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Synthesis, Structure, and Catalytic Oxidation Chemistry from the First Oxo–Imido Schiff Base Metal Complexes

Ramkrishna Ramnauth, Salih Al-Juaid, Majid Motevalli, Bernardetta C. Parkin, and Alice C. Sullivan*

Department of Chemistry, Queen Mary, University of London, Mile End Road,
London, E1 4NS U.K.

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The molybdenum oxo–imido complex, [Mo(O)(N^{t}Bu)Cl$_2$(dme)] (**1**), was obtained from the reaction between [MoO$_2$Cl$_2$(dme)] and [Mo(N^{t}Bu)$_2$Cl$_2$(dme)]. Reactions between [Mo(O)(NR)Cl$_2$(dme)] (where R = ^{t}Bu or 2,6-^{i}Pr$_2$C$_6$H$_3$) and the disodium Schiff base compounds Na$_2$(3,5-^{t}Bu$_2$)$_2$salen, Na$_2$(3,5-^{t}Bu$_2$)$_2$salpen, and Na$_2$(7-Me)$_2$salen afforded the first oxo–imido transition metal Schiff base complexes: [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salen}] (**2**), [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}] (**3**), and [Mo(O)(N-2,6-^{i}Pr$_2$C$_6$H$_3$){(7-Me)$_2$salen}] (**4**), respectively. The compounds [Mo(N^{t}Bu)$_2${(3,5-^{t}Bu$_2$)$_2$salpen}] (**5**) from [Mo(N^{t}Bu)$_2$(NH^{t}Bu)$_2$] and [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2${(7-Me)$_2$salen}] (**6**) from [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(NH^{t}Bu)$_2$] (**7**) are also reported. Compounds **1**–**7** were characterized by NMR, IR, and FAB mass spectroscopy while compounds **3**, **4**, and **5** were additionally characterized by X-ray crystallography. In conjunction with ^{t}BuOOH as oxidant, compound **3** is a catalyst for the oxidation of benzyl alcohol to benzaldehyde and *cis*-cyclooctene and 1-octene to the corresponding epoxides.

Introduction

Metal bis-imido and metal bis-oxo complexes are well-established classes,[1] but there are comparatively fewer mixed oxo−imido metal complexes. The latter can be broadly categorized according to the coordination modes the oxo and imido groups exhibit as shown by the examples in Figure 1.

Other examples of mixed oxo−imido complexes are known, for example, Cr(VI),[8a,b] W(VI),[8c] and Os(VIII)[8d] where these π-donor groups stabilize the high oxidation state of the metals. Kühn et al. have carried out theoretical and spectroscopic investigations on monomer−dimer equilibria in mixed oxo−imido rhenium compounds.[9]

In this paper, we report on the synthetic and structural aspects of the first transition metal oxo−imido Schiff base compounds of the type [Mo(O)(NR)L], where R is ^{t}Bu or 2,6-^{i}Pr$_2$C$_6$H$_3$ and L is a tetradentate Schiff base ligand (see Scheme 1). We also report results from a preliminary investigation of the catalytic activity of one of these compounds toward oxidation of the substrates benzyl alcohol, *cis*-cyclooctene, and 1-octene. Tetradentate Schiff base ligands are well-known for provision of stereo control in oxidation reactions at transition metal centers.[10]

Results and Discussion

Synthesis and Characterization. The molybdenum oxo−imido complex, [Mo(O)(N^{t}Bu)Cl$_2$(dme)] (**1**), was obtained

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* To whom correspondence should be addressed. E-mail: a.c.sullivan@qmul.ac.uk.

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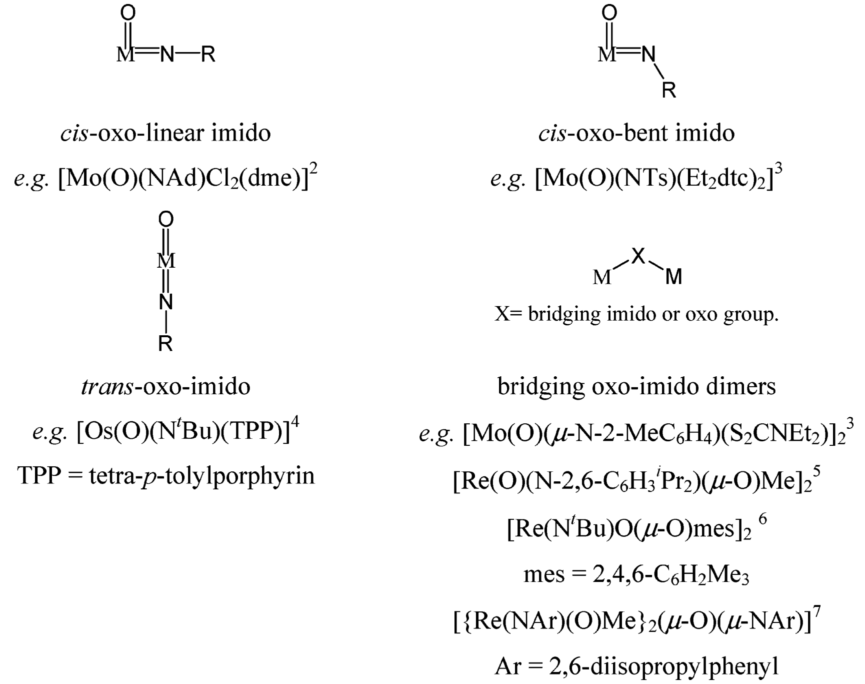


cis-oxo-linear imido

e.g. $[\mathrm{Mo(O)(NAd)Cl_2(dme)}]$[2]

cis-oxo-bent imido

e.g. $[\mathrm{Mo(O)(NTs)(Et_2dtc)_2}]$[3]

X= bridging imido or oxo group.

trans-oxo-imido

e.g. $[\mathrm{Os(O)(N^tBu)(TPP)}]$[4]

TPP = tetra-*p*-tolylporphyrin

bridging oxo-imido dimers

e.g. $[\mathrm{Mo(O)(\mu\text{-}N\text{-}2\text{-}MeC_6H_4)(S_2CNEt_2)}]_2$[3]

$[\mathrm{Re(O)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(\mu\text{-}O)Me}]_2$[5]

$[\mathrm{Re(N^tBu)O(\mu\text{-}O)mes}]_2$[6]

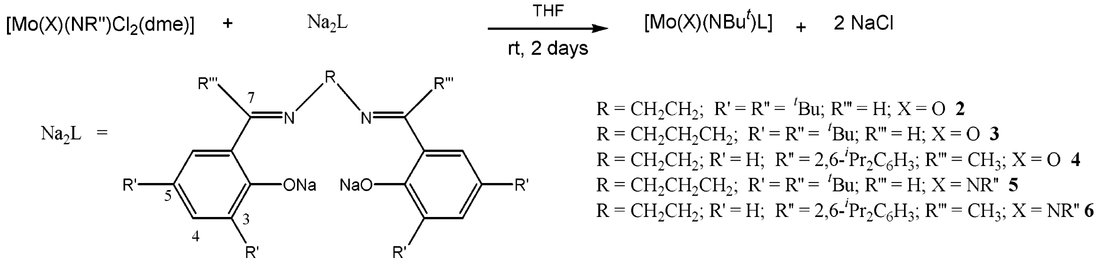
mes = $2,4,6\text{-}\mathrm{C_6H_2Me_3}$

$[\{\mathrm{Re(NAr)(O)Me}\}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{NAr})]$[7]

Ar = 2,6-diisopropylphenyl

Figure 1. Coordination modes seen in mixed oxo−imido complexes.

Scheme 1

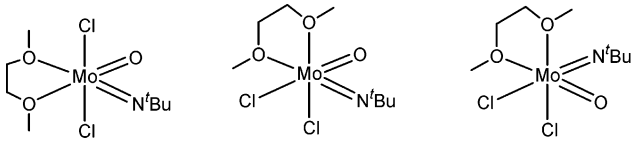


$\mathrm{R = CH_2CH_2;\ R' = R'' = {}^tBu;\ R''' = H;\ X = O}$ **2**
$\mathrm{R = CH_2CH_2CH_2;\ R' = R'' = {}^tBu;\ R''' = H;\ X = O}$ **3**
$\mathrm{R = CH_2CH_2;\ R' = H;\ R'' = 2,6\text{-}{}^iPr_2C_6H_3;\ R''' = CH_3;\ X = O}$ **4**
$\mathrm{R = CH_2CH_2CH_2;\ R' = R'' = {}^tBu;\ R''' = H;\ X = NR''}$ **5**
$\mathrm{R = CH_2CH_2;\ R' = H;\ R'' = 2,6\text{-}{}^iPr_2C_6H_3;\ R''' = CH_3;\ X = NR''}$ **6**

following the reaction between $[\mathrm{MoO_2Cl_2(dme)}]$[11a] and $[\mathrm{Mo(N^tBu)_2Cl_2(dme)}]$.[11b] The reaction between **1** and $\mathrm{Na_2(3,5\text{-}{}^tBu_2)_2salen}$ or $\mathrm{Na_2(3,5\text{-}{}^tBu_2)_2salpen}$ in THF afforded the oxo−imido compounds $[\mathrm{Mo(O)(N^tBu)\{(3,5\text{-}{}^tBu_2)_2salen\}}]$ (**2**) and $[\mathrm{Mo(O)(N^tBu)\{(3,5\text{-}{}^tBu_2)_2salpen\}}]$ (**3**). The compound $[\mathrm{Mo(O)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)\{(7\text{-}Me)_2salen\}}]$ (**4**) was obtained in low yield from the reaction between $[\mathrm{Mo(O)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2(dme)}]$[12] and $\mathrm{Na_2(7\text{-}Me)_2salen}$. The oxo−imido synthetic work is summarized in Scheme 1.

Compounds **5** and **6** were prepared from $[\mathrm{Mo(N^tBu)_2(N^tBuH)_2}]$[8c] and $[\mathrm{Mo(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2(NH^tBu)_2}]$ (**7**), respectively, and the appropriate diprotonated Schiff bases, in the manner we previously described for $[\mathrm{Mo(N^tBu)_2\{(3,5\text{-}{}^tBu_2)_2salen\}}]$.[13]

Compounds **1**−**7** were characterized by NMR, IR (vide infra), and FAB mass spectroscopy (see Experimental Section for data) while compounds **3**, **4**, and **5** were additionally characterized by X-ray crystallography. Assuming the imido−oxo pair adopts a mutual *cis* orientation, three possible stereoisomers (Figure 2) indistinguishable on the basis of available infrared and NMR data are possible for **1**. We note, however, that the related compounds $[\mathrm{Mo(}N\mathrm{\text{-}1\text{-}admantyl)(O)Cl_2(dme)}]$[2] and $[\mathrm{Mo(O)(}N\mathrm{\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2(dme)}]$[12] adopted structures with *trans* chlorine atoms similar to that of stereoisomer **1a**.



1a **1b** **1c**

Figure 2. Possible stereoisomers of $[\mathrm{MoO)(N^tBu)Cl_2(dme)}]$ (**1**).

Single-Crystal X-ray Structural Characterization of $[\mathrm{Mo(N^tBu)_2\{(3,5\text{-}{}^tBu_2)_2salpen\}}]$ (5). Crystals of $[\mathrm{Mo(N^tBu)_2\{(3,5\text{-}{}^tBu_2)_2salpen\}}]$ suitable for molecular structure determination were grown from a concentrated toluene solution at −25 °C, crystallizing in the triclinic space group $P\bar{1}$. The structure is shown in Figure 3, and selected bond distances and angles are given in Table 1. The angles subtended by mutually *cis*-ligating atoms around the six-coordinate molybdenum center are in the range 77.26(13)−105.81(12)°, while the angles between *trans*-ligating pairs of atoms are

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds **3**,[a] **3′**, **4**,[b] and **5**[c]

	3	3′		5		4
Mo(1)−O(3)	1.720(4)	1.723(5)	Mo(1)−N(1)	1.758(3)	Mo(1)−O(2)	1.717(3)
Mo(1)−N(3)	1.740(4)	1.731(4)	Mo(1)−N(2)	1.760(3)	Mo(1)−N(1)	1.772(4)
Mo(1)−O(1)	1.979(3)	1.965(4)	Mo(1)−O(1)	2.0116(18)	Mo(1)−O(3)	1.957(3)
Mo(1)−O(2)	2.105(5)	2.108(5)	Mo(1)−O(2)	2.170(2)	Mo(1)−N(2)	2.140(4)
Mo(1)−N(2)	2.176(4)	2.182(5)	Mo(1)−N(3)	2.320(4	Mo(1)−O(1)	2.150(3)
Mo(1)−N(1)	2.306(4)	2.299(4)	Mo(1)−N(4)	2.167(3)	Mo(1)−N(3)	2.319(4)
O(3)−Mo(1)−N(3)	104.9(2)	103.5(2)	N(1)−Mo(1)−N(2)	105.81(12)	O(2)−Mo(1)−N(1)	102.63(18)
O(3)−Mo(1)−O(1)	99.02(18)	99.5(2)	N(2)−Mo(1)−N(2)	105.81(12)	O(2)−Mo(1)−O(3)	105.74(12)
N(3)−Mo(1)−O(1)	101.63(19)	99.9(2)	N(1)−Mo(1)−O(1)	103.44(15)	N(1)−Mo(1)−O(3)	102.27(17)
O(3)−Mo(1)−O(2)	159.77(15)	159.92(18)	O(2)−Mo(1)−N(2)	164.56(9)	O(2)−Mo(1)−N(2)	96.33(14)
N(3)−Mo(1)−O(2)	92.31(18)	91.97(19)	N(1)−Mo(1)−N(4)	94.85(14)	N(1)−Mo(1)−N(2)	92.29(15)
O(1)−Mo(1)−O(2)	88.24(17)	89.46(18)	O(1)−Mo(1)−O(2)	82.95(10)	O(3)−Mo(1)−N(2)	149.93(14)
O(3)−Mo(1)−N(2)	88.9(2)	88.6(2)	N(2)−Mo(1)−O(1)	96.43(12)	O(2)−Mo(1)−O(1)	86.28(17)
N(3)−Mo(1)−N(2)	97.10(19)	96.3(2)	N(1)−Mo(1)−O(2)	89.27(11)	N(1)−Mo(1)−O(1)	166.89(13)
O(1)−Mo(1)−N(2)	157.05(16)	159.47(16)	O(1)−Mo(1)−N(4)	153.97(9)	O(3)−Mo(1)−O(1)	84.21(15)
O(2)−Mo(1)−N(2)	77.81(18)	77.44(19)	O(1)−Mo(1)−N(3)	81.09(14)	N(2)−Mo(1)−O(1)	77.01(12)
O(3)−Mo(1)−N(1)	84.47(17)	85.8(2)	N(2)−Mo(1)−N(4)	96.20(12)	O(2)−Mo(1)−N(3)	164.80(17)
N(3)−Mo(1)−N(1)	169.92(19)	169.0(2)	N(3)−Mo(1)−N(1)	166.80(9)	N(1)−Mo(1)−N(3)	89.44(14)
O(1)−Mo(1)−N(1)	81.07(16)	83.07(17)	O(1)−Mo(1)−N(4)	153.97(9)	O(3)−Mo(1)−N(3)	80.21(12)
O(2)−Mo(1)−N(1)	78.00(14)	77.38(17)	O(2)−Mo(1)−N(4)	78.88(10)	N(2)−Mo(1)−N(3)	73.70(13)
N(2)−Mo(1)−N(1)	78.29(16)	78.70(17)	N(3)−Mo(1)−N(4)	77.26(13)	O(1)−Mo(1)−N(3)	80.35(12)
C(31)−N(3)−Mo(1)	174.2(4)	167.6(4)	C(5)−N(2)−Mo(1)	175.7(2)	C(1)−N(1)−Mo(1)	171.5(3)
C(22)−O(2)−Mo(1)	122.4(3)	122.2(3)	C(1)−N(1)−Mo(1)	161.7(2)	C(13)−O(1)−Mo(1)	117.9(3)
C(7)−O(1)−Mo(1)	128.1(2)	129.9(3)	C(14)−O(2)−Mo(1)	119.34(17)	C(23)−O(3)−Mo(1)	137.7(3)

[a] Crystal data for **3** follow: $C_{37}H_{57}MoN_3O_3{\cdot}C_7H_8$, $M = 779.93$, monoclinic, $a = 25.299(9)$ A , $b = 11.798(5)$ Å, $c = 14.302(1)$ Å, $\alpha = 90.00°$, $\beta = 91.28(5)°$, $\gamma = 90.00°$, $V = 4268(2)$ Å^3, space group Pn, $Z = 4$, $D_c = 1.214$ Mg/m^3, $\mu = 0.347$ mm^{-1}, reflections measured 7866, reflections unique 7631 with $R_{int} = 0.0046$, $T = 160(2)$ K, final R indices [$I > 2\sigma(I)$] R1 = 0.0483, wR2 = 0.1144 and for all data R1 = 0.1234, wR2 = 0.1472. CCDC: 224292. [b] Crystal data for **4** follow: $C_{30}H_{35}MoN_3O_3{\cdot}CH_2Cl_2$, $M = 666.48$, monoclinic, $a = 7.122(2)$ Å, $b = 20.983(8)$ Å, $c = 10.758(5)$ Å, $\alpha = 90.00°$, $\beta = 108.96(4)°$, $\gamma = 90.00°$, $V = 1520.5(10)$ Å^3, space group $P2_1$, $Z = 2$, $D_c = 1.456$ Mg/m^3, $\mu = 0.643$ mm^{-1}, reflections measured 2955, reflections unique 2668 with $R_{int} = 0.0121$, $T = 160(2)$ K, final R indices [$I > 2\sigma(I)$] R1 = 0.0224, wR2 = 0.0606 and for all data R1 = 0.0265, wR2 = 0.0648. CCDC: 224293. [c] Crystal data for **5** follow: $C_{41}H_{68}MoN_4O_2$, $M = 744.93$, triclinic, $a = 10.692(2)$ Å, $b = 14.707(8)$ Å, $c = 14.983(9)$ Å, $\alpha = 116.38(8)°$, $\beta = 95.25(9)°$, $\gamma = 82.40(9)°$, $V = 2090.7(17)$ Å^3, space group $P1$, $Z = 2$, D_c=1.183 Mg/m^3, $\mu = 0.350$ mm^{-1}, reflections measured 7777, reflections unique 7330 with $R_{int} = 0.0165$, $T = 160(2)$ K, final R indices [$I > 2\sigma(I)$] R1 = 0.0385, wR2 = 0.1024 and for all data R1 = 0.0451, wR2 = 0.1066. CCDC: 224293.

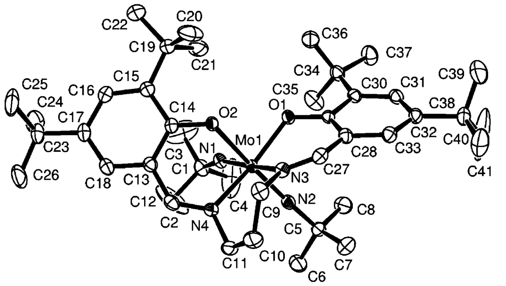

Figure 3. Crystal structure of [Mo(N^{t}Bu)$_2${(3,5-^{t}Bu$_2$)$_2$salpen}] (**5**).

considerably less than 180°. The six-membered $MoNC_3N$ ring adopts a distorted chair conformation. The overall configuration of the salpen ligand in **5** is *β-cis* (see Figure 4 for possible configurations).[14] The molybdenum−imido, Mo−N, distances are notably longer in **5** than in the related salen compound [Mo(N^{t}Bu)$_2${(3,5-^{t}Bu$_2$)$_2$salen}] (Mo−N 1.682(2), 1.686(2) Å),[13] but the molybdenum−imido angles, Mo−N−C, follow a similar pattern, where the imido *trans* to imine nitrogen is more acute. As for the salen analogue,[13] the two molybdenum to phenoxy oxygen distances are different with that *trans* to imido elongated compared to that *trans* to the imine, Mo−O(2) 2.170(2) Å, Mo−O(1) 2.0116(18) Å.

Single-Crystal X-ray Structural Characterization of [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}] (3). Crystals of [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}]•toluene suitable for molecular structure determination were obtained from a concentrated toluene solution at −25 °C. There were two crystallographically distinct [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}] molecules designated **3** and **3′** in the unit cell having slightly different structural parameters (see Table 1). The structure of **3** is shown in Figure 5, and selected bond lengths and angles for both **3** and **3′** are given in Table 1. For simplicity, only [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}] (**3**) is discussed or referred to elsewhere in the manuscript.

There is distorted octahedral geometry about the central molybdenum atom in **3** with angles between *cis*-ligating pairs of atoms in the range 77.81(18)−104.9(2) Å and angles between *trans*-ligating pairs of atoms substantially less than 180° (see Table 1). The tetradentate Schiff base clearly adopts the *β-cis* configuration in **3** (see Figure 4).[14] The MNC_3N ring is puckered with component C−C−C and N−C−C angles close to tetrahedral at C(35) and C(37) but showing distortion at C(36) 116.3(7)°. The oxo group, O(3), adopts a position *trans* to the phenoxy oxygen O(2) of the Schiff base. The molybdenum imido group Mo−N(3)−C(31) (174.2(4)°) adopts the linear coordination mode and is *trans* to the imine nitrogen N(1). Its structural parameters are very close to those in the *bis*-imido compound **5**. The Mo═O distance is within the range for Mo(VI) compounds with Mo═O bonds.[11a,15] There has been considerable discussion

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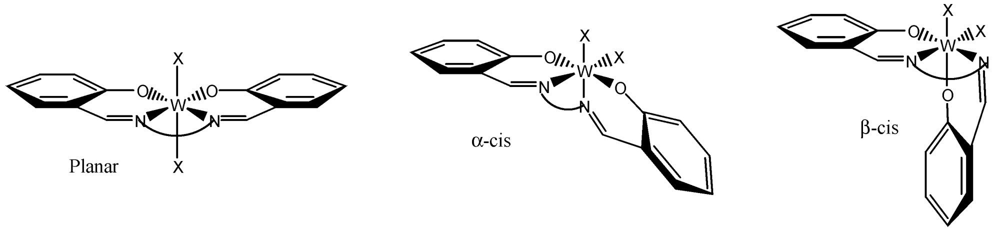

Figure 4. Geometrical configurations of tetradendate Schiff base six-coordinate complexes [MLX_2].

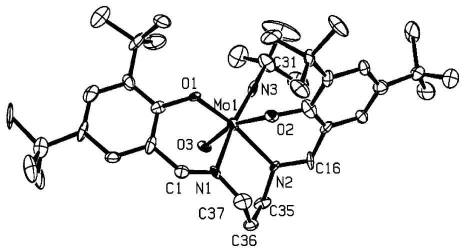

Figure 5. Crystal structure of [$Mo(O)(N^tBu)\{(3,5\text{-}^tBu_2)_2salpen\}$] (**3**).

in the literature about the relative π-donor properties of the imido and oxo groups. In the series $OsO_n(N^tBu)_{4-n}$, the Os−O stretching frequencies decrease with successive replacement of oxo groups by *tert*-butyl imido.[16]

NMR data indicate that the arylimido ligand in [$Os(N\text{-}4\text{-}NO_2C_6H_4)_2(TTP)$], where TTP is tetraphenylporphyrinato dianion, is a stronger π-donor than the oxo ligand in [$OsO_2(TTP)$].[17] The Os−O vibration in [$OsO_2(Por)$], where Por is a range of porphyrinato dianions, is reported to be at higher frequency than that in [$Os(O)(Por)(N^tBu)$].[4] In contrast to these findings, a recent theoretical and experimental study of a number of Cr(V) complexes with chromium−ligand multiple bonds predicted that the binding interaction in $Cr-O_{oxo}$ is greater than in $Cr-N_{imido}$.[18] Some observations about the relative π-donor efficiencies of the imido and oxo groups in **3** can be made. First, being *trans* to the salpen imine σ-donor nitrogen, N(1), the imido group has no *trans* competition for the d-orbitals of the metal. The linear imido angles (174.2(4)°) and the short $Mo-N_{imido}$ bond lengths (1.740(4) Å) indicate a high degree of π-delocalization. The oxo group on the other hand is positioned *trans* to the π-donating phenoxy oxygen although competitive phenoxy π-interactions are apparently limited given the bent nature of the $Mo-O-C_{phenoxy}$ bonds. It might nonetheless be concluded that this overall arrangement allows the stronger π-donor, imido in this case, to maximize π-interaction. However, the opposite arrangement is found in compound **4** (see below) so other factors are clearly important in defining these geometrical relationships. Comparison between the oxo−imido compound **3** and the related bis-imido compound **5** shows that the $Mo-O_{phenoxy}$ (2.105(3) Å) *trans* to the oxo group in **3** is significantly shorter than the corresponding $Mo-O_{phenoxy}$ (2.170(2) Å) trans to the imido group in **5**. This indicates that the imido group may have the higher *trans*-influence in this case. Crystal packing effects cannot, however, be discounted as another explanation for the observed differences in the $Mo-O_{phenoxy}$ bond lengths.

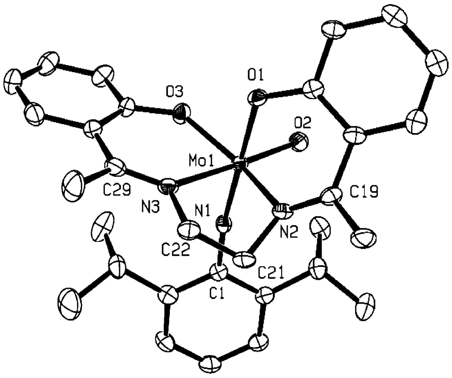

Figure 6. Crystal structure of [$Mo(O)(NAr)\{(7\text{-}Me)_2salen\}$] (**4**).

Single-Crystal X-ray Structure of [$Mo(O)(N\text{-}2,6\text{-}^iPr_2C_6H_3)\{(7\text{-}Me)_2salen\}$] (4). Crystals of **4**·CH_2Cl_2 suitable for X-ray structure determination were obtained from a concentrated dichloromethane solution at −25 °C. The distorted octahedral structure of **4** is shown in Figure 6, and selected bond distances and angles are given in Table 1. Angles associated with *cis*-ligating pairs of atoms are in the range 73.70(13)−105.74(12)° which is similar to that found for **3** and **5**. The distortion from ideal octahedral values of the angles subtended by the *trans*-ligating pairs of atoms is also similar to that in **3** and **5** (see Table 1). As for **3**, the molybdenum imido in **4** is linear, Mo−N(1)−C(1) = 171.5(3)°, and the Schiff base adopts the β-*cis* configuration. The $MoNC_2N$ ring is twisted and likely to be strained (e.g., N(2)−C(21)-C(22) 105.1(4)°).

In contrast to **3**, the imido group in **4** occupies the axial position *trans* to the Schiff base phenoxy oxygen rather than the equatorial position *trans* to the imine nitrogen. Compared to *tert*-butylimido, bulky 2,6-diisopropylarylimido is less likely, for steric reasons, to occupy the fourth position in the equatorial coordination plane alongside the ON_2 atoms of the Schiff base.

Physical and Spectroscopic Properties. Compounds **2**, **3**, **4**, **5**, and **6** are mildly moisture sensitive yellow crystalline solids while **1** and **7** are comparatively more moisture sensitive. No decomposition was observed for solutions prepared and stored under standard Schlenk conditions. Compound **2** was observed to decompose irreversibly when heated in refluxing toluene for 12 h (evidence from NMR and the appearance of new low molecular weight fragments in the GC-MS of solutions after heating). Compound **3**, however, was unchanged when treated under similar conditions. The Schiff base compounds **2**, **3**, **4**, **5**, and **6** display

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infrared and solution phase NMR spectroscopic data that are consistent with the mononuclear structures having the folded β-*cis* Schiff base configuration (see Figure 4) confirmed by X-ray crystallography for **3**, **4**, and **5**. The spectroscopic data provide no evidence for the formation of compounds with a planar Schiff base configuration but do not rule out the possibility of rearrangement from the solid state β-*cis* to α-*cis* arrangement (see Figure 4) in solution for **2**, **3**, and **4**. In particular, solution phase proton NMR spectra of compounds **2** and **3** displayed two imine N═C*H* resonances while compound **4** displayed two imine N═CCH_3 resonances, shifted upfield with respect to the free ligands. The symmetrical planar Schiff base arrangement would be expected to show one imine resonance, but the observed data could also be consistent with α-*cis* configurations. Likewise, the appearance of four distinct resonances for Schiff base ^{t}Bu in **2** and **3**, and the observation of diastereotopic protons for the Schiff base backbone methylenes in **2**, **3**, and **4**, is indicative of the strained β-*cis* geometry. However, a similar distribution of resonances might be seen for the α-*cis* configuration in **2**, **3**, and **4**. Compounds **5** and **6** also displayed features consistent with β-*cis* configuration including two imine resonances, and diastereotopic protons for the Schiff base backbone methylenes. Similar patterns were seen in our earlier reports on bis-imido Schiff base Mo(VI) and W(VI) complexes.[13,19] Such features exclude both planar and α-*cis* configurations in **5** and **6** where the higher symmetry of both configurations in this case could be expected to result in fewer resonances. Infrared spectra contain either two distinct bands at 1597 and 1583 cm^{-1} (**4**), 1645 and 1610 cm^{-1} (**5**), and 1596 and 1572 cm^{-1} (**6**), or a single broad band, 1618 cm^{-1} (**2**) and 1616 cm^{-1} (**3**) associated with the imine C═N vibration, compared to a single sharp band usually seen for the planar Schiff base arrangement. The uncertainty surrounding assignment of the M−N vibration in metal−imido compounds due to possible coupling with the N−C as well as other vibrations[5,1a] implies obvious difficulties for the interpretation of the infrared data associated with the *cis*-MO(NR) fragments in our compounds. For example, on the basis of comparison between the infrared spectrum of **2** and that of its bis-imido analogue,[13] a new infrared band at 896(s) cm^{-1} in **2** could be due to Mo−O vibration. Bands at 1251(s), 1196(m), 1171(m), 1096(m), and 1039(s) cm^{-1} in **2** are in the Mo−N/Mo−N−R vibration regions. Bands in the corresponding regions for the bis-imido analogue appeared at 1254(s), 1205(brs), 1165(m), 1106(m), and 1022(brs) cm^{-1}.[13] Our tentatively assigned Mo−O vibration is slightly lower than those quoted for *cis*-MoO_2 vibrations, 920−940 cm^{-1} (symmetric) and 900−910 cm^{-1} (asymmetric).[15] The general uncertainty concerning the Mo−N vibration precludes any firm conclusions from infrared data about relative π-interactions of the oxo and imido groups in compound **2**. Similar difficulties apply for compounds **3** and **4**, and bands due to Mo−O vibration could not be assigned with any confidence in these cases even after comparisons with infrared spectra of the bis-imido analogues **5** and **6**.

Mixed oxo−imido compounds of the type $CH_3ReO_n(NR)_{3-n}$ have been shown to readily form oxo-bridged dimers and can form them reversibly in some cases.[1d,5,9] In the present work, we found no evidence for dimer formation from the solid state structural studies nor any indication of reversible equilibria when proton NMR spectra were recorded at variable temperature. Compound **2**, however, showed evidence of irreversible decomposition when heated in refluxing toluene overnight. Peaks with masses higher than those of the molecular ions were not seen in the mass spectra of **2**, **3**, or **4**.

Oxidation Chemistry. A number of molybdenum Schiff base complexes have been investigated as catalysts for the oxidation of unsaturated organic substrates including [MoO_2(salen)], [MoO_2(salphen)],[20a] and [Mo(O)(O_2)(salophen)].[20b] Kuhn recently reported on efficient catalytic epoxidation using molybdenum bis-oxo complexes [MoO_2Lsolv] having chiral tridentate Schiff base ligands L derived from sugars, and tertiary butyl hydroperoxide, TBHP, as oxidant,[15] while an earlier report dealt with catalysts derived from Lewis base adducts of bis(halogeno)dioxomolybdenum(VI) compounds.[21] The nature of the intermediates in olefin epoxidation catalyzed by Mo(VI) compounds was discussed by Sharpless and more recently modeled using computational methods.[22] Mechanisms involving hydroperoxide intermediates were favored in comparison to those based on peroxo intermediates.

We investigated the catalytic activity of the oxo−imido compounds, [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salen}] (**2**) and [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}] (**3**), for the oxidation of a limited range of substrates including benzyl alcohol, *cis*-cylcooctene, and 1-octene. The oxidations were carried out under standard Schlenk conditions involving strict exclusion of water using predried toluene solutions of *tert*-butyl hydroperoxide[23] as oxidant and conditions as otherwise previously described by Sharpless.[23] The metal complex-to-substrate ratio was 1:250. The compound [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salen}] (**2**) gave complete conversion of the *cis*-cyclooctene to the epoxide product (isolated yield of NMR pure *cis*-cyclooctene oxide 98%). However, since we observed that compound **2** was unstable when heated in refluxing toluene, no further catalytic reactions were examined. The less strained and more thermally stable compound, [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}] (**3**), was active in the oxidation of benzyl alcohol (isolated yield of NMR pure benzaldehyde 97%), *cis*-cyclooctene (isolated yield NMR pure *cis*-cyclooctene oxide 98%), and 1-octene (the ratio of

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1-octene/1-octene oxide was 2:8 by proton NMR). No oxidized products were observed when blank reactions were carried out without catalyst. It is also noteworthy that no *cis*-cyclooctene oxide was formed when [Mo(N^{t}Bu)$_2${(3,5-^{t}Bu$_2$)$_2$salpen}] was used as catalyst under the same conditions. The lack of catalytic activity for [Mo(N^{t}Bu)$_2${(3,5-^{t}Bu$_2$)$_2$salpen}] indicates that oxo−imido exchange is unlikely to be a feature. Metal imido compounds can undergo oxo−imido exchange when treated with benzaldehyde,[1a] and so, it is possible that a bis-oxo compound is formed from **3** during the oxidation of benzyl alcohol. Further work is required to establish if this is the case.

Conclusions

We have described the syntheses and structures of the first examples of molybdenum oxo−imido Schiff base complexes. A comparison between the structural parameters of related oxo−imido and bis-imido Schiff base compounds suggests that the *tert*-butyl imido ligand exerts a stronger *trans* influence. Infrared data did not prove useful in assessing this feature. The molybdenum oxo−imido complex, [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}] (**3**), was shown to be thermally stable and an active catalyst for oxidation of some organic substrates with TBHP.

Experimental Section

General Details. Manipulations including oxidations were carried out under an atmosphere of dry nitrogen using standard Schlenk/cannula techniques and a conventional nitrogen filled glovebox. Solvents were dried over the appropriate drying agent and distilled according to the literature procedure. Deuterated solvents were refluxed in vacuo over calcium hydride before trap-to-trap distillation. All solvents were stored in nitrogen filled reservoirs, equipped with Young's taps, over the appropriate activated molecular sieves and were degassed prior to use.

The NMR spectra were recorded on JEOL 270 (^{1}H, 270 MHz; ^{13}C{^{1}H}, 67.88 MHz) and Bruker AMX400 (^{1}H, 400 MHz; ^{13}C-{^{1}H}, 100.61 MHz) and AMX600 (^{1}H, 600 MHz; ^{13}C{^{1}H}, 150.90 MHz) spectrometers and referenced using residual protio-solvent resonance. Chemical shifts are quoted in δ (ppm), and coupling constants, in hertz. Assignments (see Scheme 1 for numbering) were supported by DEPT-135 and DEPT-90 homo- and heteronuclear, two-dimensional experiments as appropriate. Infrared spectra were obtained using a Perkin-Elmer FTIR 1720X spectrometer equipped with an ATR attachment, in the range 4000−200 cm^{-1}. Microanalyses were obtained from services at Queen Mary College and University College London. Mass spectra were obtained from the EPSRC Mass Spectroscopy Service, Swansea, Wales, using LSIMS (liquid secondary ion mass spectrometry), with cesium ion bombardment at 25 kV energy onto the sample dissolved in a matrix liquid, typically 3-nitrobenzyl alcohol (NOBA), and poly(ethylene glycol) (PEG) as a mass reference.

The compounds MoCl$_5$ (used to prepare [MoO$_2$Cl$_2$]),[24] Na$_2$MoO$_4$, 2,4-di-*tert*-butylphenol, *para*-formaldehyde, ethylenediamine, 1,3-dipropylamine, 2-hydroxyacetophenone, and NaH 60% dispersion in mineral oil were purchased from Aldrich, Lancaster, Fluka, and Avocado chemical companies and used as received.

Literature methods were used for the preparation of [Mo(N^{t}Bu)$_2$(NH^{t}Bu)$_2$],[8c] [Mo(N^{t}Bu)$_2$Cl$_2$(dme)],[11b] [MoO$_2$Cl$_2$(dme)],[11a] [Mo(O)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$(dme)],[12] and the Schiff bases [14] H$_2$(3,5-^{t}Bu$_2$)$_2$salen, H$_2$(3,5-^{t}Bu$_2$)$_2$salpen, and H$_2$(7-Me)$_2$salen. The disodium salts of the Schiff bases, Na$_2$L, were prepared from the neutral ligands and NaH in THF and used in situ without further purification.

Preparation of [Mo(O)(N^{t}Bu)Cl$_2$(dme)] (1). A yellow solution of [Mo(N^{t}Bu)$_2$Cl$_2$(dme)] (2.08 g, 5.21 mmol) in dme (50 cm^3) was added to a suspension of [MoO$_2$Cl$_2$(dme)] (1.50 g, 5.21 mmol) in dme (50 cm^3), via a pressure equalized dropping funnel. The yellow mixture was heated at vigorous reflux for 6 h and was then allowed to cool to room temperature when it was dried under reduced pressure. The crude white solid [Mo(O)(N^{t}Bu)Cl$_2$(dme)] (3.58 g, 100%) was then recrystallized in dme giving colorless crystals. Mp 73−75 °C. (Found: C, 27.76; H, 5.32; N, 4.29. C$_8$H$_{19}$Cl$_2$MoNO$_3$ requires: C, 27.92; H, 5.57; N, 4.07%.) IR (cm^{-1}): 2969m, 2936w, 1453brm, 1360m, 1278w, 1231s, 1187m, 1108w, 1084s, 1039vs, 1004s, 958w, 908vs, 859vs, 824vs, 797m, 589m, 573m, 518m. ^{1}H NMR (d_6-benzene, 270 MHz, 298 K): 3.42 (s, 6H, C*H$_3$*), 3.02 (s, 4H, C*H$_2$*), 1.43 (s, 9H, ^{t}*Bu*). ^{13}C-{^{1}H} NMR (d_6-benzene, 67.88 MHz, 298 K): 75.9 (*C*H$_2$), 71.3 (*C*H$_3$ + Me$_3$*C*N), 28.1 (*Me*$_3$CN).

Preparation of [Mo(O)(N^{t}Bu){3,5-^{t}Bu$_2$)$_2$salen}] (2). To a solution of Na$_2$(3,5-^{t}Bu$_2$)$_2$salen (1.12 g, 2.08 mmol) in THF (40 cm^3) was added a solution of [Mo(O)(N^{t}Bu)Cl$_2$(dme)] (0.72 g, 2.08 mmol) in THF (40 cm^3) at 0 °C. This reaction mixture was stirred at room temperature for 2 days, after which time the volatiles and the solvent were removed under reduced pressure and the brown residue was extracted with hexane (60 cm^3). The hexane extract was concentrated to crude yellow [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salen}] which was recrystallized from toluene (1.03 g, 73%, three crops). Mp 187−189 °C (with decomposition). (Found: C, 63.89; H, 8.17; N, 5.98. C$_{36}$H$_{55}$N$_3$O$_3$Mo requires: C, 64.17; H, 8.23; N, 6.24%.) IR (cm^{-1}): 2952s, 2874m, 1618brs, 1462m, 1438s, 1388m, 1361m, 1251s, 1196m, 1171m, 1096m, 1039s, 896s, 879s, 840s, 806s, 773s, 670m, 643m, 624m, 547m, 438m. ^{1}H NMR (CDCl$_3$, 400 MHz, 300 K): δ 8.34 (s, 1H, imine-*H*), 8.31 (s, 1H, imine-*H*), 7.55 (d, $^4J_{\mathrm{H-H}} = 2.6$ Hz, 1H, *H6*), 7.45 (d, $^4J_{\mathrm{H-H}} = 2.6$ Hz, 1H, *H6*), 7.18 (d, $^4J_{\mathrm{H-H}} = 2.6$ Hz, 1H, *H4*), 7.09 (d, $^4J_{\mathrm{H-H}} = 2.6$ Hz, 1H, *H4*), 4.64 (m, 1H, C*H$_2$*), 4.10 (m, 1H, C*H$_2$*), 3.84 (m, 1H, C*H$_2$*), 3.41 (m, 1H, C*H$_2$*), 1.46 (s, 9H, ^{t}Bu), 1.33 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu), 1.05 (s, 9H, N^{t}Bu). ^{13}C-{^{1}H} (CDCl$_3$, 100.61 MHz, 300 K): 168.35 (*C2*), 164.79 (*C*═N), 163.60 (*C*═N) 160.05 (*C*2), 140.19 (*C*1), 139.56 (*C*1), 137.82 (*C*6), 137.10 (*C*6), 130.40 (*C*3), 129.28 (*C*3), 125.24 (*C*5), 123.95 (*C*5), 123.13 (*C*4), 120.55 (*C*4), 71.56 (Me$_3$*C*N═), 62.67(*C*H$_2$), 60.59 (*C*H$_2$), 35.53 (*C*H$_3$), 35.47 (*C*H$_3$), 34.08 (*C*H$_3$), 33.92 (*C*H$_3$), 31.41 (*C*H$_3$), 31.19 (*C*H$_3$), 29.83 (*C*H$_3$), 29.67 (*C*H$_3$), 29.62 (*C*H$_3$), 29.35 (*C*H$_3$), 27.84 (*C*H$_3$). MS (LSIMS) *m*/*z* 676.338; *m*/*z* calculated for C$_{36}$H$_{55}$N$_3$O$_3$Mo 676.339 [M$^+$].

Preparation of [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}] (3). To a solution of Na$_2$(3,5-^{t}Bu$_2$)$_2$salpen (0.80 g, 1.45 mmol) in THF (25 cm^3) was added a solution of [Mo(O)(N^{t}Bu)Cl$_2$(dme)] (0.50 g, 1.45 mmols) in THF (25 cm^3) at 0 °C. This reaction mixture was stirred at room temperature for 2 days, after which time the volatiles and the solvent were removed under reduced pressure and the brown residue was extracted with hexane (20 cm^3). The hexane extract was concentrated to leave crude yellow [Mo(O)(N^{t}Bu){(3,5-^{t}Bu$_2$)$_2$salpen}], which was recrystallized from toluene (0.71 g, 71.6%, 2 crops). Mp 186−189 °C (with decomposition). (Found: C, 64.51; H, 8.49; N, 6.50. C$_{37}$H$_{57}$N$_3$O$_3$Mo requires: C, 64.61; H, 8.35; N, 6.11%.) IR (cm^{-1}): 2953m, 2868w, 1616br s, 1534w, 1436m, 1411m, 1386m, 1358m, 1273m, 1237s, 1202m, 1172m, 1131w,

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1091w, 1025w, 967w, 915w, 816vs, 833vs, 810s, 776w, 744m, 730s, 695m, 618w, 575m, 546m, 530m, 487m, 430m. ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): 7.72 (d, $^{4}J_{H-H}$ = 2.8 Hz, 1H, *H*6), 7.57 (d, $^{4}J_{H-H}$ = 2.8 Hz, 1H, *H*6), 7.53 (s, 1H, imine-*H*), 7.47 (s, 1H, imine-*H*), 7.05 (d, $^{4}J_{H-H}$ = 2.8 Hz, 1H, *H*4), 6.90 (d, $^{4}J_{H-H}$ = 2.8 Hz, 1H, *H*4), 4.57 (m, 1H, C*H*$_2$), 3.58 (m, 1H, C*H*$_2$), 3.46 (m, 1H, C*H*$_2$), 3.26 (m, 1H, C*H*$_2$), 3.02 (m, 1H, C*H*$_2$), 2.08 (m, 1H, C*H*$_2$), 1.67 (s, 9H, ^{t}Bu), 1.41 (s, 9H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu), 1.33 (s, 9H, ^{t}Bu), 1.22 (s, 9H, N^{t}Bu). ^{13}C-{^{1}H} NMR (d_6-benzene, 150.90 MHz, 298 K): 166.46 (*C*2), 162.35 (*C*═N), 159.54 (*C*2), 158.10 (*C*═N), 140.03 (*C*1), 137.88 (*C*1), 136.68 (*C*6), 130.11 (*C*6), 126.87 (*C*3), 125.30 (*C*3), 125.02 (*C*5), 121.68 (*C*5), 121.45 (*C*4), 117.48 (*C*4), 63.31 (*C*H$_2$), 59.06 (*C*H$_2$), 56.74 (Me$_3$CN═), 35.04 (*C*H$_3$), 34.12 (*C*H$_3$), 31.50 (*C*H$_3$), 31.28 (*C*H$_2$), 29.69 (*C*H$_3$), 29.43 (*C*H$_3$). MS (LSIMS) *m*/*z* 684.355; *m*/*z* calculated for $C_{37}H_{57}N_3O_3Mo$ 684.355 [M$^+$].

Preparation of [Mo(O)(N-2,6-^{i}Pr$_2$C$_6$H$_3$){(7-Me)$_2$salen}] (4). To a solution of Na$_2$(7-Me)$_2$salen (0.1 g, 0.29 mmol) in THF (20 cm^3) was added a solution of [Mo(O)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$(dme)] (0.13 g, 0.29 mmol) in THF (15 cm^3) at 0 °C. This reaction mixture was stirred at room temperature for 2 days, after which time the volatiles and the solvent were removed under reduced pressure and the brown residue was extracted with hexane (10 cm^3). The hexane extract was concentrated to leave crude yellow [[Mo(O)(N-2,6-^{i}Pr$_2$C$_6$H$_3$){(7-Me)$_2$salen}] which was recrystallized from toluene (0.07 g, 34%). Mp 168−172 °C (with decomposition). (Found: C, 62.17; H, 6.24; N, 6.98. $C_{30}H_{35}MoN_3O_3$ requires: C, 61.96; H, 6.07; N, 7.23.) IR (cm^{-1}): 2959m, 2878w, 1597m, 1583m, 1527w, 1461w, 1433m, 1329m, 1258s, 1236m, 1085brs, 1014vs, 875s, 793vs, 757vs, 636m, 580m, 558m, 536m, 521m, 466m.

^{1}H NMR (CDCl$_3$, 400 MHz, 300 K): 7.64 (dt, 1H, *H*), 7.46 (m, 1H, *H*), 7.35 (t, 1H, *H*), 7.09−6.91 (m, 3H, *H*), 6.87−6.61 (m, 4H, *H*), 6.20 (t, 1H, *H*), 4.72 (m, 1H, CH$_2$), 4.41(m, 2H, CH$_2$), 4.14 (m, 1H, CH$_2$), 3.66 (sep, $^{3}J_{H-H}$ = 6.06, 2H, C*H*^{i}Pr), 2.51 (s, 3H, Me), 2.45 (s, 3H, Me), 1.20 (d, $^{3}J_{H-H}$ = 6.06, 6H, ^{i}Pr), 1.14 (d, $^{3}J_{H-H}$ = 6.06, 6H, ^{i}Pr). MS (LSIMS) *m*/*z* 584.181; *m*/*z* calculated for $C_{30}H_{35}MoN_3O_3$ 584.181 [M$^+$].

Preparation of [Mo(N^{t}Bu)$_2${(3,5-^{t}Bu$_2$)$_2$salpen}] (5). To a solution of [Mo(N^{t}Bu)$_2$(NH^{t}Bu)$_2$] (0.5 g, 1.31 mmol) in toluene (40 cm^3) was added H$_2$(3,5-^{t}Bu$_2$)$_2$salpen (0.66 g, 1.31 mmol) as a solid. The solution immediately turned orange and was then heated at reflux for 16 h. The orange reaction solution was then allowed to cool to room temperature and was dried under reduced pressure to produce an orange solid which was recrystallized from toluene (10 cm^3) at −20 °C to produce analytically pure [Mo(N^{t}Bu)$_2${(3,5-^{t}Bu$_2$)$_2$salpen}] (0.78 g, 89%). Mp 232−236 °C (with decomposition). (Found: C, 65.89; H, 8.76; N, 7.86.Calcd for $C_{41}H_{66}N_4O_2W$: C, 66.28; H, 8.95; N, 7.54%.) IR (cm^{-1}): 2959s, 2953m, 2919m, 1645m, 1610s, 1605s, 1533m, 1467m, 1444m, 1384m, 1354m, 1256s, 1241s, 1203s, 1168s, 1117m, 1089m, 1022w, 834m, 810m, 784m, 741m, 552m, 439m. ^{1}H NMR (d_6-benzene, 600 MHz, 298 K): 7.67 (d, $^{4}J_{H-H}$ = 2.6 Hz, 1H, *H*6), 7.62 (d, $^{4}J_{H-H}$ = 2.7 Hz, 1H, *H*6), δ 7.50 (s, 1H, imine-*H*), 7.46 (s, 1H, imine-*H*), 7.30 (d, $^{4}J_{H-H}$ = 2.6 Hz, 1H, *H*4), 6.98 (d, $^{4}J_{H-H}$ = 2.6 Hz, 1H, *H*4), 4.07 (m, 1H, C*H*$_2$), 3.57 (m, 1H, C*H*$_2$), 3.40 (m, 1H, C*H*$_2$), 3.29 (m, 1H, C*H*$_2$), 3.18 (m, 1H, C*H*$_2$), 1.77 (m, 1H, C*H*$_2$), 1.70 (s, 9H, ^{t}Bu), 1.58 (s, 9H, ^{t}Bu), 1.39 (s, 9H, ^{t}Bu), 1.39 (s, 9H, ^{t}Bu), 1.25 (s, 9H, N^{t}Bu), 1.15 (s, 9H, N^{t}Bu). ^{13}C-{^{1}H} NMR (d_6-benzene, 150.90 MHz, 298 K): 170.63 (*C*2), 167.50 (*C*═N), 164.74 (*C*2), 161.89 (*C*═N), 141.83 (*C*1), 139.49 (*C*1), 137.61 (*C*6), 135.30 (*C*6), 129.93 (*C*3), 128.00 (*C*3), 127.84 (*C*5), 125.76 (*C*5), 123.21 (*C*4), 122.41 (*C*4), 69.52 (Me$_3$*C*N═), 69.05 (Me$_3$*C*N═), 64.73 (*C*H$_2$), 58.32 (*C*H$_2$), 35.86 (*C*H$_3$), 35.79 (*C*H$_3$), 34.13 (*C*H$_3$), 34.05 (*C*H$_3$), 31.83 (*C*H$_3$), 31.66 (*C*H$_3$), 31.40 (*C*H$_3$), 30.80 (*C*H$_3$), 30.49 (*C*H$_3$), 30.21 (*C*H$_2$). Accurate mass FAB (liquid secondary ion mass spectroscopy): found *m*/*z* 745.431, calculated for $C_{41}H_{66}N_4O_2Mo$ 745.432 [M$^+$].

Preparation of [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2${(7-Me)$_2$salen}] (6). To a solution of [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(NH^{t}Bu)$_2$] (0.5 g, 0.85 mmol) in toluene (40 cm^3) was added H$_2$(7-Me)$_2$salen (0.25 g, 0.85 mmol) as a solid. The solution immediately turned orange and was then heated at reflux for 16 h. The orange reaction solution was then allowed to cool to room temperature and was dried under reduced pressure to produce an orange solid which was recrystallized from toluene (10 cm^3) at −20 °C to produce analytically pure [Mo(NAr)$_2$-{(7-Me)$_2$salen}] (0.42 g, 68%). Mp 254 °C (with decomposition). (Found: C, 67.95; H, 7.05; N, 7.26. Calcd for $C_{42}H_{52}N_4O_2Mo$: C, 68.09; H, 7.07; N, 7.56%.) IR (cm^{-1}): 2956w, 1596m, 1572m, 1530m, 1460w, 1434m, 1378w, 1326m, 1313m, 1256s, 1228m, 1135w, 1085brm, 1011 brs, 950m, 914w, 873m, 792s, 746vs, 637m, 615m, 584w, 469w. ^{1}H NMR (CDCl$_3$, 270 MHz, 298 K): 7.64 (dd, 1H, Schiff base *H*3), 7.50 (dd, 1H, Schiff base *H*3), 7.36 (dt, 1H, Schiff base *H*4), 7.24 (dt, 1H, Schiff base *H*4), 7.09 (dd, 1H, Schiff base *H*6), 6.94 (dd, 1H, Schiff base *H*6), 6.84 (m, 6H, Schiff base *H*5, *H*5, imido *H*3, *H*3, *H*4, *H*4), 6.64 (m, 2H, imido *H*5, *H*5), 4.47 (m, 1H, C*H*$_2$), 4.31 (m, 1H, C*H*$_2$), 3.81 (m, 1H, C*H*$_2$), 3.33 (sep, 4H, C*H* imido), 3.27 (m, 1H, C*H*$_2$), 2.60 (s, 3H, C*H*$_3$), 2.43 (s, 3H, C*H*$_3$), 1.00 (d, $^{3}J_{H-H}$ = 6.9 Hz, 6H, C*H*$_3$), 0.81 (d, $^{3}J_{H-H}$ = 6.9 Hz, 6H, C*H*$_3$), 0.75 (d, $^{3}J_{H-H}$ = 6.9 Hz, 6H, C*H*$_3$), 0.59 (d, $^{3}J_{H-H}$ = 6.9 Hz, 6H, C*H*$_3$). ^{13}C-{^{1}H} NMR (CDCl$_3$, 67.88 MHz, 298 K): 172.46 (Schiff base *C*2), 169.27 (Schiff base C═N), 168.99 (Schiff base *C*2), 163.55 (Schiff base *C*═N), 156.13 (imido *ipso* *C*═N), 152.35 (imido *ipso* *C*═N), 142.00 (imido *C*2), 137.91(imido *C*2), 135.17 (Schiff base *C*1), 133.09 (Schiff base *C*1), 130.00 (Schiff base *C*6), 129.72 (Schiff base *C*6), 126.34 (imido *C*6), 124.56 (Schiff base *C*3), 123.37 (Schiff base *C*3), 123.20 (imido *C*3), 122.87 (imido *C*6), 122.59 (imido *C*4), 122.28 (imido *C*5), 117.26 (Schiff base *C*4), 115.64 (Schiff base *C*4), 57.97 (*C*H$_2$), 54.66 (*C*H$_2$), 27.32 (*C*H$_3$), 25.13 (*C*H$_3$), 24.03 (*C*H$_3$), 23.63 (*C*H$_3$), 22.50 (*C*H$_3$), 20.41 (*C*H$_3$), 18.38 (*C*H$_3$). Accurate mass FAB (liquid secondary ion mass spectroscopy): found *m*/*z* 742.314, calculated for $C_{42}H_{52}N_4O_2Mo$ 742.314 [M$^+$].

Preparation of [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(NH^{t}Bu)$_2$] (7). A deep red solution of [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$Cl$_2$(dme)] (5.0 g, 8.23 mmol) in ether (50 cm^3) was added via a pressure equalized dropping funnel to a suspension of LiNH^{t}Bu (1.30 g, 16.46 mmol) in ether (50 cm^3) at −78 ° C. The reaction mixture was then allowed to reach room temperature and stirred for 2 h. The red/orange solution was then carefully filtered from the white solid using Watmann grade 1 filter paper. The orange-red solution was dried under reduced pressure to give crude [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(NH^{t}Bu)$_2$] which was recrystallized from hexane at −20 °C giving analytically pure [Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(NH^{t}Bu)$_2$] (1.85 g, 38%). Mp 143−146 °C. (Found: C, 64.78; H, 9.28; N, 9.16. Calcd for $C_{32}H_{54}N_4Mo$: C, 65.06; H, 9.21; N, 9.48%.) IR (cm^{-1}): 2952s, 2863m, 1616 br w, 1454m, 1424m, 1380w, 1321s, 1270s, 1200br s, 1104w, 1048w, 978 m, 690s, 930m, 916m, 846w, 776vs, 746vs, 650s, 558m, 477m. ^{1}H NMR (d_6-benzene, 270 MHz, 298 K): 7.30 (br s, 2H, imido *H*4), 7.19 (d, J_{H-H} = 2.32, 2H, imido *H*5), 7.07 (m, 2H, imido *H*6), 3.94 (sep, $^{3}J_{H-H}$, = 6.25, 2H, ^{i}Pr *H*), 1.47 (s, 18 H, ^{t}Bu), 1.37 (d, $^{3}J_{H-H}$ = 7.82, 24H, ^{i}Pr). ^{13}C-{^{1}H} NMR (d_6-benzene, 150.90, 300 K): 154.02 (imido *C1*), 140.83 (imido *C2, C6*), 128.29 (imido *C3*), 124.41 (imido *C5*), 122.75 (imido *C6*), 55.31 (NH^{t}Bu, quaternary *C*), 33.32 (^{i}Pr), 28.82 (*C*H-^{i}Pr), 23.45 (^{t}Bu).

X-ray Crystallography. The intensity data were collected on a CAD-4 diffractometer using Mo Kα radiation (λ 0.71069 Å) and

$\omega-2\theta$ scans at 160 K. The unit cell parameters were determined by least-squares refinement on diffractometer angles (**3**, $8.89° \leq \theta \leq 10.97°$; **4**, $10.23° \leq \theta \leq 12.27°$; and **5**, $12.05° \leq \theta \leq 13.84°$) for 25 automatically centered reflections.[25] All data were corrected for absorption by empirical methods (ψ scan)[26] and for Lorentz-polarization effects by XCAD4.[27] The structures were solved by heavy-atom methods using SHELXS-97,[28] and DIRDIF-99 programs,[29] and were refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on F^2 using SHELXL-97.[28] The H atoms were calculated geometrically and refined with a riding model. In the final stage of refinement, data were corrected for absorption by DIFABS.[30] The program ORTEP-3[31] was used for diagrams, and WINGX[32] was used to prepare material for publication. Crystal data and refinement details are given in Table 1.

General Procedure of Oxidation Reactions. Oxidation reactions were carried out on the organic substrates, benzyl alcohol, *cis*-cyclooctene, and 1-octene with anhydrous TBHP as oxidant and the oxo−imido complex $[Mo(O)(N^tBu)\{(3,5\text{-}^tBu_2)_2salpen\}]$ as catalyst.

Oxidation of *cis*-Cyclooctene. To a solution of $[Mo(O)(N^tBu)\text{-}(3,5\text{-}^tBu_2)_2salpen]$ (0.04 g, 0.06 mmol) and *cis*-cyclooctene (2.0 cm^3, 1.69 g, 15.35 mmol) was added Na_2HPO_4 (0.01 g). To this orange solution was added dropwise a solution of 4.8 M TBHP in toluene (6.4 cm^3, 30.7 mmol). The reaction solution was then heated at 55 °C for 12 h. The reactions were followed by TLC, and this showed that conversion was complete after 12 h. The reaction mixtures were extracted into ether, and washed with a 10% sodium sulfite solution and finally water. The ether layer was dried and evaporated (yield 98%). The product was confirmed as NMR-pure *cis*-cyclooctene epoxide by comparison with the spectrum of the known compound.

Oxidation of Benzyl Alcohol. The reaction was carried out as described using benzyl alcohol in place of *cis*-cyclooctene. Coversion was complete after 12 h by TLC. The isolated yield of NMR pure benzaldehyde was 98%.

Oxidation of 1-Octene. The reaction was carried out as above using 1-octene in place of *cis*-cyclooctene. TLC indicated that conversion was incomplete after 12 h. The reaction mixture was found to contain both 1-octene and 1-octene epoxide. Comparison of the integrated intensities of the epoxide protons at 2.9(m, 1H) and 2.75(m,1H) with the 1-octene protons at 4.95(m, 2H) gave the ratio 2:8 for 1-octene/1-octene epoxide in the mixture.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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