Activation of Bis(trimethylsilyl) Peroxide and *tert*-Butyl Hydroperoxide with Oxo and Peroxo Complexes of Vanadium, Molybdenum, and Tungsten for the Sulfoxidation of Thianthrene 5-Oxide

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Bis(trimethylsilyl) peroxide (BTSP) and *tert*-butyl hydroperoxide (*t*BuOOH) were activated by various oxo and peroxo complexes of molybdenum, tungsten, and vanadium as catalysts for the sulfoxidation of thianthrene 5-oxide (SSO). A screening of a number of phosphane oxide and amine oxide ligands revealed that BTSP was most efficiently activated by the $[MoO_5(OPtBu_3)]$ complex. The best results for *t*BuOOH as oxygen source were achieved with the vanadates $[VO(OR)_3]$ (R = *t*Bu, *i*Pr). Comparative selectivity and rate data for the stoichiometric and catalytic sulfoxidations of SSO mediated by the MoO_5L complex (L = $OPtBu_3$, $OPnOct_3$, $ONnBu_3$, $ONnOct_3$) suggest that the bisperoxo metal complex is the active oxygen transfer species.

Group -5, -6, and -7 transition metal peroxo complexes are well-established oxygen transfer agents in organic synthesis especially in view of their propensity for catalytic oxidations. Numerous reports describe their application in the activation of hydrogen peroxide and simple hydroperoxides such as *t*BuOOH for the epoxidation of olefins or the oxidation of alcohols to aldehydes and ketones[1]. Their ability to oxidize catalytically thioethers and sulfoxides and coordinated sulfur ligands continues to be a focus of current research[2,3,4].

In this type of metal-mediated oxygen transfer a large number of reactive peroxo metal oxidants, which either function stoichiometrically or catalytically, belong to the class of isoelectronically and structurally related bisperoxo complexes with an axial oxo ligand, two equatorial peroxo functionalities, and two σ-bonded ligands as in $[VO(O_2)_2(H_2O_2)]^-$[5], $[MO(O_3)_2\ (H_2O)HMPT]$ (M = Mo, W)[6], and $[ReO(O_2)_2(CH_3)(H_2O)]$[7]. Besides the peroxo functionality $[M(\eta^2\text{-}O_2)]$, other types of metal complexes with a d^0 electronic configuration are capable to serve as oxidation catalysts, for example $[M(O)_2Cl_2L_2]$[8] or $[(\eta^5\text{-}C_5Me_5)Mo(O)_2Cl]$[9]. They form the more reactive metal hydroperoxy [M(OOH)] (metal peracid) and alkyl peroxy [M(OOR)] (ester of metal peracid) functionalities by the addition of H_2O_2 or ROOH to the oxo ligand.

While *t*BuOOH is an established oxygen donor in such catalytic oxidations[1a–d], the metal-catalyzed activation of bis(trimethylsilyl) peroxide (BTSP) as oxygen donor appears to be essentially unexplored. The catalytic oxidation of secondary alcohols to ketones with BTSP, catalyzed by pyridinium dichromate, has been reported[10], but no epoxidations nor sulfoxidations by catalytically metal-activated BTSP seem to be known.

The interest of the present work was to study stoichiometric and catalytic sulfoxidations with transition metal peroxo complexes. For the stoichiometric oxidations, the Mimoun-type[6b] molybdenum bisperoxo complexes with *N*-oxide and *P*-oxide ligands instead of HMPT were to be used and compared with MoO_5(HMPT). Since the peroxo complexes with two such ligands are less reactive as oxidants than with only one, e.g. $[Mo(O)(O_2)_2(HMPT)_n]$ (n = 1, 2), the mono-substituted derivatives were to be employed. For the catalytic reactions, the oxo and peroxo complexes, which have been successfully used for the activation of H_2O_2 and *t*BuOOH[1], were chosen to test their ability to activate BTSP. For this purpose, complexes of the type $[M(O)_2Cl_2(dme)]$ (M = Mo, W)[8a] (dme = 1,2-dimethoxyethane), $[Mo(O)(O_2)_2L]$ (L = $OPtBu_3$, $OPnOct_3$, $ONiBu_3$, $ONnBu_3$, $ONnOct_3$), $[(C_5Me_5)W(O)_2nBu]$[11], and $[V(O)(OR)_3]$ (R = *i*Pr, *t*Bu) were to be used.

As substrate for the oxidation reactions, thianthrene 5-oxide (SSO) was to be employed, which is a well-established mechanistic probe for assessing the electronic character for oxygen transfer agents[12]. The oxidation of SSO leads to four products, namely the thianthrene 5,10-dioxides (*trans*- and *cis*-SOSO), thianthrene 5,5-dioxide (SSO_2), and the undesirable trioxide $SOSO_2$ (Scheme 1) as subsequent oxidation product (overoxidation) of all three dioxides.

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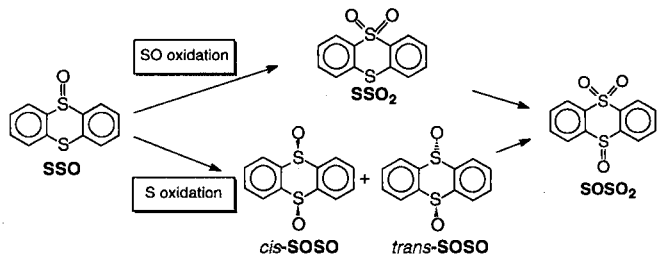
Scheme 1



$$X_{SO} = \frac{\text{SO oxidation}}{\text{total oxidation}} = \frac{SSO_2 + SOSO_2}{SSO_2 + SOSO + 2 \times SOSO_2}$$

The X_{SO} parameter was introduced (Scheme 1)[13] as differentiating measure of chemoselectivity between sulfoxide versus sulfide oxidation. Fortunately, in SSO the usually rather high reactivity difference (ca. 100-fold) between oxidation of the sulfides versus sulfoxide functionalities is sufficiently reduced (ca. fourfold)[2a], such that the X_{SO} parameter spans a convenient and accurately determinable reactivity range. For typical electrophilic oxidants ($X_{SO} \leq 0.3$), e.g. protonated hydrogen peroxide, peroxycarboxylic acids, dioxiranes, etc.[12], the X_{SO} parameter reflects differences in the electrophilic character for lone-pair oxidation at the sulfide versus sulfoxide site, while for typical nucleophilic oxidants ($X_{SO} \geq 0.7$), e.g. the deprotonated hydrogen peroxide, peroxycarboxylate anions, carbonyl oxides, etc., oxidation takes place preferentially by addition to the S=O bond.

Previous applications of the SSO probe for transition metal oxidants include the peroxo complexes of vanadium, molybdenum, and tungsten[1d,14,15], ruthenium tetraoxide, chromyl chloride, and permanganate[16]. However, since for these oxidants the previous analytical protocol was used, the quantitative results are suspect, and it was of importance to rectify this situation by reexamination with the revised analytical method[12].

Results

A number of new peroxo complexes of the Mimoun type[8b] were prepared, but instead of hexamethylphopshoric amide (HMPT) as ligand, we chose amine oxide and phosphane oxide ligands with linear alkyl chains to increase their lipophilic character and solubility in organic solvents. The latter were obtained by the addition of one equivalent of OER_3 (E = N, P; R = *t*Bu, *i*Bu, *n*Bu, *n*Oct), dissolved in an organic solvent, to a freshly prepared solution of $[MoO_5(H_2O)_2]$[6]. The water-insoluble complexes $[MoO_5(OER_3)(H_2O)]$ were dehydrated in vacuo with P_4O_{10} to yield $[MoO_5(OER_3)]$ (**1**–**5**) or an coordination oligomer of this composition. The *N*-oxide complexes were prepared in situ by adding the tertiary amines to the solution of $[MoO_5(H_2O)_2]$ in H_2O_2 (30%) as described in the preparation of pyridine *N*-oxide complexes $[MO_5(Opy)_2]$ (M = Mo, W)[17].

	$MoO_5(OER_3)$				
	1	**2**	**3**	**4**	**5**
E	P	P	N	N	N
R	*t*Bu	*n*Oct	*i*Bu	*n*Bu	*n*Oct

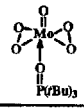
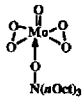
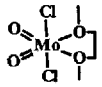
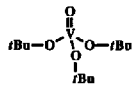
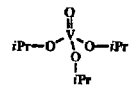
All peroxo complexes **1**–**5** are thermally labile and have a defined decomposition temperature, as established by differential thermal analysis (DTA). Peroxo complex **2** with $OPnOct_3$ as donor ligand decomposes spontaneously at 81 °C, while the analogous amine *N*-oxide complex **5** decomposes already at 60 °C. Notable is the higher thermal stability of the *n*-butyl derivative **4** (94 °C) compared to the isobutyl one **3** (72 °C). However, at room temperature (ca. 20 °C) both complexes can be handled easily and stored in the dark at −30 °C without decomposition for several months.

The IR spectra of the complexes **1**–**5** show the expected characteristic ν(O–O) absorptions for the symmetric and asymmetric valence vibrations $\nu(MoO_2)$ in the region of 850–875 and 540–595 cm^{-1}[6]. The phosphane oxide ligands of the peroxo complexes show the typical bands ν(P=O) at 1194 (**1**) and 1078 cm^{-1}(**2**)[6]. The absorptions of the ν(N–O) vibration of the amine *N*-oxide ligands in the complexes **3**–**5** overlap with those of the ν(Mo=O), which appear at 964 (**3**) and 970 cm^{-1} (**4**, **5**).

The ^{31}P-NMR spectra ($CDCl_3$, ca. 20 °C) of the phosphane oxide complexes **1** and **2** indicate coordination of the phosphorus oxygen atom (δ = 96.5 for **1** and 83.2 for **2**) to the Lewis-acidic d^0 metal center by the typical low-field shift of ca. 30 ppm compared to the free phosphane oxides (δ = 65.4 for tBu_3PO and 49.0 for $nOct_3PO$). In the ^{1}H-NMR spectra, the signals of the protons of the *tert*-butyl group in complex **1** show a doublet at δ = 1.55 and a coupling constant $^3J_{PH}$ of 13.9 Hz. While the methylene protons of the derivatives **2** and **5** possess complex multiplets in the ^{1}H-NMR spectra, the proton resonances of complexes **3** and **4** were definitively assigned. The ^{13}C-NMR spectra of the complexes **1** and **2** display characteristic J_{CP} coupling constants. While derivative **1** shows only one doublet with a coupling constant $^1J_{CP}$ = 45.3 Hz for the quaternary carbon atoms, complex **2** exhibits the three distinct couplings $^1J_{CP}$ = 62.9, $^2J_{CP}$ = 3.7, and $^3J_{CP}$ = 15.7 Hz. The ^{13}C-NMR signals for the $(CH)_\alpha$ and $(CH_2)_\alpha$ carbon atoms of the amine oxide complexes **3**–**5** are low-field shifted by ca. 10 ppm compared to the free trialkylamines.

The catalytic oxidations were performed in CH_2Cl_2 with a limiting amount (50 mol%) of BTSP or *t*BuOOH and 10 mol % of catalyst. Both oxygen donors did not react with SSO at room temperature (ca. 20 °C) even after several days when no catalyst was present. Fortunately, since SSO is a much less reactive substrate than dialkyl sulfides[18], SSO is only slowly oxidized by BTSP at 60 °C. We preferred room temperature in order to obtain convincing evidence for activation by the transition metal complex. After consumption of the peroxide as confirmed by the KI/starch test (for BTSP after hydrolysis), the samples were submitted to HPLC analyses. The results are summarized in Table 1.

Table 1. Catalytic oxidation[a] of thianthrene 5-oxide (SSO) with *t*BuOOH and BTSP

entry	catalyst (10 mol%)[b]	oxygen donor (50 mol%)[b]	conv.[c] (%)	product ratio (%)[d] SSO_2	SOSO *cis*	SOSO *trans*	$SOSO_2$	X_{SO}[e]
1a	 (1)	BTSP	58	9.7	11	74	5.9	**0.15**
1b		*t*BuOOH	35	13	12	73	2.0	**0.14**
2a	 (5)	BTSP	38	15	15	62	7.9	**0.21**
2b		*t*BuOOH	2.5	13	16	45	27	**0.31**
3a		BTSP	42	5.2	16	77	1.1	**0.06**
3b		*t*BuOOH	50	5.3	3.3	91	0.0	**0.05**
4a		BTSP	37	8.1	22	67	2.9	**0.11**
4b		*t*BuOOH	36	6.3	6.7	87	0.0	**0.06**
5a		BTSP	22	9.3	39	47	4.4	**0.13**
5b		*t*BuOOH	49	10	26	59	4.7	**0.14**
6a		BTSP	24	9.9	37	48	5.3	**0.14**
6b		*t*BuOOH	48	10	29	56	4.7	**0.14**

[a] At 25°C, 20 h. – [b] Relative to SSO. – [c] Conversion of the thianthrene 5-oxide after total consumption of the peroxide as determined by the KI/starch test. – [d] HPLC analysis: RP-18, MeOH/H_2O/MeCN (64:34:2) as eluent, error ±3% of the stated values, normalized to 100%. – [e] X_{SO} is defined in Scheme 1, error ±0.03 units.

The activation of *t*BuOOH was possible with the *P*-oxide complex [$MoO_5(OPtBu_3)$] (Table 1, entry 1b), but failed for the corresponding *N*-oxide complex $MoO_5(ONnOct_3)$ (Table 1, entry 2b) since only 2.5% conversion of SSO was achieved. While the [$M(O)_2Cl_2(dme)$] complexes (M = Mo, W) substantially activated both BTSP and *t*BuOOH (Table 1, entries 3 and 4), the [$(C_5Me_5)W(O)_2nBu$] complex was ineffective as catalyst for both oxygen donors (not in Table 1). The vanadium complexes [$VO(OR)_3$] (R = *t*Bu, *i*Pr) in Table 1 (entries 5 and 6) activated about half of the BTSP and decomposed the other half (22 and 24% conversions of SSO when 50 mol % of BTSP was applied). For comparison, the activation of *t*BuOOH leads to complete oxygen transfer (49 and 48% conversions of SSO when 50 mol % of *t*BuOOH was applied) without decomposition.

The oxidation of SSO by the BTSP/[$MoO_5(OPtBu_3)$] oxidant (Table 1, entry 1a) is quite efficient since nearly all of the available active oxygen content was transferred. The X_{SO} value (0.15; Table 1, entry 1a) was slightly higher than in the stoichiometric oxidation (0.09; Table 2, entry 1b).

This effect was also found for the activation of BTSP by the *N*-oxide complex [$MoO_5(ONnOct_3)$] (**5**), for which the X_{SO} value rose from 0.15 (Table 2, entry 2b) to 0.21 (Table 1, entry 2a).

The stoichiometric oxidations with limiting amounts (25 mol %) of the Mimoun-type molybdenum bisperoxo complexes are presented in Table 2. For comparison, the oxidation of SSO with the classical Mimoun complex

Table 2. Stoichiometric oxidation[a] of thianthrene 5-oxide (SSO) by molybdenum bisperoxo complexes

entry	MoO_5L[b] L[f]	conv.[c] (%)	product ratio (%)[d] SSO_2	SOSO *cis*	SOSO *trans*	$SOSO_2$	X_{SO}[e]
1a	**O=P(NMe$_2$)$_3$**	27	7.0	38	54	1.1	**0.08**
1b	**O=P*t*Bu$_3$**	30	4.6	29	62	4.9	**0.09**
1c	**O=P*n*Oct$_3$**	26	6.8	39	50	3.7	**0.10**
2a	**O-N*n*Bu$_3$**	9	13	22	65	0.3	**0.13**
2c	**O-N*n*Oct$_3$**	11	15	14	71	0.0	**0.15**

[a] At 25°C, 1–3 d. – [b] 25 mol % of the oxidant MoO_5L was employed. – [c] Conversion of thianthrene 5-oxide after total consumption of the peroxide as confirmed by the KI/starch test, 25% SSO conversion represents 50% oxygen transfer if both peroxo groups are active. – [d] Analyzed by HPLC: RP-18, MeOH/H_2O/MeCN (64:34:2) as eluent, error ±3% of the stated values, normalized to 100%. – [e] X_{SO} is defined in Scheme 1, error ±3% of the stated values. – [f] Complex **3** (L = ON*i*Bu$_3$) rapidly decomposed under these conditions.

[$MoO_5(HMPT)$][6] (entry 1a) at room temperature was performed, which resulted mainly in *trans*-SOSO, as previously reported[2a]. The X_{SO} value of the Mimoun complex (0.08, entry 1a) is identical within the error limit to those of the other molybdenum bisperoxo complexes with phosphane oxide ligands, namely [$MoO_5(OPtBu_3)$] (0.09, entry 1b) and

$[MoO_5(OPnOct_3)]$ (0.10, entry 1c). The X_{SO} values for the molybdenum bisperoxo complexes with the amine *N*-oxide ligands are generally slightly higher and range from 0.13 to 0.15 (Table 2, entries 2a, b).

The *P*-oxide complexes transferred about 50% of the available active oxygen content to the SSO substrate. The conversion/time profile of the SSO oxidation for $[MoO_5(OPtBu_3)]$ (**1**) is shown in Table 3.

Table 3. Conversion/time profile of the catalytic and stoichiometric SSO oxidations[a]

entry	metal complex (10 mol%)	oxygen donor (10 mol%)	conversion (%)[b] 0.4 h	5 h	23 h
1	$[MoO_5(OPtBu_3)]$	-	9.6	9.8	10.0
2	$[MoO_5(OPtBu_3)]$	*t*BuOOH	9.3	11.6	13.9
3	$[MoO_5(OPtBu_3)]$	BTSP	13.6	17.6	19.5

[a] All reactions were performed at 20 °C in CH_2Cl_2. – [b] Analyzed by HPLC: RP-18, MeOH/H_2O/MeCN (64:34:2) as eluent, error ±3% of the stated values, normalized to 100%.

For the R_3NO complexes (R = *n*Bu, *n*Oct), less than one half of the available active oxygen was transferred, the rest was lost by unproductive decomposition. With the R_3NO complexes, especially those with branched alkyl substituents (e.g. R = *i*Bu), the decomposition path of the bisperoxo complex is favored. Indeed, the isobutyl derivative **3** is the least persistent one and decomposes spontaneously under these conditions.

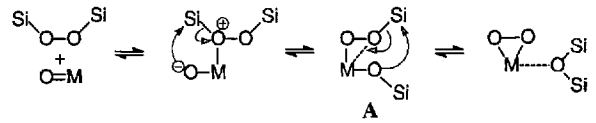
Discussion

It is apparent that the X_{SO} values of these bisperoxo complexes, which might be regarded as *metalladioxiranes*, are very similar to those measured for the authentic dioxiranes[19] of acetone (DMD), trifluoroacetone (TFD), isopropyl methyl ketone, and cyclohexanone (X_{SO} ca. 0.1). The X_{SO} values for the molybdenum bisperoxo complexes with the amine *N*-oxide ligand are generally a little bit higher (0.14 ± 0.01; Table 2, entries 2a, b) than those with *P*-oxide ligands (0.09 ± 0.01; Table 2, entries 1a–c). This seems to reflect the higher electron densities in the *N*-oxide compared to the *P*-oxide complexes. The negative charge at the oxygen donor atom of $R_3P{=}O$ is better compensated than in the purely zwitterionic $R_3N^+{-}O^-$ due to $d_\pi{-}p_\pi$ double bond character in P=O. Consequently, R_3PO ligands are less ionic and have a poorer coordinating ability as confirmed by the fact that they can be replaced by the more nucleophilic R_3NO ligands[20].

Compared to the authentic dioxiranes, for the peroxo complexes some more mechanistic alternatives have to be considered[19]. For example, precomplexation is possible, but was recently ruled out[2a]. By monitoring the oxidation by ^{1}H-NMR spectroscopy, we were also unable to detect any intermediate in which the substrate SSO is complexed as ligand to the Lewis-acidic metal center.

In the catalytic of BTSP and *t*BuOOH, the M=O functionality of the coordinatively unsaturated oxo metal complex seems to play a decisive role[21]. Thus, an oxo metal complex qualifies to be a potential catalyst if it is able to add BTSP (or *t*BuOOH) across the double bond [M=O] (Scheme 2). An intermediary silylperoxy (or hydroperoxy) functionality is presumably generated on the way to a peroxo complex.

Scheme 2



The complexes in entries 3–6 (Table 1) used for activating BTSP and *t*BuOOH are oxo and not peroxo species. Since the latter are not available, comparison is not possible between the stoichiometric and catalytic oxidations of the corresponding peroxo complexes.

The *t*BuOOH as well as BTSP oxidations, catalyzed by the oxo complexes $[M(O)_2Cl_2(dme)]$ (M = Mo, W) and $[VO(OR)_3]$ (R = *t*Bu, *t*Pr), are electrophilic in character as confirmed by the low X_{SO} values (Table 1, entries 3b–6b). The general trend in the catalytic activity of these oxo complexes is a higher efficiency in the activation of *t*BuOOH than BTSP except the tungsten complex (Table 1, entries 4a, b), for which equal activity was observed. The competing decomposition of BTSP, especially for the oxo complexes of vanadium (Table 1, entries 5a, 6a), lowers the catalytic efficacy and needs to be minimized by proper ligand design.

To elucidate the nature of the active oxygen transfer species, the conversion/time profile was measured (Tabe 3). The results reveal that compared with the stoichiometric oxidations, the rate of oxygen transfer to SSO by $[MoO_5(OPtBu_3)]$ is not accelerated significantly in the presence of BTSP or *t*BuOOH. The activation of *t*BuOOH was significantly slower than that of BTSP (see Experimental Section). Apparently, BTSP and *t*BuOOH affect only the regenration of the bisperoxo complex, but it cannot be ruled out that other not detected intermediate metal peroxide species derived from the reaction of BTSP (e.g. intermediate **A**, Scheme 2) with the metal complex are also involved in the oxygen transfer. This is expecially likely for *t*BuOOH, which is known to form very active *tert*-butylperoxy complexes of vanadium(V) and molybdenum(VI)[1c,21]. In this context, Thiel et al. reported[22] that species of the type [MO*t*Bu] proposed in the activation of *t*BuOOH are more reactive for epoxidation than the bisperoxo complex itself.

In summary, some of the catalyst/oxygen donor combinations in Table 1 are entirely new, especially those with BTSP, which for the first time could be activated for catalytic oxidation. Definitely all of these oxygen transfer agents are electrophilic in character, as confirmed by the low X_{SO} values for the oxidation of thianthrene 5-oxide. Thus, the activation of BTSP by oxo and bisperoxo complexes provides a novel method for catalytic sulfoxidation.

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Experimental

NMR: Bruker AC 200 (^{1}H at 200.1, ^{31}P at 81.0, ^{13}C at 50.3 MHz), room temp. (ca. 20°C), if not noted otherwise. All ^{31}P and ^{13}C NMR spectra are proton broad-band decoupled, and the carbon multiplicities are not given. The methylene resonances in the ^{13}C-NMR spectra were confirmed by DEPT measurements. Standards CD_2Cl_2 (δ = 5.32), $CDCl_3$ (δ = 7.24) for the ^{1}H-NMR and CD_2Cl_2 (δ = 54.20), $CDCl_3$ (δ = 77.00) for the ^{13}C-NMR spectra. For the ^{31}P-NMR spectra, 85% H_3PO_4 served as external standard. – IR: Bruker IFS 25, software package "Spektrafile IR plus" of Heyden & Son GmbH, and Perkin-Elmer 283 or 1420. The solids were recorded as nujol mulls, liquids as a film between KBr plates. Abbreviations: weak (w), medium (m), strong (s), very strong (vs), broad (br), out of plane (op) vibration of the aromatic ring. – HPLC analyses: Carried out as described elsewhere[1b], system equipped with a C-18 reversed-phase column, $CH_3OH/H_2O/CH_3CN$ (64:34:2) as eluent. Detection was performed at λ = 254 nm, and the identification of the peaks was verified by their UV spectra (250–450 nm) on a Kontron detector 430. As internal standard *trans*-1-phenyl-1-penten-3-one was added as chloroform solution after the reaction in the dark to avoid photoisomerization.

The weighing of the extremely air- and moisture-sensitive substances as well as the preparation of the spectroscopic samples was performed in a Glovebox (Type MB 150 BG-I, Fa. Braun) under a thoroughly cleaned argon. All solvents were purified by standard methods and were dried and stored over activated molecular sieves (Fluka 3 or 4 Å).

Oxidations were performed in distilled solvents ($CHCl_3$ and CH_2Cl_2 were distilled over P_4O_{10}). The catalysts were added as stock solutions.

The compounds $[Mo(O)_2Cl_2(dme)]$[23], $[W(O)_2Cl_2(dme)]$[23], $[MoO_5(HMPT)]$[6], and $OPtBu_3$[24] were prepared as described in the literature. The syntheses of the new complexes are described below.

Preparation of $[Mo(O)(O_2)_2(OPtBu_3)]$ (**1**): MoO_3 (660 mg, 4.59 mmol) was suspended in 30% H_2O_2 (3.0 ml, 26.5 mmol) at 40°C for 4 h. After a clear, yellow solution had formed, tBu_3PO (990 mg, 4.54 mmol) was added as finely powdered solid. A pale yellow precipitate was obtained, which after 1 h was collected by filtration and washed with water (3 × 5 ml). The crude product was dried for 16 h at 25°C/5 · 10^{-5} mbar with P_4O_{10} to yield 1.72 g (96%) of a pale yellow amorphous solid. – DTA: 140°C (dec.). – ^{1}H NMR (25°C, CD_2Cl_2, TMS): δ = 1.55 [d, 27H, CH_3, ^3J(P,H) = 13.9 Hz]. – ^{13}C NMR (25°C, CD_2Cl_2, TMS): δ = 29.4 (CH_3), 41.5 [d, $C(CH_3)_3$, ^1J(C,P) = 45.3 Hz]. – ^{31}P NMR (25°C,CD_2Cl_2, H_3PO_4): δ = 96.5 (s). – IR (Nujol): $\tilde{\nu}$ = 1194 cm^{-1} s, [ν(P=O)], 1154 (vs), 1071 (vs), 1019 (m), [963 vs, ν(Mo=O)], 927 (m), [873 vs, ν(O–O)], 807 (vs), 717 (w), 658 (s), 636 vs), [593 s, $\nu_{as}(MoO_2)$], [554 m, $\nu_s(MoO_2)$], 518 (m), 499 (s), 427 (w). – $C_{12}H_{27}MoO_6P$ (394.3): calcd. C 36.56, H 6.90; found C 36.33, H 6.82.

Preparation of $[Mo(O)(O_2)_2(OPnOct_3)]$ (**2**): MoO_3 (371 mg, 2.58 mmol) was suspended in 30% H_2O_2 (1.46 ml, 12.9 mmol) at 40°C for 4 h. After a clear, yellow solution had formed, a solution of $nOct_3PO$ (500 mg, 1.29 mmol) in 4 ml of THF was added. After 2 h, the solution was concentrated to 3 ml under reduced pressure (25°C/10^{-2} mbar), and a yellow oil separated. The reaction mixture was extracted with CH_2Cl_2 (3 × 5 ml), and the combined extracts were evaporated to dryness (25°C/10^{-2} mbar). The residue was washed with water (2 × 2 ml) and dried for 6 h at 25°C/5 · 10^{-5} mbar to yield 675 mg (93%) of a pale yellow wax. – DTA: 81°C (dec.). – ^{1}H NMR (25°C, $CDCl_3$, TMS): δ = 0.85 [t, 9H, CH_3, ^2J(H,H) = 6.6 Hz], 1.12–1.50 [m, 30H, CH_2-(3–7)], 1.51–79 (m, 6H, CH_2-2), 2.04–2.18 (m, 6H, CH_2-(1). – ^{13}C NMR (25°C, $CDCl_3$, TMS): δ = 14.7 (C-8), 21.9 [d, C-2, ^2J(C,P) = 3.7 Hz], 26.3 [d, C-1, ^1J(C,P) = 62.9 Hz], 23.2, 29.6, 29.7, 32.4, 31.5 [d, C-3, ^3J(C,P) = 15.7 Hz]. – ^{31}P NMR (25°C, $CDCl_3$, H_3PO_4): δ = 83.2. – IR (Nujol): $\tilde{\nu}$ = 1245 cm^{-1} (m), 1228 (w), 1203 (m), [1078 s, ν(P=O)], [969 vs, ν(Mo=O)], [868 vs, ν(O–O)], 718 (s), 695 (s), 609 (w), [592 vs, $\nu_{as}(MoO_2)$], [551 m, $\nu_s(MoO_2)$], 526 (m), 509 (m), 454 (w). – $C_{24}H_{51}PMoO_6$ (562.6): calcd. C 51.24, H 9.14; found C 51.68, H 9.45.

Preparation of $[Mo(O)(O_2)_2(ONiBu_3)]$ (**3**): MoO_3 (350 mg, 2.43 mmol) was suspended in 30% H_2O_2 (2.75 ml, 24.3 mmol) at 40°C for 4 h. After a clear, yellow solution had formed, $NiBu_3$ (300 mg, 1.62 mmol) was added dropwise, and a dark yellow oil separated. After stirring for 2 h at 25°C, a yellow precipitate had formed. The precipitate was collected by filtration, washed with water (3 × 5 ml) and pentane (2 × 2 ml), and dried 6 h at 25°C/5 · 10^{-5} mbar to yield 580 mg (95%) of a pale yellow, amorphous solid. – DTA: 72°C (dec.). – ^{1}H NMR (25°C, $CDCl_3$, TMS): δ = 1.08 [d, 18H, CH_3, ^2J(H,H) = 6.7 Hz], 2.00–2.19 (m, 3H, CH), 3.01–3.21 (br, 6H, CH_2). – ^{13}C NMR (25°C, $CDCl_3$, TMS): δ = 21.4 (CH_3), 24.9 (CH), 62.3 (CH_2). – IR (Nujol): $\tilde{\nu}$ = 1273 cm^{-1} (m), 1172 (m), 1106 (m), 1014 (m), 1004 (m), [964 vs, ν(Mo=O)], 938 m, [852 vs, ν(O–O)], 817 (w), 720 (m), 639 (vs), [583 vs, $\nu_{as}(MoO_2)$], [538 m, $\nu_s(MoO_2)$], 520 (m). – $C_{12}H_{27}MoNO_6$ (377.3): calcd. C 38.20, H 7.21, N 3.71; found C 38.12, H 7.22, N 3.78.

Preparation of $[Mo(O)(O_2)_2(ONnBu_3)]$ (**4**): MoO_3 (613 mg, 4.26 mmol) was suspended in 30% H_2O_2 (5.60 ml, 49.4 mmol) at 40°C for 4 h. After a clear, yellow solution had formed, nBu_3N (464 mg, 2.50 mmol) was added dropwise. After stirring for 48 h, a pale yellow precipitate formed. The precipitate was collected by filtration, washed with water (3 × 5 ml) and pentane (3 × 5 ml), and dried for 6 h at 25°C/5 · 10^{-5} mbar to yield 830 mg (88%) of a pale yellow, amorphous solid. – DTA: 94°C (dec.). – ^{1}H NMR (25°C, $CDCl_3$, TMS): δ = 0.95 [t, 9H, CH_3, ^2J(H,H) = 6.8 Hz], 1.10–1.45 (sex, 30H, CH_2-3), 1.71–1.78 (m, 6H, CH_2-2), 3.57–3.66 (m, 6H, CH_2-1). – ^{13}C NMR (25°C, $CDCl_3$, TMS): δ = 13.7 (C-4), 19.54 (C-3), 24.6 (C-2), 63.9 (C-1). – IR (Nujol): $\tilde{\nu}$ = 1722 cm^{-1} (w), 1096 (m), 1320 (w), [970 vs, ν(Mo=O)], 911 (m), [851 vs, ν(O–O)], 820 (w), 768 (m), 724 (m), 642 (vs), [593 vs, $\nu_{as}(MoO_2)$], [541 s, $\nu_s(MoO_2)$], 519 (m). – $C_{12}H_{27}MoNO_6$ (377.3): calcd. C 38.20, H 7.21, N 3.71; found C 38.41, H 7.04, N 3.91.

Preparation of $[Mo(O)(O_2)_2(ONnOct_3)]$ (**5**): MoO_3 (309 mg, 2.15 mmol) was suspended in 30% H_2O_2 (2.45 ml, 21.5 mmol) at 40°C for 4 h. After a clear, yellow solution had formed, $NnOct_3$ (570 mg, 1.61 mmol) was added dropwise, and a dark yellow oil separated, which solidified after stirring for 48 h. The yellow precipitate was collected by filtration, washed with water (3 × 5 ml), and dried 6 h at 25°C/5 · 10^{-5} mbar to yield 877 mg (75%) of a pale yellow, amorphous solid. – DTA: 60°C (dec.). – ^{1}H NMR (25°C, $CDCl_3$, TMS): δ = 0.84 [t, 9H, CH_3, ^2J(H,H) = 6.2 Hz], 1.10–1.45 [m, 30H, CH_2-(3–7)], 1.60–1.85 (m, 6H, CH_2-2), 3.31–3.51 (m, 6H, CH_2-1). – ^{13}C NMR (25°C, $CDCl_3$, TMS): δ = 14.0 (C-8), 22.6, 22.7, 26.09, 29.0, 29.4, 31.6 (C-2), 64.0 (C-1). – IR (Nujol): $\tilde{\nu}$ = 1096 cm^{-1} (m), 1320 (w), [970 vs, ν(Mo=O)], 911 (m), [851 vs, ν(O–O)], 820 (w), 768 (m), 724 (m), 642 (vs), [593

vs, $\nu_{as}(MoO_2)$], [541 s, $\nu_s(MoO_2)$], 519 (m) cm^{-1}. – $C_{24}H_{51}MoNO_6$ (545.6): calcd. C 52.83, H 9.42, N 2.57; found C 52.52, H 9.50, N 2.53.

Stoichiometric Oxidations of Thianthrene 5-Oxide with the Molybdenum Bisperoxo Complexes **1**–**5**: To a solution of 19.0 mg (0.0818 mmol) thianthrene 5-oxide in 2 ml CH_2Cl_2 was added at room temp. (ca. 20°C) a stock solution of the bisproxo complex (ca. 0.02–0.04 M, 25 mol %). After 1–3 d, the peroxide was consumed (as tested by KI/starch paper), and the samples were analyzed directly by HPLC without workup. The results are summarized in Table 2.

Catalytic Oxidations of Thianthrene 5-Oxide with tBuOOH and $Me_3Si-O-O-SiMe_3$ (BTSP): To a solution of 17.0 mg (0.0733 mmol) thiantrene 5-oxide in 1.8 ml CH_2Cl_2 was added at room temp. a stock solution of BTSP or *t*BuOOH (ca. 0.08 M, 0.0367 mmol, 50 mol %) followed by a stock solution of the catalyst (ca. 0.02–0.17 M, 10 mol %). After 20 h, the peroxide was consumed (as tested by KI/starch paper), and the samples were directly analyzed by HPLC without workup. The results are summarized in Table 1.

Conversion/Time Profile of the Thianthrene 5-Oxide Oxidation by $[MoO_5(OPtBu_3)]$: To a solution of 100 mg (0.430 mmol) thianthrene 5-oxide in 1.8 ml CH_2Cl_2 was added at room temp. (ca. 20°C) a stock solution of BTSP or *t*BuOOH (0.05 M, 10 mol %), followed by a stock solution (0.02 M, 10 mol %) of $[MoO_5(OPtBu_3)]$ (Table 3, entries 2, 3). The conversions were determined by HPLC analysis, in which small aliquots of the reaction mixtures were directly injected. For comparison, the conversion for the bisperoxo complex alone was also determined. The results are collected in Table 3.

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