\% [WO(O}_2\text{) (CPHA)}_2\text{] (5)}} \text{Epoxide}$$

Entry	Substrate	Product	Time	Conversion [%] ^[a]	Yield [%] GC ^[b] Isolated	Yield [%] ^[c]	Selectivity [%] ^[d]	TON ^[e] (TOF) ^[f]
1			20 min	96	96	—	30	100 14400(43200) ^[g]
2			30 min	72	72	65	35	100 7200 (14400) ^[g]
3			1 h	86	86	—	24	100 4300 (4300)
4			2.2 h	74	74	—	23	100 3700 (1682)
5			1 h	75	75	68	27	100 1500 (1500)
6			15 min	94	94	89	26	100 9400 (37600) ^[g]
7			3 h	86	83	—	59	98 4150 (1383)
8			2 h	84	84	—	44	100 4200 (2100)
9			1.25 h	98	98	—	36	100 4950 (3960)
10			1 h	96	96	—	35	100 4800 (4800)
11			1.5 h	93	93	—	37	100 4650 (3100)
12			45 min	94	94	86	51	100 4700 (6265) ^[g]
13			1.5 h	92	92	—	47	100 4600 (3066)
[h]14			1.25 h	96	96	—	26	100 4800 (3840)
[h]15			2.5 h	92	92	—	42	100 4600 (1840)
[h]16			1.5 h	96	96	—	25	100 1920 (1280)
[h]17			1.25 h	90	90	81	25	100 1800 (1440)
[h]18			2 h	97	97	—	26	100 1940 (970)
[h]19			2.5 h	95	95	94	17	100 950 (380)

[a] A control experiment (omission of **2** as well as HCO_3^-) does not show any conversion to epoxide or other probable products. The mol ratio of catalyst/substrate was 1:15000 (for entry 1), 10000 (for entries 2 and 6), 5000 (for entries 3, 4 and 7–15), 2000 (for entries 5, 16, 17 and 18) and 1000 (for entry 19). For entries 16, 17, 18 and 19, acetonitrile and acetone solvent mixtures were used in a 2:1 volume ratio. [b] The detailed calculation of GC yield is given in the Supporting Information. [c] This is the yield of control experiment, excluding catalyst **2** only, but not NaHCO_3 , which remains in the reaction solution at the same 25 mol-% concentration. When the control experiment uses NaHCO_3 at a catalytic concentration, the conversion and yield become negligible. [d] Selectivity is really spectacular in the given time frame. If the stirring is continued for still longer periods, entries 5, 7, 8 and 9 start showing a peak due perhaps to the formation of diols. [e] TON: ratio of mol of product (here epoxide) obtained to the mol of catalyst used. [f] The corresponding TOFs (TON h^{-1}) are shown in parentheses. [g] Extrapolated values. [h] A temperature that is slightly above room temp. (30°C) was used for these substrates.

Catalytic Properties of the Complexes

The complexes show prolific catalytic activity in the hydrogen peroxide oxidation of various olefins, alcohols, sulfides and amines to their corresponding epoxides, aldehydes or ketones, sulfoxides and sulfones and nitro compounds, respectively. The details of catalytic activity with respect to epoxidation of olefins with complex **5** as a catalyst are recorded in Table 3. Table 4 includes details for the oxidation of alcohols, sulfides and amines with complexes **3** and **5**

as catalysts, for the sake of comparison. The comparative efficiency of all the seven catalysts **1–5**, **6A** and **8**, towards epoxidation of cyclohexene and styrene is shown in Table 5. A similar efficiency comparison in the case of alcohol oxidation (using benzyl alcohol and 2-octanol as representative substrates) is presented in Table 6. The efficiency of catalysts **1–4** towards all the substrates is *almost* the same, which indicates that the electron-repelling methyl substituent has very little effect on the catalytic process, since this

Table 4. Details of the catalytic oxidation of functionalized organic compounds in refluxing^[a] acetonitrile^[b,c] with^[d] **5** or **3** as catalyst^[e] and H₂O₂^[f] as oxidant.

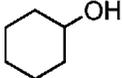
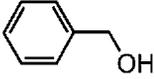
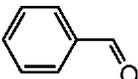
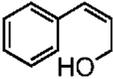
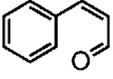
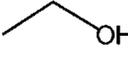
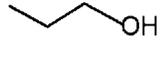
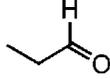
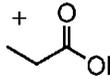
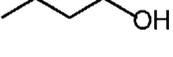
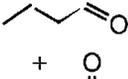
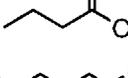
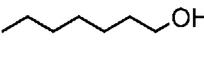
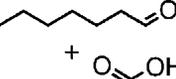
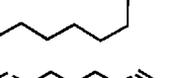
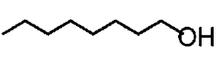
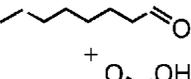
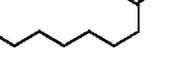
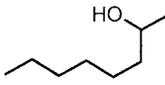
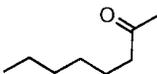
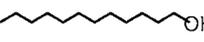
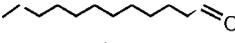
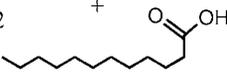
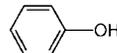
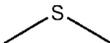
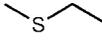
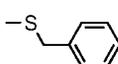
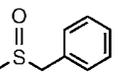
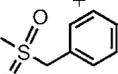
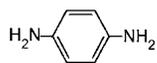
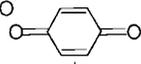
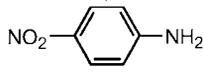
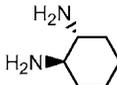
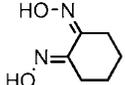
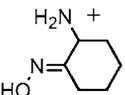
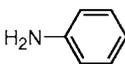
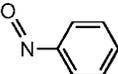
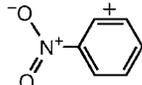
Entry	Substrate ^[g]	Time [h]	Product	Yield [%] ^[h]		Turnover number ^[i]	
				5	3	5 (TON)	3
1		17		94 (83)	89	940	890
2		15		95 (86)	91	950	910
3		14		92 (84)	88	920	880
4	CH ₃ OH	13	HCHO	51	50	510	500
			+ HCOOH	36	33	360	330
5		13		55	52	550	520
			+ 	30	28	300	280
6		12		64 (58)	62	640	620
			+ 	23 (19)	22	230	220
7		11		94	88	940	880
8		14		67	64	670	640
			+ 	23	22	230	220
9		17		72	67	720	670
			+ 	17	17	170	170
10		18		78	74	780	740
			+ 	9	9	90	90

Table 4. (Continued).

Entry	Substrate ^[g]	Time [h]	Product	Yield [%] ^[h]		Turnover number ^[i] (TON)	
				5	3	5	3
11		20		89	84	890	840
12		22		82	78	820	780
				1	1	10	10
13		12		91(86)	87	910	870
14		1		6 (4)	10	60	100
				94 (89)	90	940	900
15		1		30	35	300	350
				70	65	700	650
16		1		60	58	600	580
				35	32	350	320
17		6		66 (63)	63	660	630
				28 (25)	27	280	270
18		10		67	63	670	630
				31	30	310	300
19		7		84	80	840	800
				16	17	160	170

[a] Reflux at 78 °C (in acetonitrile) or 40 °C (in dichloromethane). [b] 10 mL. [c] For entries 14–16, 15 mL dichloromethane was used as solvent. [d] Blank experiments were performed, i.e. only the catalyst was excluded from the reaction mixture while all other parameters remained the same: oxidation for entries 1–3 and 8–12 was found to be negligible, but ca. 8% oxidation was observed for 4 and 5, 4% for 6 and 7, 5% for 13 and 17, 10% for 14–16 and 3% for 18 and 19 (when 100% oxidation was obtained by using catalyst). [e] 0.025 mmol. [f] Total amount used: 35–205 mmol; 35 mmol (entries 14–16), 70 mmol (entries 17 and 19), 109 mmol (entries 4–7, 13, 18), 157 mmol (entries 1–3, 8–10) and 205 mmol (entries 11 and 12) mmol. [g] 25 mmol. [h] Based on substrate concentration. [i] Turnover number (TON) is defined as the ratio of the number of moles of product obtained to the number of moles of catalyst used. Results in parentheses show the isolated yield. In case of ethanol (entry 5) oxidation, some ester is formed along with the aldehyde and acid.

is a resultant effect of steric vs. electronic interactions on the substrates. However, as the yield and TON suggest, (which here act in the opposite direction) of these catalysts complexes **5** and **8** are superior to **1** and **4** as catalysts; be-

Table 5. Comparative catalytic efficiency of all the catalysts (entries 1–7) in the oxidation of some representative olefins keeping all the parameters same as in Table 3.

Entry	Catalyst	Oxidation of cyclohexene ($t = 1$ h)		Oxidation of styrene ($t = 2.5$ h)	
		Yield [%]	TON	Yield [%]	TON
1	[W(O)(O ₂)(BPHA) ₂] (1)	76	3800	65	2600
2	[W(O)(O ₂)(BOTH A) ₂] (2)	80	4000	67	2680
3	[W(O)(O ₂)(BMTH A) ₂] (3)	82	4100	69	2760
4	[W(O)(O ₂)(BPTH A) ₂] (4)	78	3900	64	2560
5	[W(O)(O ₂)(CPHA) ₂] (5)	86	4300	72	2880
6	[W(O) ₂ (BPHA) ₂] (6A)	74	3700	63	2520
7	PPh ₄ [W(O)(O ₂) ₂ (PhCOO)] (8)	89	4450	74	2960

Table 6. Comparative catalytic efficiency of the catalysts in the oxidation of some representative functionalized organic compounds in refluxing^[a] acetonitrile^[b] with H₂O₂^[c] as oxidant.

Entry	Catalyst ^[d]	Substrate ^[e]	Product	Time	Conversion [%]	Yield ^[f] [%]	Selectivity [%]	TON ^[g]
1	[WO(O ₂)(BPHA) ₂] 1			15 h	86	86	100	860
2	[WO(O ₂)(BOTH A) ₂] 2	"	"	"	89	89	100	890
3	[WO(O ₂)(BMTH A) ₂] 3	"	"	"	91	91	100	910
4	[WO(O ₂)(BPTH A) ₂] 4	"	"	"	88	88	100	880
5	[WO(O ₂)(CPHA) ₂] 5	"	"	"	95	95	100	950
6	[WO ₂ (BPHA) ₂] 6A	"	"	"	81	81	100	810
7	[PPh ₄][WO(O ₂) ₂ (PhCOO)] 8	"	"	"	99	99	100	990
8	[WO(O ₂)(BPHA) ₂] 1			20 h	80	80	100	800
9	[WO(O ₂)(BOTH A) ₂] 2	"	"	"	82	82	100	820
10	[WO(O ₂)(BMTH A) ₂] 3	"	"	"	84	84	100	840
11	[WO(O ₂)(BPTH A) ₂] 4	"	"	"	81	81	100	810
12	[WO(O ₂)(CPHA) ₂] 5	"	"	"	89	89	100	890
13	[WO ₂ (BPHA) ₂] 6A	"	"	"	76	76	100	760
14	[PPh ₄][WO(O ₂) ₂ (PhCOO)] 8	"	"	"	94	94	100	940

[a] Reflux at 78 °C. [b] 10 mL. [c] 100 mmol. [d] 0.025 mmol. [e] 25 mmol. [f] Based on concentration. [g] Turnover number is defined as the ratio of the number of moles of product obtained to the number of moles of catalyst used.

tween **5** and **8**, complex **8** possesses a bit higher efficiency than **5**, since **8** contains two peroxido groups and **5** contains one. In case of **5**, this increase in efficiency may be due to an extended conjugation of the aromatic ring with the planar

Table 7. Efficiency of the catalyst **5** for different amounts of H₂O₂ as oxidant keeping all other parameters the same as those in Table 3.

Equiv. of H ₂ O ₂ used (with respect to substrate)	Oxidation of cyclohexene (<i>t</i> = 1 h)		Oxidation of styrene (<i>t</i> = 2.5 h)	
	Yield [%]	TON	Yield [%]	TON
1	61	3050	39	1560
2	75	3750	59	2360
3	86	4300	72	2880
4	92	4600	80	3200
5	95	4750	83	3320

aliphatic residue $-C=C-C=O$, which implies that the low-lying and delocalized empty antibonding orbital in the catalyst makes the oxidation reactions more facile. The efficiency of catalyst **5** with different amounts of H₂O₂ in olefin oxidation has also been studied (Table 7), and the results indicate that 3–4 equiv. H₂O₂ is suitable for an effective epoxidation process.

Probable Reaction Pathways

We have noted that **1–4** and **5** are capable of accomplishing stoichiometric oxidation by transferring one of the peroxido oxygen atoms to the substrates. Those peroxido compounds can function as catalyst precursors and, in the presence of H₂O₂, catalyze the oxidation of the substrate with good yield and TON. Similarly [WO₂(hydroxamato)₂] (**6**) also can be regarded as a catalyst precursor in the presence of a considerable amount of H₂O₂, whereby **1–4** and **5** are generated in situ and react with the available H₂O₂ to form the active catalyst.

Catalytic

When H₂O₂ is used as a sole oxidant the catalytic efficiency is rather poor, but when NaHCO₃ is added as an additive (a cocatalyst) the efficiency of the system becomes enormous. The key aspect^[40,41] of such a reaction is that H₂O₂ and hydrogen carbonate react in an equilibrium process to produce peroxydicarbonate, HCO₄⁻, which is a more reactive nucleophile than H₂O₂ and speeds up the epoxidation reaction. Though WO(O₂)₂·2BMTHAH (also true for BPHAH, BOTHAH, BPTHAH) is not isolable in the present case, it was noted earlier^[42] that the corresponding product with QOH as ligand, namely, WO(O₂)₂·2QOH, was not only isolated, but the attempted crystallization of the QOH adduct afforded the less reactive monoperoxido complex, [WO(O₂)(QO)₂]. So, it may be safely presumed that the diperoxido adduct behaves as the active catalyst,^[42] and the monooxidomonoperoxido complex [WO(O₂)(hydroxamato)](**1–5**) as the catalyst precursor in the presence of a moderate excess of H₂O₂. However, in the presence of a large excess of H₂O₂, we suggest that **7C** or **8** become the active catalyst and the diperoxido adduct is the catalyst precursor. Hence, considering all the experimental results, observations and logical inferences, we find it appropriate to frame Scheme 3 and Scheme 4 to highlight the reaction route of catalytic oxidation of olefins and alcohols to the respective epoxides and carbonyl compounds in the pres-

ence of moderate to large excesses of H₂O₂ as well as at conditions of nearly spent up H₂O₂. Interestingly, as shown in Scheme 3 and Scheme 4, the original catalyst becomes isolable in spite of the hydrolysis of the anionic complex, indicating that **8** functions as a surrogate for **7**. It may be important to emphasize that all the vitally important starting materials specified in Scheme 3 are structurally characterized. Hence the catalytic cycles drawn have solid foundations.

Scheme 4 can be applied to sulfide → sulfoxide → sulfone, amine → nitro conversions by substituting the alcohol with these substrates. It may also be noted that the use of the HCO₃⁻ → HCO₄⁻ conversion for olefin → epoxide and the H₂O₂ → H₂O conversion for other substrates occur two times, because the scheme covers two reaction conditions: (1) minimal usage of H₂O₂ (2) use of the maximum amount of H₂O₂.

This catalytic system of epoxidation comprising oxidoperoxidotungsten catalysts in presence of NaHCO₃ as promoter and H₂O₂ as terminal oxidant is better than other known catalytic systems with tungsten in terms of yield, TON, TOF, selectivity, temperature and cost-effective reaction conditions. The method^[17] involving Na₂WO₄ as catalyst in chlorinated or aromatic solvents required high temperature reflux, and the yield, selectivity and TON were less than those observed in our system. The solvent-free system^[12b] consisting of Na₂WO₄ as catalyst required stirring at high temperature, and the yield and selectivity were good, but the TON was much less than ours. In heteropolytungstate-catalyzed epoxidations,^[43,44] the time of the reaction was too long, the selectivity and TON were lower, but the H₂O₂ economy was better in comparison to our results. The apparently better TON reported by Nishiyama et al.^[43] in the case of cyclooctene (7200 vs. 10000) is due to the involvement of 10 W centres, as opposed to 1, per mol of the catalyst in our case. Moreover, our catalyst can accomplish the conversion at a much shorter time than that required by their heteropolytungstate. In our case, the selectivity is also much better.

The catalytic oxidation of alcohols, sulfides and amines in the given conditions showed good efficiency in terms of yield, TON, selectivity, temperature and cost-effective reaction conditions. Alcohol and sulfide oxidation with other oxido- or oxidoperoxidotungsten catalysts^[24–27] was less efficient than our system in terms of yield and TON. In heteropolytungstate-catalyzed alcohol and amine oxidations,^[28–30] the yield, TON and selectivity are much lower than our results.

Conclusions

The catalysts described in this paper are used in the epoxidation of olefins, and oxidation of alcohols, sulfides and amines to their respective oxidation products and are very efficient in terms of catalyst economy, selectivity, yield, TON, TOF, greenness and cost-effectiveness. These catalysts can also be recovered easily once the reaction is completed and can be used for subsequent reactions, although a loss of efficiency is observed, as the catalyst gets deactivated. Heterogenization of these homogeneous catalysts in mesoporous materials or polymers in high concentrations would be important from the commercial standpoint, and we will report such a study very soon.

Experimental Section

Physical Measurements: The IR spectra were recorded by using KBr pellets with a Perkin–Elmer 597 IR spectrophotometer (4000–200 cm^{-1}). Electronic spectra were recorded with a Hitachi U-3410 UV/Vis/NIR spectrophotometer. ^1H and ^{13}C spectra were recorded with a Bruker AV 300 spectrometer, and ^{183}W NMR spectra were recorded with a Bruker AMX 400 spectrometer, the equipment being operated at 300 MHz by using TMS and Na_2WO_4 as reference, respectively. Electrospray mass spectra were recorded with a Q-TOF MicroMass Spectrometer (Waters). A Systronics (India) model 335 digital conductivity bridge with a bottle-type cell was used to determine the molar conductance values of the isolated complexes at 25 °C by using a thermostatic arrangement. A SUNVIC (U. K.) apparatus was used to measure the melting points of the organic substrates as well as those of their oxidized products. Magnetic susceptibilities were obtained by the Gouy method with $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a standard. Elemental analyses were performed with the help of a Perkin–Elmer 240C elemental analyzer, and the amount of tungsten was estimated gravimetrically as its 8-quinolinolate.^[45] HPTLC tests were performed with a CAMAG HPTLC system (Switzerland). GLC measurements were done with an Agilent model 6890 gas chromatograph by using HP-1 and IN-NOWAX capillary columns in the FID mode with dinitrogen as carrier gas.

Materials: The compounds $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, dinitrophenylhydrazine and zinc dust were of extra pure grade and were obtained from Loba Chemie (India). Hydrogen peroxide (30%), hydrochloric acid, ammonium chloride, sodium hydrogen carbonate, cyclohexanol, cyclohexanone, *n*-butyl alcohol, benzaldehyde, cinnamaldehyde, cinnamic acid, acetonitrile, dichloromethane, light petroleum (40–60), diethyl ether and acetone were of analytical grade and were obtained from E. Merck (India). Acetonitrile, dichloromethane and acetone were further purified by a literature method^[46] before use. 1-Buten-3-ol, 4-penten-1-ol, *cis*-2-penten-1-ol, 1-hexene, 1-heptene, *trans*-5-decene and 9-decen-1-ol were from Sigma-Aldrich Chemie GmbH, Germany and were used without further purification. Styrene, cinnamyl alcohol and allyl alcohol were obtained from E. Merck (Germany). All the epoxides of the corresponding olefins were the products of Aldrich, Germany. Nitrobenzene and *o*-, *m*- and *p*-nitrotoluenes of laboratory reagent grade were obtained from B.D.H. (India). Benzyl alcohol, phenol, methanol, *n*-propyl alcohol, dimethyl sulfoxide, isopropyl alcohol, *n*-heptyl alcohol, *n*-octyl alcohol, 2-octanol, *n*-dodecyl alcohol, aniline, *p*-phenylenediamine and nitrobenzene were of G. R. grade and obtained from Sisco Chemical Laboratories (SRL, India). Ethyl methyl sulfide,

benzyl methyl sulfide, *trans*-1,2-diamino cyclohexane, cyclopentene, cyclohexene, *cis*-cyclooctene, norbornene, cinnamyl alcohol, 1-octene, 1-hexene, 1-decene, 1-dodecene and *trans*-2-hexen-1-ol were obtained from Lancaster (England). Benzoyl chloride and thionyl chloride of synthetic reagent grade were obtained from Ranbaxy (India). Ethanol (95%) was obtained from Bengal Chemical and Pharmaceutical Works (Calcutta) and was lime-distilled before use. IOLAR II grade dioxygen, dihydrogen, zero-air and dinitrogen gas used for chromatographic analysis were obtained from Indian Refrigeration Stores, Calcutta. Triply distilled (all glass) water was used whenever necessary. The hydroxamic acid ligands, *N*-benzoyl-*N*-phenylhydroxamic acid (BPHAH), *N*-benzoyl-*N*-*o*/*m*/*p*-tolylhydroxamic acid (BOTHAH/BMTHAH/BPTHAH) and *N*-cinnamyl-*N*-phenylhydroxamic acid (CPHAH) were prepared following the literature method^[47] and characterized by elemental analysis, melting point and IR spectroscopic data. All the solvents used for chromatographic analysis were either of HPLC, spectroscopic or GR grade.

Preparation of the Complexes: $[\text{WO}(\text{O}_2)(\text{BPHA})_2]$ (1): An aqueous solution (10 cm^3) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.825 g; 2.5 mmol) was acidified with HCl solution (6 M), and a white precipitate of $\text{WO}_3 \cdot n\text{H}_2\text{O}$ was obtained. It was filtered off and washed several times with water and ethanol. The precipitate was transferred quantitatively into a beaker and was dissolved in H_2O_2 (30% w/v, 6.95 mmol, 5 cm^3) by stirring at room temperature (25 °C) to get a clear and colourless solution. *N*-benzoyl-*N*-phenylhydroxamic acid (BPHAH; 1.02 g, 5.0 mmol) dissolved in a minimum volume of ethanol (ca 5 cm^3) was added to the above solution with stirring (5 min), and a light-yellow solid separated out. The solid was filtered off, washed thoroughly with water, ethanol and diethyl ether and dried in vacuo. The compound crystallized as pale-yellow rectangles from dichloromethane/*n*-hexane (1:1) solvent mixture. Yield 1.38 g (2.1 mmol, 84%). $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_7\text{W}$ (656.29): calcd. C 47.57, H 3.05, N 4.27, W 28.03; found C 47.82, H 3.16, N 4.35, W 27.65. ^{183}W NMR (300 MHz, CD_2Cl_2 , 27 °C): $\delta = -313.909$ ppm. The compound is soluble in acetone, acetonitrile, dichloromethane, but insoluble in ether and carbon tetrachloride.

$[\text{WO}(\text{O}_2)(\text{BOTH})_2]$ (2), $[\text{WO}(\text{O}_2)(\text{BMTH})_2]$ (3), $[\text{WO}(\text{O}_2)(\text{BPTH})_2]$ (4), $[\text{WO}(\text{O}_2)(\text{CPHA})_2]$ (5): These compounds were prepared and crystallized by following the same method as that described for **1** with the corresponding hydroxamic acid ligands instead of BPHAH. $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_7\text{W}$ (684.34 for **2**, **3**, **4**): calcd. C 49.13, H 3.51, N 4.09, W 26.88; found C 49.40, H 3.65, N 4.25, W 26.35 (for **2**); C 49.05, H 3.72, N 4.16, W 26.55 (for **3**); C 49.56, H 3.62, N 4.18, W 26.52 (for **4**). For **5**: $\text{C}_{60}\text{H}_{48}\text{N}_4\text{O}_{14}\text{W}_2$ (1416.72): calcd. C 50.87, H 3.42, N 3.95, W 25.95; found C 51.05, H 3.52, N 3.90, W 25.70. For **2**: ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 2.47$ (s, 3 H, $-\text{CH}_3\{\text{C}14\}$), 2.36 (s, 3 H, $-\text{CH}_3\{\text{C}21\}$), 7.17–7.50 (m, 18 H, Ar) ppm. ^{13}C NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 17.39$ (C-14, C-21); 126.33, 127.20, 127.38, 127.67, 128.18, 128.26, 128.38, 128.57, 128.89, 129.07, 129.41 (C-4–C-6, C-10, C-11, C-17, C-18, C-25–C-27); 130.86, 131.47, 131.59, 131.77, 132.82 (C-3, C-7, C-9, C-12, C-16, C-19, C-24, C-28); 136.49 (C-2, C-23); 137.62 (C-13, C-20); 138.44 (C-8, C-15); 164.64 (C-1, C-22) ppm. For **3**: ^{183}W NMR (300 MHz, CD_2Cl_2 , 27 °C): $\delta = -313.746$ ppm. For **4**: ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 2.43$ (s, 3 H), 2.39 (s, 3 H), 7.06–7.54 (m, 18 H) ppm. ^{13}C NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 21.23$, 21.28, 126.27, 126.51, 126.72, 127.19, 127.37, 128.16, 128.36, 128.53, 129.38, 129.43, 129.59, 130.01, 130.18, 131.85, 132.22, 132.70, 136.07, 136.53, 137.25, 140.23, 141.02, 163.69, 164.87 ppm. ^{183}W NMR (300 MHz, CD_2Cl_2 , 27 °C): $\delta = -313.778$ ppm. MS: $m/z = 684.82$ $[\text{M}]^+$ (calcd. for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_7\text{W}$: 684.11), 707.78 $[\text{M} + \text{Na}]^+$ (calcd. for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_7\text{WNa}$: 707.10),

722.75 [M + K]⁺ (calcd. for C₂₈H₂₄N₂O₇WK: 723.07), 725.77 [M + CH₃CN]⁺ (calcd. for C₃₀H₂₇N₃O₇W: 725.14), 682.82 [M – 2H]⁺ (calcd. for C₂₈H₂₂N₂O₇W: 682.09), 585.8 [M – C₄H₃ – 3O]⁺ (calcd. for C₂₄H₂₁N₂O₄WNa: 585.10), 498.94 [M – CH₃CN + H – L]⁺ (calcd. for C₁₆H₁₆N₂O₅W: 500.06), 463.81, 249.98 [L + Na]⁺ (calcd. for C₁₄H₁₂NO₂Na: 249.08), 210.01 [L – O]⁺ (calcd. for C₁₄H₁₂NO: 210.09), 107.01 [L – MePhNHO + 2H]⁺ (calcd. for C₇H₆O: 106.04). For **5**: ¹⁸³W NMR (300 MHz, CD₂Cl₂, 27 °C): δ = –315.613 ppm. Solubility of the complexes **2–5** is similar to that of **1**. Yield: on average 83% (for **2**, **3** and **4**) and 81% for **5**.

[W(O)₂(BPHA)₂](6A): An aqueous solution (10 cm³) of Na₂WO₄·2H₂O (0.825 g; 2.5 mmol) was acidified with HCl solution (6 M), and a white precipitate of WO₃·*n*H₂O was obtained. Hydrated sodium tungstate, Na₂WO₄·2H₂O (0.825 g, 2.5 mmol), was dissolved in a minimum volume of water (5 mL). An ethanol solution of *N*-benzoyl-*N*-phenylhydroxamic acid (BPHAH; 1.02 g, 5.0 mmol) was added dropwise to this aqueous solution with stirring. A light-yellow solid separated out after addition of two drops of hydrochloric acid (6 M). The solid was filtered off and washed thoroughly with distilled water, ethanol and diethyl ether and finally dried in vacuo. The yield was 0.677 g (82%). C₂₆H₂₀N₂O₆W (640.29): calcd. C 48.75, H 3.12, N 4.37, W 28.72; found C 48.92, H 3.16, N 4.15, W 27.95. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.21–8.06 (m, 20 H) ppm. ¹³C NMR (300 MHz, CDCl₃, 25 °C): δ = 126.39, 126.65, 128.21, 128.57, 129.41, 129.62, 129.86, 130.50, 131.98, 132.80, 138.58, 139.75, 163.94 ppm. ¹⁸³W NMR (300 MHz, CD₂Cl₂, 27 °C): δ = +85.783 ppm. The compound is soluble in acetone, acetonitrile, dichloromethane, but insoluble in ether and carbon tetrachloride. All the dioxidotungsten complexes can be prepared by the above procedure and the respective complexes are named **6A**, **6B**, **6C** and **6D**.

[PPh₄][WO(O₂)₂(C₆H₅-COO)] (8): [WO(O₂)(BMTHA)₂] (2.50 mmol; 1.64 g) was dissolved in a minimum volume of acetonitrile (15 mL) in a round-bottomed flask and heated at reflux for 1 h after addition of an excess of H₂O₂ (30% w/v; 20 mL). A uniform and clear solution was obtained. Acetonitrile was then separated by distillation, and to the aqueous solution that was left was added an aqueous solution (10 mL) of PPh₄Cl (2.50 mmol; 0.86 g) dropwise with constant stirring over 30 min. A reddish solid separated. The solid was filtered off, washed thoroughly with water, ethanol, diethyl ether and dried in vacuo. The compound was found to be soluble in acetonitrile, acetone, dichloromethane and chloroform but insoluble in diethyl ether and benzene. Yield 1.08 g (65%). C₃₁H₂₅O₇WP (724.34): C 51.39, H 3.45, W 25.39; found C 51.12, H 3.16, W 24.74.

X-ray Crystallographic Data Collection and Refinement: Suitable single crystals of complexes **1–3** and **5** were selected and mounted on a Bruker P4 single-crystal X-ray diffractometer for intensity data collection. Accurate cell parameters were determined from diffractometer setting angles in the usual way. Intensity data were collected at room temperature (20 °C) by using Mo-*K*_α radiation (λ = 0.71073 Å) with the ω-2θ scan mode. Data were corrected for Lorentz and Polarization effects. An empirical absorption correction based on ψ scan was applied. A summary of relevant crystal data for complexes **1–3** and **5** is listed in Table 1. The structures were solved by the Patterson method with SHELXS-97^[48] and refined by full-matrix least-squares on *F*² with SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were included in calculated positions and allowed to ride on the atoms to which they were attached, with thermal parameters tied to those of the parent atoms.

Experimental Procedure for Catalysis and Isolation of Products

Procedure for Epoxidation of Olefins

The experimental procedure for the epoxidation of olefins is as follows: An acetonitrile solution (10 cm³) containing a given substrate (ca. 10–15 mmol), NaHCO₃ (2.5–3.75 mmol), tungsten catalyst (0.01–0.001 mmol) and H₂O₂ (25–35 mmol, 30%) was placed in a flat-bottom, two-neck reaction flask. One neck was fitted with a reflux condenser (to check evaporation), and the other neck was closed with a septum. The reaction mixture was stirred at room temperature (25 °C) for a definite period of time as quoted in the Table 3.

As and when required, an aliquot of the reaction solution was withdrawn from, and H₂O₂ added to, the contents of the flask with the help of a syringe through the septum. The 0.5-cm³ solution withdrawn was subjected to multiple ether extraction, and the extract was also concentrated down to 0.5 cm³ from which 1 μL was withdrawn with the help of a gas syringe and injected to the GC port. The retention times of the peaks were compared with those of commercial standards, and nitrobenzene was used as an internal standard for GC yield calculation. In a few cases, especially for olefin alcohols, the identities of the products were confirmed by GC–MS analysis.

When the GC yield of the product was very high, the isolated yield (Table 3) was obtained by multiple ether extraction of the reaction solution after the reaction was over, and then evaporation of the ether and acetonitrile by distillation in a rotary evaporator at room temperature. The solid thus produced was kept over P₂O₅ in a desiccator and directly weighed by a microbalance. Then, the identity of the products was confirmed by IR and NMR probing.

For lower yields, the liquid (the solid products obtained from reaction solution were simply dried and weighed) products were subjected to preparative TLC, and the highly intense spot was cut out and plunged in CH₂Cl₂ which served as an eluant. Then the resulting solution was dried with MgSO₄, filtered through a short silica gel pad and finally the solvents were removed by rotary evaporation as described above. The residue was then kept over P₂O₅ for 15 min and then weighed.

Procedure for Oxidation of Alcohols, Sulfides and Amines

The experimental procedure for oxidation of alcohols, sulfides and amines is as follows: An acetonitrile (dichloromethane for sulfides) solution (10 cm³) containing a given substrate (25 mmol), tungsten catalyst (0.02–0.025 mmol) and 30% H₂O₂ (35–205 mmol) was placed in a flat-bottom, two-neck reaction flask. One neck was fitted with a reflux condenser (to check evaporation), and the other neck was closed with a septum. The reaction mixture was heated at reflux for a definite period of time as quoted in Table 4.

Workup procedure I was used for isolating aldehydes or ketones, and procedures II and III were used for isolating carboxylic acids and other compounds.

Procedure I: Carbonyl compounds were isolated as their respective yellow-orange solid 2,4-dinitrophenylhydrazone derivatives, and the corresponding carbonyl compounds were generated from the derivatives by acid hydrolysis. The purity of the DNPH derivatives was checked by the integration of the respective ¹H NMR spectra.

Procedure II: The reaction solutions assumed to contain carboxylic acids were treated with aqueous NaHCO₃, and the aqueous layer was concentrated to near dryness and allowed to stand for 30 min.; then the corresponding acids were isolated as their colourless Na salts.

Procedure III: Sulfones were crystallized out as solids after concentrating the aqueous layer, while unreacted sulfides and sulfoxides remaining in the CH_2Cl_2 layer were separated by fractional distillation. 1,4-benzoquinone (from phenol) was extracted out from the reaction solution by diethyl ether and evaporation of ether deposits on the off-white material. The mixture of products, 1,4-benzoquinone and 4-nitroaniline, obtained from 1,4-diaminobenzene was separated by steam distillation, since the former is steam volatile. Other amines and their oxidized products were separated by column chromatography, and their identities were checked by NMR spectroscopic analysis. It may be mentioned that for all the above procedures the amount of products chemically separated correspond closely to the G.C. results.

Recovery of Catalyst: The residue left after distilling the ether and acetonitrile off at mildly reduced pressure was thoroughly shaken with diethyl ether repeatedly to extract the substrates and products almost quantitatively from the ether solvent, and the yellow solid residue left was verified by IR spectroscopy to be the catalyst.

Supporting Information (see footnote on the first page of this article): The detailed chemical reactions for Scheme 3 and Scheme 4 as mentioned in the text, the list of IR and UV/Vis spectral values, the bond lengths and angles for all complexes, the method of determination of GC yield and the ^{183}W NMR and mass spectra.

CCDC-662003, CCDC-662004, CCDC-662005 and CCDC-662006 for the structures of complexes **1**, **2**, **3** and **5**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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