Heteropolyperoxo- and Isopolyperoxo-tungstates and -molybdates as Catalysts for the Oxidation of Tertiary Amines, Alkenes and Alcohols†

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The catalytic oxidation of tertiary amines to the corresponding *N*-oxides by $[XO_4\{MO(O_2)_2\}_4]^{3-}$ (X = P or As, M = Mo or W) and by $[M_2O_3(O_2)_4]^{2-}$ with H_2O_2 as co-oxidant has been studied. Epoxidation of alkenes and oxidation of alcohols by $[M_2O_3(O_2)_4]^{2-}$ with H_2O_2 as co-oxidant has also been examined and compared with that effected by $[XO_4\{MO(O_2)_2\}_4]^{3-}$. A possible structure for $[M_2O_3(O_2)_4]^{2-}$ is suggested.

Polyoxo-[2] and polyperoxo-metalates[3] are currently of considerable interest as catalysts for a variety of organic oxidations with the environmentally acceptable H_2O_2 as co-oxidant. One of the most effective homogeneous catalysts for the epoxidation of alkenes, using H_2O_2 as co-oxidant, is Venturello's compound, $[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$ **1**, used in a biphasic aqueous H_2O_2–benzene mixture.[1,4–6] We have recently reported analogues of **1**, *viz*. $[N(C_6H_{13})_4]_3[AsO_4\{WO(O_2)_2\}_4]$ **2**, $[N(C_6H_{13})_4]_3[PO_4\{MoO(O_2)_2\}_4]$ **3** and $[N(C_6H_{13})_4]_3[AsO_4\{MoO(O_2)_2\}_4]$ **4**, and have shown, for a wide variety of cyclic and linear mono-alkenes, that **2** is superior to **1** as an epoxidation catalyst while **3** and **4** are markedly inferior to both **1** and **2**.[1]

In this paper we show that both complexes **1** and **2** are effective catalysts for the oxidation of tertiary amines R_3N to R_3NO, and report similar oxidations by the dimeric isopolyperoxo complexes $[N(C_6H_{13})_4]_2[M_2O_3(O_2)_4]$ (M = W **5** or Mo **6**). We also compare the efficiencies of **1**–**6** for alkene epoxidations, and propose structures for the anions of **5** and **6** which are, in effect, fragments of the structure of **1**.

Results and Discussion

Oxidation of Tertiary Amines by Complexes **1**–**4**.—Venturello's compound **1** has been used, with H_2O_2 as co-oxidant, to catalyse alkene epoxidation;[1,4,5] with large lipophilic quaternary ammonium cations it similarly *cis*-hydroxylates internal alkenes,[7] oxidises internal alkynes to α,β-epoxy ketones,[8,9] and will also oxidise primary and secondary alcohols to aldehydes and ketones respectively.[1] The stoichiometric oxidation of alkenes to epoxides[10] and sulfides to sulfoxides[10–12] by $[C_5H_5N(CH_2)_{15}Me]_3[PO_4\{MoO(O_2)_2\}_4]$ has been reported. The tungsten analogue, $[C_5H_5N(CH_2)_{15})Me]_3[PO_4\{WO(O_2)_2\}_4]$, will catalyse, under biphasic or homogeneous conditions, the oxidation of primary amines to oximes[13] and secondary amines to nitrones[13,14] (aromatic amines give nitroso compounds or nitrobenzenes[13]).

Our work was prompted by a report that $H_3[PW_{12}O_{40}]$ and, less effectively, $H_3[PMo_{12}O_{40}]$ would catalyse the oxidation by aqueous H_2O_2 of a number of such amines to the amine oxides.[15] Since it is known[16–18] that H_2O_2 reacts with $H_3[PM_{12}O_{40}]$ to give, amongst other species, $[PO_4\{MO(O_2)_2\}_4]^{3-}$ and $[M_2O_3(O_2)_4]^{2-}$, it was of interest to study such oxidations. Our results for amine oxidations are summarised in Table 1. In all cases the reactions were carried out in a toluene–15% aqueous H_2O_2 biphasic mixture over 6 h at 85 °C. All products were isolated and their purities checked by their melting points and IR spectra. The yields are in most cases superior to those found for the $H_3[PW_{12}O_{40}]$–H_2O_2 system.[15] Whereas complex **2** is markedly superior to **1** for alkene epoxidations,[1] there is only a very slight difference in their efficiencies for amine oxidations; as with alkene epoxidations, however, the molybdenum complexes **3** and **4** are far less effective than **1** and **2** and data for these are not tabulated. Blank experiments (*i.e.* in the absence of metal catalyst) yielded no substantial quantity of *N*-oxide.

It is interesting that some of the organic substrates can function as effective coligands with η^2-peroxide in a number of complexes (*e.g.* in pyridine-2-carboxylato and pyridine-2,6-dicarboxylato complexes of molybdenum and tungsten);[19] nevertheless such potential complex formation does not seem to impede their oxidation, perhaps because of the forcing conditions used.

Stoichiometrically one would expect 1 mol of complex **1** to oxidise 8 mol of substrate. With pyridine-2,5-dicarboxylic acid, chosen because it gave the best yield and turnover on catalytic oxidation with **1** and **2**, the result was in agreement with expectation.

The mechanism of the reaction is likely to be complex and no attempts were made to study this aspect. As with the reaction between Venturello's compound **1** and cyclooctene in the absence of H_2O_2,[1] the ^{31}P NMR spectrum (in $CDCl_3$) of **1** with an equimolar amount of pyridine-2,6-dicarboxylic acid showed a number of peaks arising presumably from a number of partially peroxidised species. On addition of an excess of H_2O_2 the normal ^{31}P NMR spectrum of **1** was observed, again as is the case with the reaction of cyclooctene with **1**.[1]

The Dimeric Species $[M_2O_3(O_2)_4]^{2-}$.—Dimeric species of the form $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ (M = W or Mo) have long been known. There are X-ray data on $K_2[M_2O_3(O_2)_4(H_2O)_2]$ (M = W[20] or Mo[21]), $[C_5H_5NH]_2[Mo_2O_3(O_2)_4(H_2O)_2]$[22] and $[C_3H_5N_2]_2[Mo_2O_3(O_2)_4(H_2O)_2]$,[23] and we have measured the vibrational spectra of such species and shown by Raman spectroscopy that they are likely to retain their structures in aqueous solution.[24] We have also prepared, however, a water-free species, $[PPh_4]_2[W_2O_3(O_2)_4]$,[24] and Mimoun and co-workers[25] have isolated $[PPh_3(CH_2Ph)]_2[W_2O_3(O_2)_4]$. The latter complex has been shown to be an active epoxidant of alkenes with H_2O_2 as co-oxidant.[25]

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† Studies on Polyoxo- and Polyperoxo-metalates. Part 2.[1]

Table 1 Oxidation of tertiary amines catalysed by $[N(C_6H_{13})_4]_2[XO_4\{WO(O_2)_2\}_4]$ and $[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$ with H_2O_2 as co-oxidant*

	Yield (%) [Turnover]		
Substrate	$[PO_4\{WO(O_2)_2\}_4]^{3-}$	$[AsO_4\{WO(O_2)_2\}_4]^{3-}$	$[W_2O_3(O_2)_4]^{2-}$
Pyridine-2-carboxylic acid	62 [137]	65 [147]	18 [41]
Nicotinic acid	73 [161]	77 [174]	72 [159]
Isonicotinic acid	83 [184]	86 [195]	64 [145]
Pyridine-2,3-dicarboxylic acid	68 [151]	75 [169]	65 [147]
Pyridine-2,5-dicarboxylic acid	94 [208]	96 [215]	83 [184]
Pyridine-2,6-dicarboxylic acid	76 [168]	79 [178]	50 [112]
Pyridine-3,4-dicarboxylic acid	79 [175]	82 [182]	71 [156]

* Product is the corresponding *N*-oxide in each case.

Table 2 Spectroscopic characteristics (cm^{-1}) of $[W_2O_3(O_2)_4]^{2-}$

Species		ν(M=O)	ν(O–O)	$\nu_{asym}(M_2O)$	$\nu_{sym}[M(O_2)]$	$\nu_{asym}[M(O_2)]$
$[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$[a]	IR	967vs	855s	764s	616m	560s
	Raman	968(10)	849(5)	768(1)	615(1)	552(3)
$[W_2O_3(O_2)_4(D_2O)_2]\cdot 2D_2O$[b]	IR	967vs	855vs	764vs	617s	559s
	Raman	963(10)	863(6)	760(2)	621(3)	559(6)
$[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$	IR	962vs	840vs	749(sh)	616s	562s
	Raman	948(10)	868(5)	—	—	579(3)
$[N(C_6H_{13})_4]_2[Mo_2O_3(O_2)_4]$	IR	978vs	858vs	768s	633m	579s
	Raman	982(10)	880(8)	—	642(2)	586(4)
$[PPh_4]_2[W_2O_3(O_2)_4]$	IR	962vs	840vs	759s	616s	561s
	Raman	973(10)	869(4)	734(2)	629(6)	575(4)
$[AsPh_4]_2[W_2O_3(O_2)_4]$[c]	IR	963vs	843vs	760s	612m	562s
	Raman	954(10)	864(5)	—	619(6)	569(3)
$[PPh_3(CH_2Ph)]_2[W_2O_3(O_2)_4]$	IR	955vs	839vs	751vs	624s	557s
	Raman	971(10)	871(5)	735(2)	625(7)	568(3)
$[N\{(CH_2)_{13}Me\}(CH_2Ph)Me_2]_2[W_2O_3(O_2)_4]$	IR	955vs	835vs	755vs	619s	567s
	Raman	950(10)	876(4)	—	623(3)	573(2)

[a] IR $\nu[W(OH_2)]$ 329m, $\delta(W_2O)$ 259w, ν(OH) 3400vs, 3335vs, δ(HOH) 1631s; Raman $\nu[W(OH_2)]$ 323(3), $\delta(W_2O)$ 255(1), ν(OH) 3538(3), 3422(2) cm^{-1}. [b] IR $\nu_{sym}(W_2O)$ 451m, $\nu[W(OH_2)]$ 325m, $\delta(W_2O)$ 264m, ν(OD) 2618s, 2477s, δ(HOD) or δ(DOD) 1385m, 1207m; Raman $\nu_{sym}(W_2O)$ 444(1), ν(OD) 2617(2) cm^{-1}. [c] $\nu[W(OH_2)]$ 328(2) cm^{-1}.

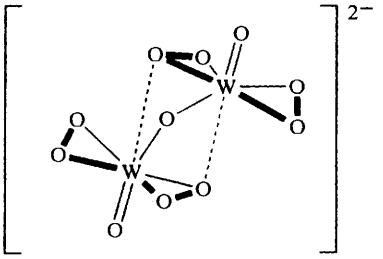

Fig. 1 Proposed structure of the $[W_2O_3(O_2)_4]^{2-}$ anion

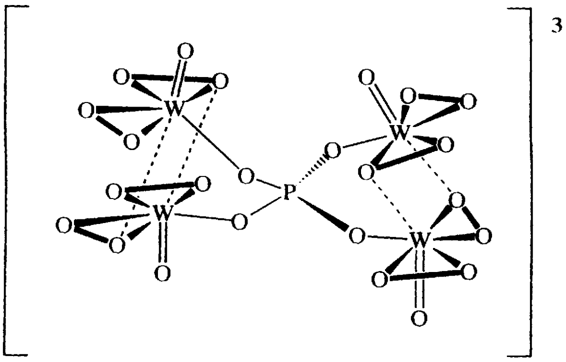

Fig. 2 Structure of the $[PO_4\{WO(O_2)_2\}_4]^{3-}$ anion in Venturello's compound **1**

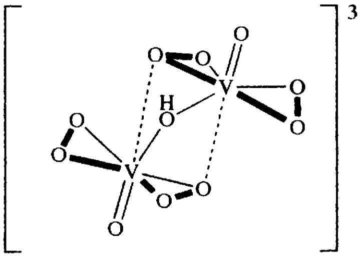

Fig. 3 Structure of the anion in $[NH_4]_3[V_2(OH)O_2(O_2)_4]$

Although we have prepared pure samples of $[N(C_6H_{13})_4]_2[M_2O_3(O_2)_4]$ (M = W **5** or Mo **6**), $[PPh_4]_2[W_2O_3(O_2)_4]$ **7** and $[AsPh_4]_2[W_2O_3(O_2)_4]$ **8**, no crystals suitable for X-ray structural analysis could be obtained despite numerous attempts. It is quite clear, however, from microanalyses and from vibrational spectra (Table 2) that these salts, all of which contain large cations, do not contain co-ordinated water and we suggest that they have the structure shown in Fig. 1; this may be regarded as related to one of the dimeric fragments in Venturello's compound **1** (Fig. 2). Indeed, we have earlier reported the crystal structure of a related complex, $[NH_4]_3[V_2(OH)O_2(O_2)_4]$ (Fig. 3), in which the structure of the anion is close to that proposed here for $[W_2O_3(O_2)_4]^{2-}$, the only difference being that the bridging oxo atom is protonated in the vanadium complex.[26] Recently an analogue of this, $[NH_4]_5[PO_4\{V_2O_2(O_2)_4\}]\cdot H_2O$ has been reported.[27]

In Table 2 we list infrared and Raman spectra for complexes **5**–**8** together with those for $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ and $K_2[W_2O_3(O_2)_4(D_2O)_2]\cdot 2D_2O$, with tentative assignments for the vibrational modes. Bands due to water (or D_2O) modes are quite clear for the potassium salts but are not present for the

Table 3 Epoxidation of monoalkenes by *trans*-$[XR_4]_2[W_2O_3(O_2)_4]$ with H_2O_2 as co-oxidant

Substrate	Product	Yield (%) [Turnover] $[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$	Yield (%) [Turnover] $[PPh_4]_2[W_2O_3(O_2)_4]$
Cyclopentene	Epoxycyclopentane	50 [195]	1 [4]
Cyclohexene	Epoxycyclohexane	10 [39]	10 [40]
Cycloheptene	Epoxycycloheptane	86 [300]	86 [346]
Cyclooctene	Epoxycyclooctane	86 [300]	77 [321]
Cyclododecene	Epoxycyclododecane	20 [83]	5 [21]
trans-Stilbene	*trans*-2,3-Diphenyloxirane	91 [355]	72 [300]
cis-Stilbene	*cis*-2,3-Diphenyloxirane	83 [324]	68 [283]
Styrene	Phenyloxirane	1 [4]	1 [4]
Bicyclo[2.2.1]hept-2-ene	2,3-Epoxybicyclo[2.2.1]heptane	—	9 [38]
Hex-1-ene	1,2-Epoxyhexane	12 [27]	—
Hept-1-ene	1,2-Epoxyheptane	10 [23]	—
Oct-1-ene	1,2-Epoxyoctane	19 [44]	—
Non-1-ene	1,2-Epoxynonane	27 [72]	—
Dec-1-ene	1,2-Epoxydecane	24 [61]	—
Undec-1-ene	1,2-Epoxyundecane	22 [56]	—
Dodec-1-ene	1,2-Epoxydodecane	29 [83]	—

Table 4 Alcohol oxidations catalysed by $[W_2O_3(O_2)_4]^{2-}$

Substrate	Product	Yield (%) [Turnover] $[PPh_4]_2[W_2O_3(O_2)_4]$	Yield (%) [Turnover] $[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$
Benzyl alcohol	Benzaldehyde	38 [63]	96 [160]
4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	87 [145]	> 99 [167]
3,4-Dimethoxybenzyl alcohol	3,4-Dimethoxybenzaldehyde	99 [166]	> 99 [167]
2-Methylbenzyl alcohol	2-Methylbenzaldehyde	24 [40]	> 99 [167]
4-Methylbenzyl alcohol	4-Methylbenzaldehyde	52 [87]	> 99 [167]
(±)-Menthol	Menthone	10 [17]	85 [142]
Cyclohexanol	Cyclohexanone	20 [34]	81 [135]
Cyclooctanol	Cyclooctanone	6 [10]	> 99 [167]
1,2,3,4-Tetrahydronaphthol	3,4-Dihydro-2*H*-naphthalen-l-one	27 [45]	0.2 [0.3]
Diphenylmethanol	Benzophenone	99 [166]	> 99 [167]

other species, again indicating the absence of either co-ordinated water or of molecules of water of crystallisation in **5–8**.

Oxidations of Amines, Alkenes and Alcohols with Complexes **5–8**.—The complex $[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$ **5** was treated with tertiary amines in the presence of a biphasic toluene–15% aqueous H_2O_2 mixture under the same conditions as those successfully used for catalytic oxidations with **1** and **2** (see Table 1). In general **5** is a reasonably effective catalyst, though rather less efficient than **1** and **2** in respect of yields and turnovers.

It seems likely that the efficiency of $[N(C_6H_{13})_4]_2$-$[W_2O_3(O_2)_4]$ **5** as an alkene epoxidant (Table 3) derives from the presence of the two asymmetrically bound η^2-peroxide ligands, which renders one W–O bond weaker and thus easier to break followed by heterolytic O–O bond cleavage to epoxidise the alkene (a similar proposal has been made for the catalytic efficiency of **1**[1]). It has recently been suggested[28] that the effectiveness of **1** may be related to ion-pairing effects; such a possibility would also exist for the dimeric species **5–8**. Changing the counter ion from $N(C_6H_{13})_4^+$ to PPh_4^+, (giving **7**), the latter being a much less efficient phase-transfer agent, resulted in good yields of the epoxide, although lower than those observed for **5**. Use of $AsPh_4^+$ (known to be less soluble than PPh_4^+ in organic media) gave poor yields and lower turnovers for epoxidation of both cyclic and terminal linear alkenes and data for these are not tabulated. A salt of $[W_2O_3(O_2)_4]^{2-}$ with $N[(CH_2)_{13}Me](CH_2Ph)Me_2^+$, a well established phase-transfer cation, was prepared, though it could not be obtained pure; it gave disappointing yields of epoxides. As with the molybdenum analogues of **1** and **2**, $[N(C_6H_{13})_4]_2$-$[Mo_2O_3(O_2)_4]$ **6** was found to be very inefficient for epoxidation of monoalkenes. Proton NMR spectra of the reaction mixtures show that epoxides only are produced.

Both complexes **5** and **7** were found to catalyse the oxidation of primary and secondary alcohols to aldehydes and ketones respectively (Table 4). The reactions were in all cases carried out in a benzene–15% aqueous H_2O_2 biphasic mixture at 75 °C, over a period of 3 h. Yields were determined by gas chromatography. Again, in most cases, the yields obtained with **5** as catalyst are markedly superior to those observed for **7** emphasising the importance of the counter ion in these reactions. By using gas chromatography–mass spectrometry it was evident that only carbonyl products were formed.

Conclusion

We conclude that the tetrameric Venturello complexes $[N(C_6H_{13})_4]_3[XO_4\{WO(O_2)_2\}_4]$ (X = P or As) and the dimer $[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$ are effective catalysts for the oxidation of tertiary amines to their *N*-oxides with H_2O_2 as co-oxidant in a biphasic benzene–water system. The dimeric anions $[M_2O_3(O_2)_4]^{2-}$ (M = Mo or W) with large cations are likely to have the structure shown in Fig. 1, and the tungsten complex $[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$ is an effective catalyst for epoxidation of alkenes and oxidation of alcohols. The former **5** is rather less effective than $[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$ for alkene epoxidations but for alcohol oxidations it is comparable in efficiency.

Experimental

General.—Sodium tungstate dihydrate and sodium molybdate dihydrate were obtained from BDH Chemicals and used without further purification. Tetrahexylammonium chloride, tetraphenylphosphonium chloride, tetraphenylarsonium chloride, benzyltriphenylphosphonium chloride and hydrogen peroxide (30% w/v) were used as supplied by Aldrich Chemical Company. Complexes **1–4**[1] and $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$[24] were synthesised as previously described.

$[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$ **5**.—A solution of sodium tungstate dihydrate (1.65 g, 5 mmol) in water (10 cm^3) was treated with 30% H_2O_2 (6 cm^3). The yellow solution formed was treated with dilute hydrochloric acid dropwise until it just turned colourless (pH 2.5). Tetrahexylammonium chloride (3.9 g, 10 mmol) in water (20 cm^3) was added dropwise giving rise to a white precipitate. The solid was filtered off, washed with water (10 cm^3) and diethyl ether (2 × 10 cm^3) and air dried. The product is slightly hygroscopic and was stored *in vacuo*. Yield 2.91 g, 2.4 mmol (96%) (Found: C, 46.0; H, 8.3; N, 2.2; O_2^{2-}, 10.1. Calc. for $C_{48}H_{104}N_2O_{11}W_2$: C, 46.0; H, 8.4; N 2.2; O_2^{2-}, 10.2%).

$[N(C_6H_{13})_4]_2[Mo_2O_3(O_2)_4]$ **6**.—A solution of sodium molybdate dihydrate (1.21 g, 5 mmol) in water (10 cm^3) was treated with 30% H_2O_2 (6 cm^3). The orange-red solution formed was treated with dilute hydrochloric acid dropwise until it just turned yellow (pH 4.2). Tetrahexylammonium chloride (3.9 g, 10 mmol) in water (20 cm^3) was added dropwise giving rise to a pale yellow precipitate. The solid was filtered off, washed with water (10 cm^3) and diethyl ether (2 × 10 cm^3) and air dried. The product is slightly hygroscopic and was stored *in vacuo*. Yield 2.42 g, 2.3 mmol (92%) (Found: C, 53.2; H, 9.5; N, 2.6; O_2^{2-}, 11.7. Calc. for $C_{48}H_{104}Mo_2N_2O_1$: C, 53.5; H, 9.7; N, 2.6; O_2^{2-}, 11.9%).

$[PPh_4]_2[W_2O_3(O_2)_4]$ **7**.—Potassium hydroxide (1.0 g, 17 mmol) was dissolved in the minimum amount of water and hydrated tungsten trioxide, $WO_3\cdot H_2O$ (2.0 g, 7 mmol), added. The solution was stirred until the $WO_3\cdot H_2O$ had dissolved. It was often cloudy, so if necessary it was centrifuged and the supernatant then cooled to 0 °C in an ice-bath. Hydrogen peroxide (30% w/v, 7 cm^3) was added dropwise and the resulting yellow solution treated with dilute hydrochloric acid until a colourless solution was formed (pH 2.5). On cooling white crystals of the potassium dimer $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$, precipitated. To an aqueous solution of this dimer (3.47 g, 5 mmol) in water (20 cm^3) was added tetraphenylphosphonium chloride (3.74 g, 10 mmol) and the solution was stirred until clear. After allowing to stand for 30 min a white solid was deposited. Yield 5.45 g, 4.4 mmol (89%) (Found: C, 46.2; H, 3.3; O_2^{2-}, 10.1. Calc. for $C_{48}H_{40}O_{11}P_2W_2$: C, 46.2; H, 3.0; O_2^{2-}, 10.4%).

$[AsPh_4]_2[W_2O_3(O_2)_4]$ **8**.—A solution of sodium tungstate dihydrate (1.65 g, 5 mmol) in water (10 cm^3) was treated with 30% H_2O_2 (6 cm^3). The yellow solution formed was treated with dilute hydrochloric acid dropwise until it just turned colourless (pH 2.5). Tetraphenylarsonium chloride (4.2 g, 10 mmol) in water (20 cm^3) was added dropwise giving rise to a cream precipitate. The solid was filtered off washed with water (10 cm^3) and diethyl ether (2 × 10 cm^3) and air dried. The product is slightly hygroscopic and was stored *in vacuo*. Yield 3.17 g, 2.4 mmol (97%) (Found: C, 43.3; H, 3.3; O_2^{2-}, 9.5. Calc. for $C_{48}H_{40}As_2O_{11}W_2$: C, 43.0; H, 3.1; O_2^{2-}, 9.8%).

$[PPh_3(CH_2Ph)]_2[W_2O_3(O_2)_4]$.—This was obtained as a white solid by a method[25] similar to that described above for the synthesis of complex **7**. Yield 5.2 g, 4.2 mmol (83%) (Found: C, 48.3; H, 3.2; O_2^{2-}, 10.0. Calc. for $C_{48}H_{40}O_{11}P_2W_2$: C, 48.0; H, 3.6; O_2^{2-}, 10.2%).

Oxidation of Tertiary Amines by Complex **1**.—The oxidation of isonicotinic acid is typical. The complex $[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$ (0.1 g, 0.045 mmol) was dissolved in toluene (10 cm^3) and isonicotinic acid (0.93 g, 10 mmol) added. Hydrogen peroxide (15% w/v, 15 cm^3) was added to the resulting suspension and the mixture was refluxed at 90 °C for 6 h. Upon cooling the solid was filtered off, washed with water (10 cm^3), diethyl ether (2 × 10 cm^3) and air dried. Yield 1.00 g, 8.3 mmol (83%).

General Procedure for Oxidation of Tertiary Amines by Complexes **1**, **2** *or* **5**.—The catalyst (**5**) (0.06 mmol) was dissolved in toluene (10 cm^3) and the pyridine (10 mmol) added. Hydrogen peroxide (15% w/v, 15 cm^3) was added to the resulting suspension and the mixture was refluxed at 90 °C for 6 h. Upon cooling the solid was filtered off, washed with water (5 cm^3), diethyl ether (2 × 10 cm^3) and air dried. The yield, IR spectrum and melting point of the product were recorded.

General Procedure for Epoxidation of Cycloalkenes by Complex **5** *or* **7**.—The catalyst (**5** or **7**) (0.06 mmol) was dissolved in benzene (5 cm^3) and the cycloalkene (25 mmol) added. Hydrogen peroxide (15% w/v, 6 cm^3) was added to the organic component and the biphasic mixture refluxed at 70 °C for 3 h. The resulting organic layer was then analysed by gas chromatography (GC).

General Procedure for Epoxidation of Linear Alkenes by Complex **5**.—The catalyst (**5**) (0.06 mmol) was dissolved in benzene (5 cm^3) and the alkene (10 mmol) added. Hydrogen peroxide (15% w/v, 12 cm^3) was added to the benzene solution and the biphasic mixture refluxed at 70 °C for 20 h. The resulting organic layer was then analysed by GC and / or by ^1H NMR spectroscopy.

General Procedure for Oxidation of Primary and Secondary Alcohols by Complex **5** *or* **7**.—The catalyst (**5** or **7**) (0.06 mmol) was dissolved in benzene (5 cm^3) and the alcohol (10 mmol) added. Hydrogen peroxide (15% w/v, 10 cm^3) was added to the benzene solution and the biphasic mixture refluxed at 70 °C for 3 h. The resulting organic layer was then analysed by GC and/or GC–mass spectrometry.

Instrumentation.—Infrared spectra were measured as KBr discs on a Perkin-Elmer 1720 FT instrument. Raman spectra were recorded on spinning discs on a KBr matrix on a Spex Ramalog 5 instrument, with a Datamate data acquisition unit using excitation at 647.1 nm from a Coherent Radiation Innova 90 krypton-ion laser, and as powders on a Perkin-Elmer 1760 X FT-IR instrument fitted with a 1700 X NIR FT-Raman accessory (Spectron Nd:YAG laser, 1064 nm excitation). Proton and $^{31}P-\{^1H\}$ NMR spectra were measured on a JEOL EX-270 spectrometer (^1H, 270.05 MHz; ^{31}P, 109.25 MHz).

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