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Molybdenum(VI) Dioxo Complexes Employing Schiff Base Ligands with an Intramolecular Donor for Highly Selective Olefin Epoxidation

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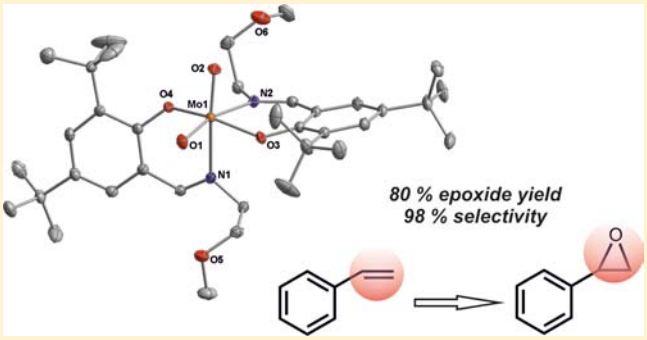
Supporting Information

ABSTRACT: Reaction of $[MoO_2(\eta^2\text{-}tBu_2pz)_2]$ with Schiff base ligands HL^X (X = 1−5) gave molybdenum(VI) dioxo complexes of the type *cis*-$[MoO_2(L^X)_2]$ as yellow to light brown solids in moderate to good yields. All ligands coordinate via its phenolic O atom and the imine N atom in a bidentate manner to the metal center. The third donor atom (R_2 = OMe or NMe_2) in the side chain in complexes **1**−**4** is not involved in coordination and remains pendant. This was confirmed by X-ray diffraction analyses of complexes **1** and **3**. Complexes **1**, **3**, and **5** exist as a mixture of two isomers in solution, whereas complexes **2** and **4** with sterically less demanding substituents on the aromatics only show one isomer in solution. All complexes are active catalysts in the epoxidation of various internal and terminal alkenes, and epoxides in moderate to good yields with high selectivities are obtained. In the challenging epoxidation of styrene, complexes **1** and **2** prove to be very active and selective. The selectivity seems to be influenced by the pendant donor arm, as complex **5** without additional donor in the side chain is less selective. Experiments prove that the addition of *n*-butyl methyl ether as intermolecular donor per se has no influence on the selectivity. The basic conditions induced by the NMe_2 groups in complexes **3** and **4** lead to lower activity.



INTRODUCTION

Alkene epoxidation is one of the main routes for the production of epoxides, which are of high importance in both synthetic organic chemistry and chemical technology.[1] Among them, styrene oxide represents one of the most interesting compounds as it is used for the manufacture of important commercial products (e.g., epoxy resins, cosmetics, surface coatings, sweeteners, perfume, drugs, etc.).[2] To overcome the limitations of traditional processes using stoichiometric amounts of peracids, research has focused on the development of new synthetic methods. Metal catalyzed alkene to epoxide conversion in the presence of softer oxidants, such as H_2O_2, alkyl hydroperoxides, or air, has attracted considerable interest and led to the development of highly active catalysts.[3−5] Molybdenum complexes with various types of ligands have been tested in the epoxidation of alkenes and among them, *cis*-$[MoO_2L_2]$ complexes by Schiff base ligands prove to be active catalysts.[6−11] Most of these complexes show high catalytic activity in the epoxidation of internal alkenes such as cyclooctene and cyclohexene. The epoxidation of terminal alkenes like styrene is more challenging because of favored ring-opening reactions of the epoxide,[12,13] leading usually to relatively low conversions and poor selectivity. Only a very limited number of highly selective molybdenum(VI) catalysts employing other ligands in the epoxidation of styrene were reported,[14−16] a prominent example being molybdenum(VI) dioxo half sandwich complexes with cyclopentadienyl derivatives.[15] Thus, it is still worthwhile to develop further homogeneous catalysts for selective epoxidation of styrene and other olefins.

We have an ongoing interest in oxygen atom transfer (OAT) chemistry mediated by high valent molybdenum compounds.[17−20] Only recently we started to investigate the catalytic behavior in epoxidation reactions.[13] These molybdenum dioxo complexes contain a bidentate phenol based ligand with an adjacent pyrazole substituent. We found them to be highly reactive epoxidation catalysts for various substrates but unselective for styrene leading to several ring-opened products. The high reactivity prompted us to develop molybdenum dioxo compounds with phenol based ligands having a higher denticity to influence the selectivity. From rhenium based epoxidation catalysis with MTO it was shown that the addition of Lewis bases (e.g., pyridines and pyrazoles) modulates the Lewis acidity of the rhenium center and thereby increases the selectivity.[21] We adopt this concept to molybdenum chemistry by introducing an intramolecular donor in the ligand design. We focused on Schiff base ligands as they are known to be effective ligands in oxidation catalysis.[4] Furthermore, synthetic procedures for Schiff base ligands are widely published and are easy to modify. Here, we report the preparation of a set of new molybdenum(VI) dioxo complexes with bidentate phenol imine ligands equipped with a

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pendant donor functionality and their highly selective catalytic epoxidation behavior toward various olefins.

RESULTS AND DISCUSSION

Synthesis of the Ligands. Syntheses of ligands HL^1 to HL^5 follow a single step procedure as described for ligand HL^3 in the literature.[22] Condensation of aromatic aldehydes with the appropriate secondary amines in methanol at room temperature results in the formation of the Schiff base ligands as yellow viscous oils (HL^1–HL^4) or solid (HL^5) in quantitative yields (see Figure 1). All ligands were characterized by common

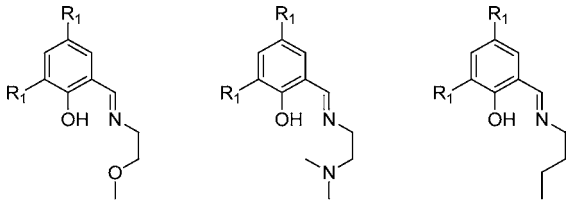


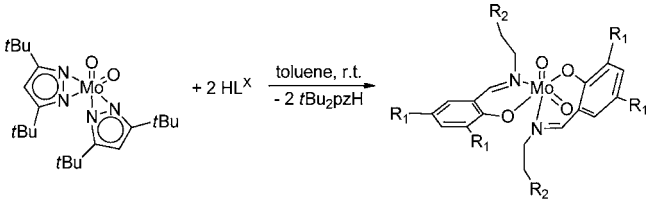
Figure 1. Ligands HL^1–HL^5 employed in this study. The ligands HL^3 and HL^5 were previously described in the literature.[22,23]

spectroscopic techniques and used without further purification. The proton of the imine group (Ar–C*H*N) at the aromatic ring is indicated by a single peak in the region between 8.14 and 8.39 ppm in the ^{1}H NMR spectra. The resonance of the corresponding C atom (Ar-CHN) is found between 166 and 168 ppm in the ^{13}C NMR spectra. IR measurements show a strong absorption between 1631 cm^{-1} and 1634 cm^{-1} attributed to the stretching vibration of the $\nu_{C=N}$ group, which is in good agreement with the literature.[22,23] Mass spectrometry confirmed the formation of the expected ligands.

Ligands HL^3 and HL^5 were previously described in the literature and have been used for the syntheses of several metal complexes.[22−27]

Synthesis of Molybdenum(VI) Dioxo Complexes. Molybdenum(VI) dioxo complexes $[MoO_2(L^X)_2]$ (X = **1**–**5**) are readily accessible by reaction of $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$[17] with 2 equiv of the ligand in dry toluene at room temperature. The pyrazolate ligands are easily displaced by two Schiff base ligands HL^X (X = **1**–**5**), leading to disubstituted complexes in moderate to good yields (Scheme 1). All ligands coordinate via the

Scheme 1. Synthetic Procedure for the Preparation of Di-substituted *cis*-$[MoO_2(L^X)_2]$ Complexes 1–5



phenolic O atom and the imine N atom to the metal center, the third donor atom (R_2 = OMe or NMe_2) in complexes **1**–**4** remains pendant. The formation of the complex is indicated by a color change from light yellow to orange (for **1**, **3**, and **5**) or brown (for **2** and **4**) of the solution. The unusual starting material $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$ offers the advantage of a very easy workup procedure, as the formed side product, bis-*tert*-butylpyrazole, together with residual ligand traces can be easily separated from the complexes via extraction with pentane or heptane. The pure compounds are isolated as yellow to light brown solids.

Complexes **1**–**5** can be also prepared by more conventional methods using either $[MoO_2Cl_2(dme)]$[28] or commercially available $[MoO_2(acac)_2]$ as starting materials (Scheme 2). Both reaction pathways would be favorable as they involve fewer synthetic steps, but the obtained yields and purities were significantly lower. Furthermore, we were not able to isolate complexes **2** and **4** using $[MoO_2(acac)_2]$.

All molybdenum complexes **1**–**5** are well soluble in common organic solvents such as toluene, tetrahydrofuran (THF), chloroform, and methanol at room temperature, but much less so in aliphatic hydrocarbons like pentane or heptane. The compounds are stable in the absence of moist air and can be stored under inert conditions for several weeks (complexes **3** and **4**) to months (complexes **1**, **2**, and **5**). In general complexes **1** and **2** with a methoxy group in the pendant arm prove to be more stable in solution than their NMe_2 based counterparts **3** and **4**. The latter compounds tend to decompose after a few days in solution. We suspect that the amine group leads to more basic conditions in comparison to the ether functionality and therefore traces of water may have a more pronounced effect, thus preferring the formation of polymeric molybdenum compounds.

Complexes **1**–**5** were characterized by NMR and IR spectroscopy, mass spectrometry, and elemental analyses. Crystals suitable for X-ray diffraction analyses were obtained in the case of complexes **1** and **3**.

^{1}H NMR spectra of the free ligands HL^1 to HL^5 show a broad resonance between 13.34 and 14.00 ppm for the aromatic OH proton. Disappearance of this signal indicates a coordination of the phenolic O atom to the metal center. The sharp signal of the imine proton in the ligand (8.14 to 8.39 ppm) is shifted to higher field and appears between 8.09 and 8.38 ppm upon complexation. Mass spectrometry as well as elemental analyses confirmed the formulation of complexes **1**–**5** as $[MoO_2(L^X)_2]$.

In principle, the design of the ligand would allow the formation of several isomers in solution, with respect to the ligand trans to the terminal oxygen ligands. Both ligands can coordinate via the phenolic O atom and the imine N atom either in a symmetric way (*N,N* and *O,O* isomer) or in an asymmetric way (*N,O* isomer) as shown in Figure 2.

For complexes **2** and **4** only one isomer could be observed in solution. NMR spectra show one set of sharp resonances for just one type of ligand, indicating a symmetric coordination of the ligand to the metal center. Formation of the *N,N* isomer (Figure 2) is probably favored over the *O,O* isomer because the steric clash of the substituents on the aromatic rings is avoided. On the other hand, ^{1}H NMR spectra of complexes **1**, **3**, and **5** show together with a set of sharp resonances, a set of broad resonances for another coordination environment.

Low temperature NMR measurements of complexes **1** and **3** resolve the broad signals and indicate the formation of a symmetric (major isomer) and an asymmetric isomer (minor isomer) in solution in a 4:1 (complex **1**) and a 2:1 (complex **3**) ratio. Figure 3 shows a comparison of the aromatic region of complex **3** at 25 °C and −35 °C. The formation of a symmetric isomer *S* (*N,N* or *O,O* isomer) is indicated by the existence of one set of

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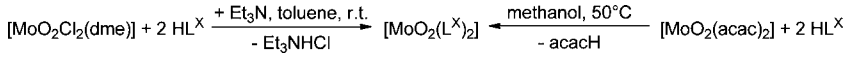
Scheme 2



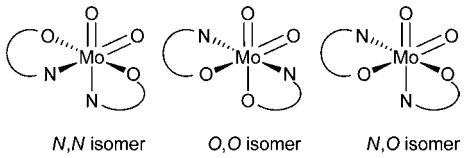


Figure 2. Possible symmetric and asymmetric isomers in solution.

resonances for both coordinated ligands. The broad signals resolve into two sets of resonances of equal intensity at low temperature (e.g., two signals for the imine groups at 8.09 and 8.36 ppm) and can thus be assigned to the asymmetric isomer *AS* (*N,O* isomer). Molecular structures determined by X-ray diffraction analyses of complexes **1** and **3** reveal exclusively the symmetric *N,N* isomer. In several attempts we dissolved such single crystals in benzene-d_6. Their ^{1}H NMR spectra show always the two isomers in solution in the same ratio as in the bulk material, pointing to a dynamic equilibrium in solution.

The three compounds **1**, **3**, and **5** that are found in the two isomeric forms (*N,N* and *N,O* isomer) in solution represent derivatives with two sterically demanding *t*Bu groups in *o*- and *p*-positions of the phenolic ring. From a steric point of view **1**, **3**, and **5** are expected to form exclusively the *N,N* isomer. On the other hand, from an electronic point of view, the *O,O* isomer with the more electronegative phenolic oxygen coordinated trans to the metal oxo bond is predicted to be favored. We exclusively find such a bonding situation in $[MoO_2(L)_2]$ complexes where L represents ß-ketiminates.[19,20] For this reason, we attribute the occurrence of two isomers in complexes **1**, **3**, and **5** to the higher electron-donating capacity of the *t*Bu groups, rendering the phenolic oxygen more nucleophilic so, at least partially, overruling the steric hindrance.

The IR spectra of all $[MoO_2(L^X)_2]$ complexes **1**−**5** exhibit two strong $\nu_{Mo=O}$ bands in the region 900−904 cm^{-1} and 914−928 cm^{-1}, characteristic for the symmetric and asymmetric stretching mode of the *cis*-$[MoO_2]^{2+}$ fragment.[14,29,30] The absence of a broad band around 3250 cm^{-1} in the spectra of the molybdenum complexes compared to the Schiff base ligands indicates the coordination of the phenolic oxygen atom after deprotonation. The characteristic stretching frequencies of the $\nu_{C=N}$ band in the free ligand (1631−1634 cm^{-1}) are shifted to lower wave numbers upon coordination of the imine nitrogen to the metal center and appears at 1625−1628 cm^{-1}.[7,8,29]

Molecular Structure in the Solid State. Single crystals suitable for X-ray diffraction analysis of complex **1** and **3** were obtained from concentrated solutions in methanol at room temperature. Complexes **1** and **3** crystallized in the monoclinic space group *Cc* (**1**) and *C*2 (**3**) in the form of light yellow parallelepipeds (**1**) or yellow tablets (**3**). Molecular views of both compounds are shown in Figure 4. Selected bond lengths and angles are given in Table 1 and crystallographic data in Table 2.

The X-ray structures of complexes **1** and **3** are very similar and confirm the formation of the symmetric *N,N* isomer (Figure 2). Both compounds exhibit a six-coordinate Mo atom in a distorted octahedral geometry. The metal center is ligated by two terminal oxygen atoms and two Schiff base ligands, each of them coordinating via the phenolic oxygen atom and the imine N atom to the metal center. The third donor atom in the side chain (R_2 = OMe in **1** and R_2 = NMe_2 in **3**) is not involved in coordination and hence the arm remains pendant. The molybdenum oxo groups show the expected mutual cis configuration and are located trans to the imine N atoms. All Mo−O bond lengths [1.9556(12) Å and 1.9611(11) Å for **1** and 1.942(4) Å for **3**] as well as all Mo=O bond lengths [1.7013(11) Å and 1.7059(11) Å for **1** and 1.714(4) Å for **3**] are in the expected range of *cis*-$[MoO_2]^{2+}$ complexes. The Mo−N bonds [2.3303(12) Å and 2.37454(12) Å for **1** and 2.334(5) Å for **3**] are somewhat longer because of the influence of the trans Mo=O ligand.[7,14,29]

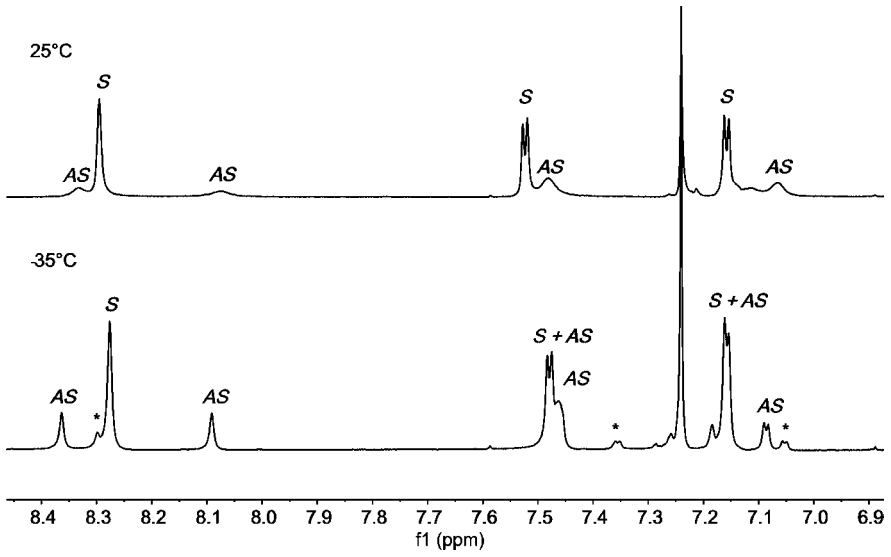


Figure 3. ^{1}H NMR spectra of complex **3** in chloroform-*d* at 25 °C (top) and −35 °C (bottom). The asterisk (*) denotes residual free ligand. *S* corresponds to the symmetric isomer (*N,N* or *O,O* isomer), and *AS* corresponds to the asymmetric *N,O* isomer shown in Figure 2.

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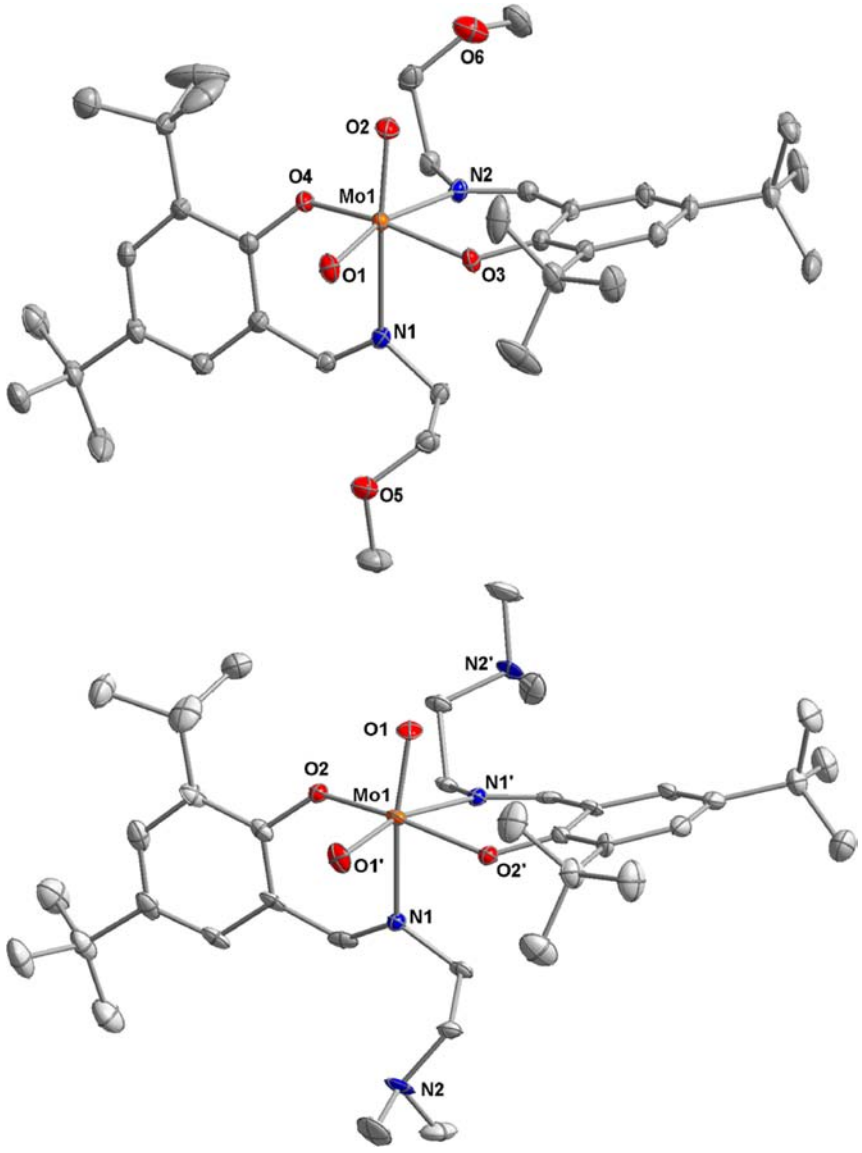

Figure 4. Molecular structure and atom labeling scheme for complexes **1** (top) and **3** (bottom). Thermal ellipsoids have been drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complexes 1 and 3

		Complex **1**			
Mo1—O1	1.7013(11)	Mo1—O3	1.9556(12)	Mo1—N1	2.3303(12)
Mo1—O2	1.7059(11)	Mo1—O4	1.9611(11)	Mo1—N2	2.3754(12)
O1–Mo1—O2	106.15(6)	O3–Mo1—O4	158.44(4)	O1–Mo1—N2	164.36(5)
O1–Mo1—O3	93.77(5)	O1–Mo1—N1	86.58(5)	O2–Mo1—N2	89.00(5)
O1–Mo1—O4	97.62(5)	O2–Mo1—N1	166.75(5)	O3–Mo1—N2	79.90(5)
O2–Mo1—O3	98.35(5)	O3–Mo1—N1	84.17(5)	O4–Mo1—N2	84.35(5)
O2–Mo1—O4	95.98(5)	O4–Mo1—N1	78.33(5)	N2–Mo1—N1	78.60(4)
		Complex **3**[a]			
Mo1—O1	1.714(4)	Mo1—O2	1.942(4)	Mo1—N1	2.334(5)
O1–Mo1—O1′	107.0(3)	O2–Mo1—O2′	161.2(2)	O2–Mo1—N1	80.23(16)
O1–Mo1—O2	94.96(19)	O1–Mo1—N1′	90.1(2)	O2–Mo1—N1′	84.70(16)
O1–Mo1—O2′	96.18(19)	O1–Mo1—N1	162.8(2)	N1–Mo1—N1′	73.1(3)

[a]Symmetry equivalent atoms are generated by the symmetry operator $1 - x, y, 2 - z$.

Epoxidation of Alkenes. Complexes **1**–**5** have been tested as catalysts in the epoxidation of several internal and terminal alkenes using *tert*-butyl hydroperoxide (TBHP, 5.5 M in decane) as oxygen source. Optimal reaction conditions regarding

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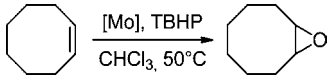
Table 2. Crystallographic Data and Structure Refinement for Complexes 1 and 3

	1	3
empirical formula	$MoO_6N_2C_{36}H_{56}$	$MoO_4N_4C_{38}H_{62}$
formula weight	708.77	734.86
crystal description	parallelepiped, light yellow	tablet, yellow
crystal size (mm)	0.70 × 0.31 × 0.25	0.69 × 0.15 × 0.07
crystal system, space group	monoclinic, *Cc*	monoclinic, *C*2
unit cell dimensions	a = 31.098(3) Å	a = 19.606(2) Å
	b = 10.1937(8) Å	b = 6.8112(7) Å
	c = 11.9756(9) Å	c = 15.1333(16) Å
	α = 90°	α = 90°
	β = 107.044(2)°	β = 98.025(4)°
	γ = 90°	γ = 90°
volume (Å^3)	3629.5(5)	2001.1(4)
Z, calculated density (g cm^{-3})	4, 1.297	2, 1.223
F(000)	1504.0	788.0
linear absorption coefficient μ (mm^{-1})	0.406	0.368
absorption correction	multiscan	multiscan
temperature	100(2) K	100(2) K
wavelength (MoK$_\alpha$)	0.71073 Å	0.71073 Å
θ range for data collection	2.11 to 30.00°	2.10 to 26.09°
limiting indices	$-42 \le h \le 43$	$-24 \le h \le 0$
	$-14 \le k \le 14$	$-8 \le k \le 0$
	$-16 \le l \le 16$	$-18 \le l \le 18$
reflections collected/unique	36836/9485	58693/2133
	[R(int) = 0.0233]	[R(int) = 0.0967]
completeness to θ max.	0.999	0.983
refinement method	full matrix least-squares on F^2	full matrix least-squares on F^2
data/restraints/parameters	9485/2/421	2133/1/211
goodness-of-fit on F^2	1.034	1.085
final R1,[a] wR2[b] [$I > 2\sigma(I)$]	R1 = 0.0221	R1 = 0.0478
	wR2 = 0.0576	wR2 = 0.1288
R indices (all data)	R1 = 0.0225	R2 = 0.0496
	wR2 = 0.0579	wR2 = 0.1305
largest diff. peak and hole (e Å^{-3})	1.033 and −0.576	2.254 and −1.458
CCDC deposition no.	837295	837296

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

Scheme 3. Epoxidation of Cyclooctene



temperature, solvent, oxidant loading, and catalyst loading were evaluated by using the substrate cyclooctene and complex **1** as catalyst (Scheme 3). Table 3 summarizes the results of temperature and solvent screening. The highest conversions were obtained at 50 °C in chloroform or without additional cosolvent. At higher temperature (75 °C) similarly high conversions were also reached in heptane or toluene. No conversion of epoxide is observed in methanol, *tert*-butanol, or THF. Our results are in good accordance with the literature, where higher temperatures and chlorinated solvents[7,14,30] or solvent free conditions[9,10] are preferred. For these reasons all further experiments were performed in chloroform at 50 °C.

The catalyst loading can be reduced down to 0.25 mol % in the presence of 2 equiv of TBHP without affecting efficiency of the

Table 3. Epoxidation of Cyclooctene Catalyzed by 1: Effect of Cosolvent and Temperature

	conversion (%)		
cosolvent[a]	35 °C	50 °C	75 °C
CH_2Cl_2	80		
$CHCl_3$		93	
$C_2H_4Cl_2$			88
heptane		57	96
toluene		63	97
TBHP/decane[b]		95	
TBHP/H_2O[b]		<10	
diethylether	25		
*t*BuOH or MeOH		<10	

[a] Reaction conditions: 0.5 mol % complex **1**, 1.41 mmol alkene, 2.82 mmol (2 equiv) TBHP. Conversions were determined by GC/MS measurements after 60 min. Mesitylene was used as internal standard. Complete selectivity toward the epoxide was observed. [b] Reaction was performed without additional cosolvent (5.5 M TBHP in decane or 70 w% TBHP in water).

system (see Table 4). A further lowering to 0.1 mol % led to lower yields with 1 or 2 equiv of TBHP. Some $[MoO_2]^{2+}$

Table 4. Epoxidation of Cyclooctene Catalyzed by 1: Effect of Catalyst and Oxidant (TBHP) Loading

		conversion (%)[a]	
mol % **1**	Mo:substrate ratio	TBHP (1 equiv)[b]	TBHP (2 equiv)[b]
1	1:100	89	99
0.5	1:200	87	98
0.25	1:400	85	95
0.1	1:1000	74	84
0.05	1:2000	56	53
0.01	1:10000	31	33

[a] Reactions were carried out at 50 °C in chloroform (5 mL) using 1.41 mmol alkene, 1.41 mmol (1 equiv), or 2.82 mmol (2 equiv) TBHP. Conversions were determined by GC/MS measurements after 120 min. Mesitylene was used as internal standard. [b] Complete selectivity toward the epoxide was observed.

complexes allow lower catalyst concentrations without loss of efficiency.[7,10,31] For subsequent epoxidation reactions we chose 0.5 mol % of catalyst loading and 2 equiv of TBHP at 50 °C in chloroform.

To evaluate the stability of the catalysts an experiment with three consecutive catalytic runs was performed. Complex **1** shows full conversion in the epoxidation of cyclooctene after 60 min in the first run. After 120 min additional substrate (1.41 mmol) and oxidant (2.82 mmol) are added for the second run and after 24 h for the third run. The results are displayed in Figure 5. The catalytic activity of complex **1** in the second run is quite similar to that of the first run. After one hour reaction time almost full conversion (93% of cyclooctene oxide) of cyclooctene is obtained. The catalytic activity in the third run (addition of substrate and TBHP after 24 h) is good, but the conversion rate is lower than in the former two runs, presumably because of the increase of *tert*-butanol concentration. In each run we only observe the formation of the corresponding epoxide and no other products caused by subsequent ring-opening reactions.

We then tested further substrates with complexes **1**−**5**, namely, cyclooctene, cyclohexene, and the more challenging substrates styrene and 4-phenyl-1-butene. All reactions are performed in

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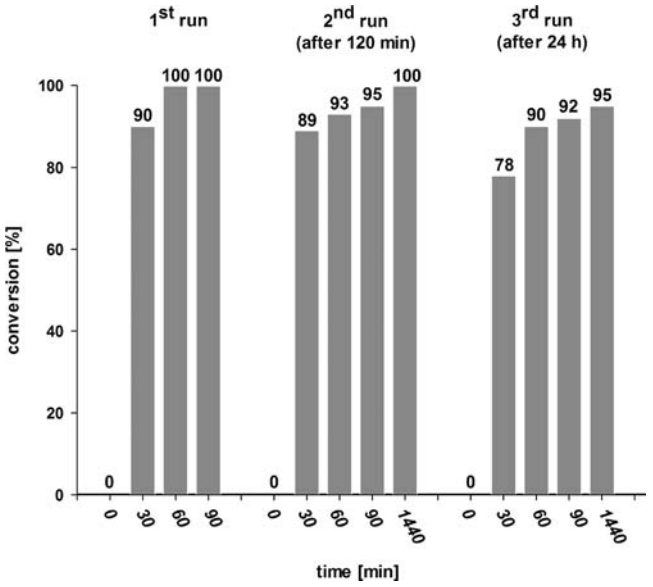
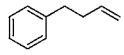


Figure 5. Activity test of complex **1** via epoxidation of cyclooctene in three consecutive runs. After 2 and 24 h 1.41 mmol cyclooctene and 2.82 mmol TBHP were added to the initial reaction mixture. Reactions were performed in chloroform (5 mL) at 50 °C with 0.5 mol % catalyst loading.

chloroform at 50 °C using 0.5 mol % catalyst, 1.41 mmol substrate, and 2.82 mmol TBHP. In all cases control experiments confirmed low conversion of substrate (<10%) in the absence of catalyst.

Generally complexes **1**−**5** oxidize the different olefins in fairly high yields. While complete conversion to the corresponding epoxide is observed for cyclohexene and cyclooctene, lower conversions are observed for both terminal alkenes styrene and 4-phenyl-1-butene. As shown in Table 5, the pendant donor arms as well as the substituents on the aromatic ring influence the catalytic activity. Complexes **1** and **2** with an additional OMe group in the side chain are more active than their NMe_2 (**3**, **4**) and Et (**5**) based counterparts (e.g., in the epoxidation of cyclooctene for **1** TOF = 359 h^{-1} for **3** TOF = 46 h^{-1} and for **5** TOF = 133 h^{-1}). The epoxidation of styrene or 4-phenyl-1-butene is more challenging as these substrates are less electron rich. Herein again, the OMe based complexes **1** and **2** prove to be more active catalysts than their NMe_2 (**3**, **4**) and Et (**5**) based counterparts. Among them, both complexes **1** (R_1 = *t*Bu) and **2** (R_1 = Me) with substituents in *ortho* and *para* position on the aryl ring show excellent catalytic activities and conversions up to 80% (**1**) and 76% (**2**) for styrene and 88% (**1**) and 70% (**2**) for 4-phenyl-1-butene are obtained after 24 h, respectively (see Table 5). Furthermore, catalysts **1**−**4** are highly selective, as ring-opening of the styrene epoxide to the corresponding diol or aldehyde is not significant under the applied reaction conditions. In contrast, complex **5** without a donor atom in the pending arm shows dramatically lower conversions and poorer selectivity in the epoxidation of styrene (39% yield after 24 h and 57% selectivity). Such poor selectivity has been previously reported in the literature with a similar *cis*-$[MoO_2]^{2+}$ complex coordinated to bidentate Schiff base ligand.[7] The conversions obtained with complexes **1** and **2** in the epoxidation of styrene and 4-phenyl-1-butene are quite high and in the same range as for some other selective catalysts in the literature.[15,32] Commercially available $[MoO_2(acac)_2]$ reacts faster in the epoxidation catalysis, as cyclooctene or cyclohexene are converted within a few minutes

Table 5. Epoxidation of Aliphatic and Aromatic Alkenes with Complexes 1−5 and $[MoO_2(acac)_2]$

substrate	catalyst[a]	conversion (%)	time (h)	selectivity[b] (%)
Cyclohexene[c]	**1**	100	1	99
	**2**	100	1	99
	3	23	1	99
	4	25	1	99
	5	100	1.5	99
Cyclooctene[c]	**1**	100	1	99
	**2**	100	1	99
	3	22	1	99
	4	30	1	99
	5	100	1.5	99
	$[MoO_2(acac)_2]$	100	0.17	99
	$[MoO_2(acac)_2]$[d]	10	1	99
Styrene[c]	**1**	75 / 80	5 / 24	98
	**2**	71 / 76	5 / 24	97
	3	15	24	99
	4	17	24	99
	5[e)]	41 / 39	5 / 24	57
	$[MoO_2(acac)_2]$[e]	42 / 46	5 / 24	66
	$[MoO_2(acac)_2]$[e,f]	44	24	65
4-Phenyl-1-butene[c]	**1**	75 / 88	5 / 24	99
	**2**	42 / 70	5 / 24	99
	3	9	24	99
	4	7	24	99
	5	13 / 27	5 / 24	99
	$[MoO_2(acac)_2]$	70 / 79	5 / 24	99

[a]Reaction conditions: 0.5 mol % catalyst, 1.41 mmol alkene (1 equiv), 1.41 mmol internal standard (1 equiv), 2.82 mmol (2 equiv) TBHP, chloroform (5 mL), 50 °C. [b]Selectivity after 24 h. [c]Reaction yields were determined by GC/MS measurements; mesitylene was used as internal standard. [d]Addition of Et_3N (1 mol %). [e)]Due to ring-opening, benzaldehyde and diols as side products. [f)]Addition of *n*-butyl methyl ether (1 mol %).

to the corresponding epoxide.[11,33,34] Nevertheless, in the epoxidation of styrene the formation of benzaldehyde and further ring-opening products is observed.[34]

Quite similar epoxide yields for complexes **3** and **4** were obtained by reactions performed under inert conditions (Ar). Furthermore, the addition of molecular sieves during catalysis has no significant effect. All catalytic reaction mixtures are homogeneous single liquid phases.

As shown in the reaction profile of complexes **1**−**5** in the epoxidation of styrene (see Figure 6), a sterically more

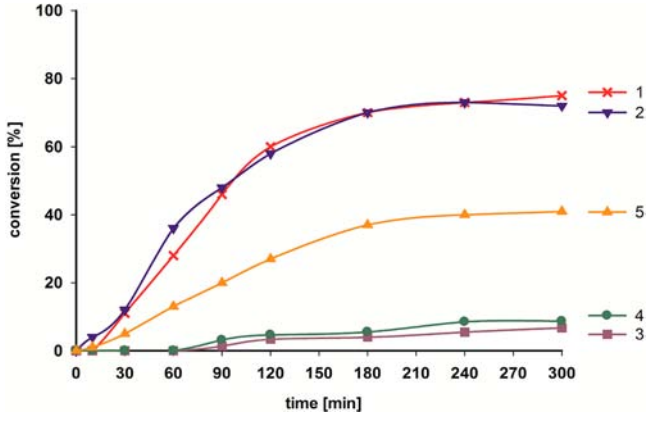


Figure 6. Reaction profile of complexes **1**−**5** in the epoxidation of styrene.

demanding substituent on the aromatic ring has a negligible influence on the catalytic activity, since similar reaction curves are

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obtained for complexes **1** (R_1 = *t*Bu) and **2** (R_1 = Me) as well as for complexes **3** (R_1 = *t*Bu) and **4** (R_1 = Me). Nevertheless, the reaction profile clearly demonstrates the influence of the pendant arm in the side chain. Both complexes **1** and **2** with a OMe group are more active than their NMe_2 based counterparts **3** and **4** and the Et based counterpart complex **5**.

The reaction mechanism in the epoxidation of alkenes is still under debate.[9,35−37] However, the more likely mechanism includes the addition of TBHP across one terminal Mo═O group, leading to the formation of Mo−OH and Mo−O−O-*t*Bu moieties.[38] After coordination of the *t*Bu-O-O to the metal center its α-O atom is transferred to the alkene, producing the epoxide under concomitant elimination of *tert*-butyl alcohol, yielding the initial complex. Theoretical studies evidence the importance of H bond formations at various steps of the catalytic cycle.[35,37] Thus, not only the oxygen atom transfer represents a barrier but also the hydrogen atom transfers. It is noteworthy that the release of the formed epoxide was calculated to have almost no barrier whereas a significant energy barrier was found for the release of the side product *tert* - butyl alcohol.[35]

The design of our complexes with pendant donor groups in the side chain allows in principle the formation of H bonds during the catalytic cycle, which may explain the different catalytic activities of complexes **1**−**5**. Both NMe_2 based complexes **3** and **4** are less active, and lower epoxide conversions are observed. It seems that the more basic NMe_2 donor group is more prone toward protonation leading to the formation of a less active species and hence slowing down the catalytic activity. We tested the influence of an amine (NEt_3, 1 mol %) in the epoxidation of cyclooctene using $[MoO_2(acac)_2]$ (0.5 mol %) as catalyst and TBHP as oxidants. Without amine, full conversion to the corresponding epoxide is observed within 10 min of reaction time, whereas the addition of the amine considerably slows down the catalytic activity and only 10% yield of cyclooctene-oxide is observed within 1 h of reaction time (see Table 5). An increase in the selectivity accompanied by a decrease in the efficiency is also observed in the rhenium based MTO system upon addition of pyridines or pyrazoles, because of the reduced Lewis acidity of the catalytic system.[39] Such inhibiting behavior is not evident in complexes **1**, **2**, and **5**.

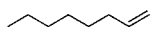
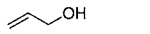
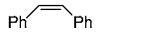
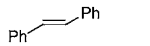
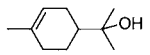
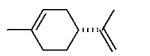
On the other hand, the higher catalytic rates of complexes **1** and **2** compared to **5** may be explained by the influence of the OMe group on the formation of hydrogen bonds. Such bonds may be stable enough to lower the activation barriers but not too strong as in the case of NMe_2 groups. Furthermore, the potential coordination of the OMe group to the molybdenum may facilitate the release of *tert*-butanol.

Additionally, we tested the effect of an intermolecular donor in the epoxidation of styrene catalyzed by $[MoO_2(acac)_2]$ (0.5 mol %) in presence of *n*-butyl methyl ether (1 mol %). Again, a selectivity of only 65% concerning styrene epoxide is observed, thereby proving that a donor per se does not increase the selectivity as observed in complexes **1**−**4**, but it requires an intramolecular donor (see Table 5).

With complexes **1**, **3**, and **5** epoxidation of a variety of different other aliphatic and aromatic alkenes was explored. Results are summarized in Table 6. All alkenes are oxidized in moderate to high yields, with complexes **1** and **5** to be generally more reactive than **3**.

Both aliphatic alkenes, 1-octene and 2-propenol, are epoxidized in high yields and good selectivities. The hydroxyl group of 2-propenol is accepted under these reaction conditions as we do not observe further products. The range of the observed

Table 6. Epoxidation of Aliphatic and Aromatic Alkenes with Complexes 1, 3, and 5

substrate	catalyst[a]	conversion (%)	time (h)	selectivity[b] (%)
1-octene[c] 	**1**	63	24	99
	3	16	24	99
	5	71	24	99
2-propenol[c] 	**1**	50 / 73	8 / 24	99
	3	22	24	99
	5	56 / 70	8 / 24	99
cis-stilbene[d] 	**1**	25 / 68	2 / 24	97
	3	9	24	99
	5	17 / 61	2 / 24	96
trans-stilbene[d] 	**1**	13 / 51	4 / 24	97
	3	7	24	99
	5[f]	27 / 58	4 / 24	88
α-terpineol[e] 	**1**	86 / 100	4 / 24	99
	3	30 / 35	4 / 24	99
	5	89 / 100	4 / 24	99
R-(+)-limonene[e] 	**1**[g]	78 / 61	4 / 24	61
	3	50 / 86	4 / 24	99
	5[g]	78 / 63	4 / 24	63

[a]Reaction conditions: 0.5 mol % catalyst, 1.41 mmol alkene (1 equiv), 1.41 mmol internal standard (1 equiv), 2.82 mmol (2 equiv) TBHP, chloroform (5 mL), 50 °C. [b]Selectivity after 24 h. [c]Reaction yields were determined ^{1}H NMR spectroscopy; dichloroethane was used as internal standard. [d]Reaction yields were determined by HPLC chromatography; mesitylene was used as internal standard. [e]Reaction yields were determined by GC/MS measurements; mesitylene was used as internal standard. [f]Due to ring-opening, benzaldehyde and acetophenone as side products. [g]Dipentene dioxide (limonene dioxide) as side product.

yields is in good accordance with the literature.[7,8,30] Significantly higher conversions are obtained in the epoxidation of *cis*-stilbene with respect to the epoxidation of *trans*-stilbene but in both cases with high stereoselectivities for complex **1**. Similar results have been observed in the literature, in some cases with higher epoxide conversions.[8,30] After 24 h, the formation of side products because of ring-opening in the epoxidation of *trans*-stilbene is apparent for complex **5**. α-Terpineol and limonene are interesting substrates, as both are naturally occurring. After 24 h we observe full conversion of α-terpineol to the corresponding epoxide. The remaining hydroxyl group is not affected, as already shown by others in the literature.[7] The epoxidation of limonene is more challenging, as the substrate includes two quite different alkene moieties, one internal and one terminal. For complexes **1** and **5**, complete conversion is obtained, but selectivities are low as the formation of the double epoxide, dipentene dioxide (limonene dioxide), occurs after 4 h. Complex **3** is more selective, as only the formation of 1,2 epoxy limonene is observed. Nevertheless, this is most probably caused by the low epoxidation rate of complex **3**. Some catalysts in the literature are more selective, as only the formation of 1,2 epoxy limonene is observed.[14] Negligible conversions with all catalysts are observed using ally phenyl ether as substrate. To sum up, complex **1** with a OMe substituent in the pendant arm is more reactive than its NMe_2 based counterpart complex **3**. Complex **5** is as reactive as complex **1**.

After one catalytic run catalyst **1** could be isolated as a solid material after evaporation of the solvent and subsequent addition of heptane. Both, IR and MS (EI) measurements of this material

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indicate that complex **1** remains unchanged. Furthermore we were concerned with possible decomposition reactions based on the more reactive N atom in complexes **3** and **4**. Therefore, we investigated the possible oxidation of the NMe_2 moiety by addition of TBHP to solutions of the ligand as well as the complex **3**. However, no formation of N oxide could be observed as NMR spectra remained unchanged. Attempts to isolate any intermediate molybdenum(VI) *tert*-butyl hydroperoxide complex have not yet been successful. The synthesis of molybdenum peroxo complexes by treatment of **1** with H_2O_2 or reaction of HL^1 with $[MoO(O_2)_2{\cdot}DMF]$[40] have likewise been unsuccessful. Furthermore, the use of H_2O_2 as terminal oxidant did not yield significant amounts of the corresponding epoxide.

Lastly, it is noteworthy that the formation of heterogeneous catalysts with our $[MoO_2(L^X)_2]$ complexes should be possible. The noncoordinated donor group in the side chain seems to be a good linking moiety for their immobilization onto inorganic solids or organic polymers. Such polymer supported Schiff base complexes of different metal ions are well-known in the literature and serve as highly active catalysts in various types of reactions (e.g., polymerizations, oxidations).[5,24,26,27,41]

■ CONCLUSIONS

We have been able to prepare a series of new $[MoO_2(L^X)_2]$ complexes with Schiff base ligands using the uncommon η^2 coordinated $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$ complex as starting material. All complexes are readily accessible in moderate to good yields. With the more sterically demanding *t*Bu substituent on the aryl ring (complexes **1**, **3**, and **5**) a mixture of two isomers in solution is obtained, whereas only one isomer in solution is detected for both methyl substituted complexes **2** and **4**. Low temperature NMR measurements of complexes **1** and **3** clearly indicate the formation of one symmetric (major isomer) and one asymmetric isomer (minor isomer). X-ray diffraction analyses show the ligands to be, in all cases, symmetrically coordinated to the metal center. Complexes **1**−**5** have been tested as catalysts in the epoxidation of various alkenes using TBHP as oxidants. Among them, complexes **1** and **2** prove to be highly selective in the epoxidation of styrene, and epoxide conversions up to 80% are obtained after 24 h. They belong to a rare group found in the literature, which undergo selective epoxide formation of this challenging substrate in high yields. Complex **5** with no side chain functionality is significantly less selective in the epoxidation of styrene. Both NMe_2 based complexes **3** and **4** are less active. Further research concerning the mechanism of such epoxidation reactions is in progress.

■ EXPERIMENTAL SECTION

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry argon using standard Schlenkline or glovebox techniques. $[MoO_2(acac)_2]$ and *tert*-butyl hydroperoxide (TBHP, 5.5 M in decane, over molecular sieves 4 Å) were purchased from Sigma Aldrich and used as received. All other chemicals were obtained from different suppliers and used without further purification. Solvents were purified via a Pure-Solv MD-4-EN solvent purification system from Innovative Technology, Inc. Methanol was refluxed over activated magnesium for at least 24 h and then distilled prior to use. Chloroform was extracted three times with water and then stirred for 24 h over $CaCl_2$. After filtration, the solvent was refluxed over P_2O_5 for 2 h and then distilled. 3,5-Dimethyl-2-hydroxybenzaldehyde,[42] the ligands (HL^3 and HL^5)[22,23] as well as the metal precursors $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$[17] and $[MoO_2Cl_2(dme)]$[28] were prepared according to literature procedures.

All ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III Spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C NMR). The ^1H NMR spectroscopic data are reported as s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constants are reported in hertz (Hz), and chemical shifts are given in parts per million (ppm) relative to the solvent residual peak. All deuterated solvents were purchased from Deutero GmbH and dried over molecular sieves. IR spectra were measured as solid samples on a Bruker Alpha B Diamond FTIR spectrometer. Mass spectra have been measured on an Agilent 5973 MSD-Direct Probe using the EI ionization technique. GC-MS measurements were performed on an Agilent 7890A with an Agilent 19091J-433 column coupled to a mass spectrometer type Agilent 5975C. Elemental analyses were carried out using a Heraeus Vario Elementar automatic analyzer at the Institute of Inorganic Chemistry at the University of Technology in Graz.

Syntheses of the Ligands. Ligand HL^1. 2-Methoxyethylamine (1.05 g, 14 mmol) was added to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (3.28 g, 14 mmol) in 50 mL of MeOH. The mixture was refluxed overnight. After cooling to room temperature, the solution was dried with Na_2SO_4. The solvent was removed under vacuum to afford a yellow viscous oil, which was used without further purification. Yield: 3.80 g (93%).

^1H NMR (300 MHz, chloroform-*d*, 298 K): δ 1.30 (s, 9H, Ar−C(CH_3)$_3$), 1.44 (s, 9H, Ar−C(CH_3)$_3$), 3.36 (s, 3H, OCH_3), 3. 66 (t, $^3J_{H-H}$ = 5.4 Hz, 2H, N(CH_2)$_2$OCH$_3$), 3.74 (t, $^3J_{H-H}$ = 5.4 Hz, 2H, N(CH_2)$_2$OCH$_3$), 7.09 (d, $^4J_{H-H}$ = 2.4 Hz, 1H, Ar-*H*), 7.37 (d, $^4J_{H-H}$ = 2.4 Hz, 1H, Ar-*H*), 8.37 (s, 1H, Ar−C*H*N), 13.70 (s, 1H, Ar−O*H*). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K): δ 29.64 (Ar−C(CH_3)$_3$), 31.71 (Ar−C(CH_3)$_3$), 34.33 (Ar-*C*(CH_3)$_3$), 35.22 (Ar-*C*(CH_3)$_3$), 59.16 (N(CH_2)$_2$OCH$_3$), 59.23 (N(CH_2)$_2$OCH$_3$), 72.16 (N(CH_2)$_2$OCH$_3$), 118.06 (*Ar*), 126.18 (Ar-H), 127.12 (*Ar*-H), 136.83 (*Ar*), 140.18 (*Ar*), 158.29 (*Ar*−OH), 167.63 (Ar-CHN). IR (ATR, cm^{-1}): 1632 (s, C═N), 1467 (m), 1458 (m), 1440 (s), 1390 (m), 1361 (m), 1273 (m), 1239 (m), 1121 (s), 971 (w), 923 (w), 904 (w), 877 (w), 839 (m), 827 (m). MS (EI) (70 eV) *m*/*z* (%): 291.2 (36.5) [M]$^+$, 276.3 (100.0) [M-CH_3]$^+$, 260.2 (3.8) [M-OCH_3]$^+$, 57.1 (8.7) [C_4H_9]$^+$.

Ligand HL^2. The synthesis of the ligand followed the procedure described above. 2-Methoxyethylamine (1.26 g, 16.8 mmol) was added to a solution of 3,5-dimethyl-2-hydroxybenzaldehyde[42] (2.10 g, 14 mmol) in 50 mL of methanol. After workup, the ligand was obtained as a light orange viscous oil, which was used without further purification. Yield: 2.76 g (95%).

^1H NMR (300 MHz, chloroform-*d*, 298 K): δ 2.24 (s, 6H, 2x Ar-CH_3), 3.34 (s, 3H, N(CH_2)$_2$OCH_3), 3.63 (t, $^3J_{H-H}$ = 5.5 Hz, 2H, N(CH_2)$_2$OCH$_3$), 3.71 (t, $^3J_{H-H}$ = 5.4 Hz, 2H, N(CH_2)$_2$OCH$_3$), 6.86 (s, 1H, Ar-*H*), 6.98 (s, 1H, Ar-*H*), 8.25 (s, 1H, Ar−C*H*N), 13.35 (s, 1H, Ar−O*H*). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K): δ 15.49 (Ar-CH_3), 20.35 (Ar-CH_3), 58.94 (N(CH_2)$_2$OCH_3), 59.13 (N(CH_2)$_2$OCH$_3$), 72.00 (N(CH_2)$_2$OCH$_3$), 117.75 (*Ar*), 125.57 (Ar), 126.95 (*Ar*), 129.05 (*Ar*-H), 134.28 (*Ar*-H), 157.26 (*Ar*−OH), 166.54 (Ar-*C*HN). IR (ATR, cm^{-1}): 1632 (s, C═N), 1605 (m), 1474 (m), 1438 (m), 1266 (s), 1120 (s), 1033 (m), 969 (w), 956 (w), 857 (m), 837 (m). MS (EI) (70 eV) *m*/*z* (%): 207.2 (91.2) [M]$^+$, 192.1 (2.4) [M-CH_3]$^+$, 176.1 (16.7) [M-OCH_3]$^+$, 162.1 (83.8) [M-CH_2OCH_3]$^+$, 149.1 (25.5) [(M-(CH_2)$_2$OCH$_3$)+H]$^+$, 135.1 (100.0) [(M-N(CH_2)$_2$OCH$_3$)+H]$^+$.

Ligand HL^4. The ligand HL^4 was prepared in analogous manner to the ligand HL^1. *N*,*N*-Dimethylethylene-diamine (1.48 g, 16.8 mmol) was added to a solution of 3,5-dimethyl-2-hydroxybenz-aldehyde[42] (2.10 g, 14 mmol) in methanol (50 mL). The product was obtained as a dark brown viscous oil, which was used without further purification. Yield: 2.96 g (96%).

^1H NMR (300 MHz, chloroform-*d*, 298 K): δ 2.16 (s, 3H, Ar−CH_3), 2.17 (s, 3H, Ar−CH_3), 2.20 (s, 6H, N(CH_3)$_2$), 2.51 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, N(CH_2)$_2$N(CH_3)$_2$), 3.57 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, N(CH_2)$_2$N-(CH_3)$_2$), 6.75 (s, 1H, Ar-*H*), 6.89 (s, 1H, Ar-*H*), 8.14 (s, 1H, Ar−C*H*N), 13.34 (s, 1H, Ar−O*H*). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K): δ 15.30 (Ar-CH_3), 20.15 (Ar-*C*H$_3$), 45.56 (N(CH_2)$_2$N(CH_3)$_2$), 57.55 (N(CH_2)$_2$N(CH_3)$_2$), 59.83 (N(CH_2)$_2$N(CH_3)$_2$), 117.55 (*Ar*), 125.27 (Ar), 126.56 (*Ar*), 128.75 (*Ar*-H), 133.97 (*Ar*-H), 157.08 (*Ar*−OH), 165.52 (Ar-CHN). IR (ATR, cm^{-1}): 1631 (s, C═N), 1605 (m), 1460 (m),

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1438 (m), 1266 (s), 1040 (m), 1020 (m), 958 (w), 935 (w), 905 (w), 855 (m). MS (EI) (70 eV) *m/z* (%): 220.1 (11.7) $[M]^+$, 176.1 (2.5) $[M\text{-}N(CH_3)_2]^+$, 162.1 (2.6) $[M\text{-}CH_2N(CH_3)_2]^+$, 135.1 (6.8) $[(M\text{-}N(CH_2)_2N(CH_3)_2)+H]^+$, 58.1 (100.0) $[CH_2N(CH_3)_2]^+$.

General Synthetic Procedure for Molybdenum(VI) Dioxo Complexes. The respective ligand (0.62 mmol, 2 equiv) was dissolved in 2 mL of dry toluene and slowly added to a solution of 150 mg of $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$ (0.31 mmol, 1 equiv) in 10 mL of toluene. The formation of the complex was immediately indicated by a change of color. To ensure complete formation of the complex, the solution was stirred overnight at room temperature. The mixture was then filtered through a pad of Celite, and the solvent was removed in vacuo. The residue was washed twice with 5 mL of pentane or heptane, affording the pure compounds as yellow to light brown solids.

$[MoO_2(L^1)_2]$ (1). The synthesis of complex **1** followed the general procedure described above. A solution of the ligand HL^1 (0.18 g, 0.63 mmol) was slowly added to a solution of $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$ (0.15 g, 0.31 mmol) in toluene. After purification, compound **1** was obtained as a yellow solid. Yield: 0.17 g (77%).

^{1}H NMR (300 MHz, chloroform-*d*, 238 K, A (major isomer), B (minor isomer) A:B = 4:1) δ 1.25 (s, 9H, $C(CH_3)_3$, B), 1.27 (s, 9H, $C(CH_3)_3$, B), 1.29 (s, 18H, $C(CH_3)_3$, A+B), 1.41 (s, 18H, 2x $C(CH_3)_3$, A+B), 3.14 (s, 3H, $N(CH_2)_2OCH_3$, B), 3.26 (s, 3H, $N(CH_2)_2OCH_3$, A), 3.34 (s, 3H, $N(CH_2)_2OCH_3$, B), 3.46 (m, $N(CH_2)_2OCH_3$, overlapping signals A+B), 3.67 (m, $NCH_2CH_2OCH_3$, overlapping signals A+B), 3.83 (m, 2H, $NCH_2CH_2OCH_3$, B), 4.15 (m, 1H, $N(CH_2)_2OCH_3$, B), 4.29 (m, 1H, $N(CH_2)_2OCH_3$, B), 7.10 (d, $^4J_{H-H}$ = 2.2 Hz, 1H, Ar-*H*, B), 7.21 (d, $^4J_{H-H}$ = 2.5 Hz, 2H, Ar-*H*, A+B), 7.48 (d, $^4J_{H-H}$ = 2.2 Hz, 2H, Ar-*H*, B), 7.50 (d, $^4J_{H-H}$ = 2.5 Hz, 1H, Ar-*H*, A), 8.10 (s, 1H, Ar−*CH*N, B), 8.30 (s, 1H, Ar−*CH*N, A), 8.38 (s, 1H, Ar−*CH*N, B). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K, major isomer A) δ 30.24 ($C(CH_3)_3$), 31.63 ($C(CH_3)_3$), 34.50 ($C(CH_3)_3$), 35.36 ($C(CH_3)_3$), 59.11 ($N(CH_2)_2OCH_3$), 59.17 ($N(CH_2)_2OCH_3$), 71.51 ($N(CH_2)_2OCH_3$), 121.54 (*Ar*), 128.63 (Ar-H), 129.93 (*Ar*-H), 138.84 (*Ar*), 142.53 (*Ar*), 160.33 (*Ar*-O), 168.99 (Ar-CHN). IR (ATR, cm^{-1}): 1628 (s, C═N), 1440 (m), 1414 (w), 1390 (w) 1268 (m), 1252 (s), 1236 (m), 1178 (m), 1178 (m), 1124 (m), 1072 (m), 928 (m, Mo═O), 904 (s, Mo═O), 841 (s), 752 (m), 617 (m), 594 (w), 547 (br, s), 482 (m), 429 (m). MS (EI) (70 eV) *m/z* (%): 710.5 (2.3) $[M]^+$, 694.5 (0.7) $[M\text{-}O]^+$, 678.5 (0.4) $[M\text{-}2O]^+$, 625.4 (6.5) $[(M\text{-}CHN(CH_2)_2OCH_3)+H]^+$, 420.1 (100.0) $[M\text{-}C_{18}H_{28}NO_2]^+$, 404.1 (1.7) $[M\text{-}C_{18}H_{28}NO_3]^+$, 291.1 (7.0) $[(C_{18}H_{28}NO_2)+H]^+$, 57.1 (12.5) $[C_4H_9]^+$. Anal. Calcd. for $MoO_6N_2C_{36}H_{56}\cdot 0{,}37\ CH_2Cl_2$: C, 59.00, H, 7.72; N, 3.78. Found: C, 59.24; H, 7.50; N, 3.89%.

$[MoO_2(L^2)_2]$ (2). The synthesis of complex 2 followed the general procedure described above. A solution of the ligand HL^2 (0.13 g, 0.63 mmol) in toluene was slowly added to a solution of $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$ (0.15 g, 0.31 mmol) in toluene. After purification, compound **2** was obtained as a light brown solid. Yield: 0.066 g (82%).

^{1}H NMR (300 MHz, chloroform-*d*, 298 K) δ 2.24 (s, 3H, Ar-CH_3), 2.28 (s, 3H, Ar-CH_3), 3.26 (s, 3H, OCH_3), 3.53 (m, 3H, $N(CH_2)_2OCH_3$), 3.72 (m, 1H, $N(CH_2)_2OCH_3$), 7.01 (d, 1H, Ar-*H*), 7.16 (d, 1H, Ar-*H*), 8.20 (s, 1H, Ar−*CH*N). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K) δ 16.48 (CH_3), 20.45 (CH_3), 59.18 ($N(CH_2)_2OCH_3$), 61.00 ($N(CH_2)_2OCH_3$), 71.59 ($N(CH_2)_2OCH_3$), 120.53 (*Ar*), 127.99 (Ar-H), 129.57 (*Ar*-H), 131.70 (*Ar*), 136.90 (*Ar*), 158.81 (*Ar*-O), 167.79 (Ar-CHN). IR (ATR, cm^{-1}): 1626 (s, C═N), 1571 (m), 1473 (m), 1267 (m), 1229 (m), 1110 (s), 988 (w), 959 (w), 921 (s, Mo═O), 901 (s, Mo═O), 839 (s), 829 (s), 749 (m), 612 (m), 550 (s), 516 (s), 470 (m), 421 (s). MS (EI) (70 eV) *m/z* (%): 542.2 (4.3) $[M]^+$, 510.1 (0.4) $[M\text{-}2O]^+$, 457.1 (3.4) $[(M\text{-}CHN(CH_2)_2OCH_3)+H]^+$, 336.1 (100.0) $[M\text{-}C_{12}H_{16}NO_2]^+$, 207.1 (7.8) $[(C_{12}H_{16}NO_2)+H]^+$, 59.1 (7.9) $[(CH_2)_2OCH_3]^+$. Anal. Calcd. for $MoO_6N_2C_{24}H_{32}\cdot 0.4\ CH_2Cl_2$: Found: C, 51.00; H, 5.75; N, 4.87. Found: C, 51.05; H, 5.46; N, 4.97%.

$[MoO_2(L^5)_2]$ (3). The synthesis of complex **3** followed the general procedure described above. A solution of the ligand HL^3 (0.19 g, 0.63 mmol) was slowly added to a solution of $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$ (0.15 g, 0.31 mmol) in toluene. After purification, compound **3** was obtained as a yellow solid. Yield: 0.16 g (68%).

^{1}H NMR (300 MHz, chloroform-*d*, 238 K, A (major isomer) and B (minor isomer) A:B = 2:1) δ 1.24 (s, 18H, 2x $C(CH_3)_3$, B), 1.28 (s, 9H, $C(CH_3)_3$, A), 1.40 (s, 9H, $C(CH_3)_3$, B), 1.42 (s, 9H, $C(CH_3)_3$, A), 1.98 (s, 6H, $N(CH_2)_2N(CH_3)_2$, B), 2.09 (s, 6H, $N(CH_2)_2N(CH_3)_2$, A), 2.19 (m, 3H, $N(CH_2)_2N(CH_3)_2$, B), 2.29 (s, 6H, $N(CH_2)_2N(CH_3)_2$, B), 2.40 (m, 1H, $N(CH_2)_2N(CH_3)_2$, A), 2.61 (m, 1H, $N(CH_2)_2N(CH_3)_2$, A), 2.96 (m, 2H, $N(CH_2)_2N(CH_3)_2$, B), 3.52 (m, 3H, $N(CH_2)_2N(CH_3)_2$, 2A+B), 4.00 (m, 1H, $N(CH_2)_2N(CH_3)_2$, B), 4.25 (m, 1H, $N(CH_2)_2N(CH_3)_2$, B), 7.08 (s, 1H, Ar-*H*, B), 7.15 (d, $^4J_{H-H}$ = 3.0 Hz, 2H, Ar-*H*, A+B), 7.46 (s, 1H, Ar-*H*, B), 7.49 (d, $^4J_{H-H}$ = 3.0 Hz, 2H, Ar-*H*, A+B), 8.09 (s, 1H, Ar−*CH*N, B), 8.28 (s, 1H, Ar−*CH*N, A), 8.36 (s, 1H, Ar−*CH*N, B). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K, major isomer A) δ 30.34 ($C(CH_3)_3$), 31.66 ($C(CH_3)_3$), 34.51 ($C(CH_3)_3$), 35.34 ($C(CH_3)_3$), 45.72 ($N(CH_2)_2N(CH_3)_2$), 56.95 ($N(CH_2)_2N(CH_3)_2$), 59.95 ($N(CH_2)_2(CH_3)_2$), 121.69 (*Ar*), 128.45 (Ar-H), 129.81 (*Ar*-H), 138.80 (*Ar*), 142.45 (*Ar*), 160.49 (*Ar*-O), 168.46 (Ar-CHN). IR (ATR, cm^{-1}): 1625 (C═N), 1561 (m), 1439 (m), 1413 (m), 1392 (m), 1360 (m), 1266 (m), 1246 (m), 1202 (m); 1174 (m), 1039 (m), 993 (w), 914 (s, Mo═O), 902 (s, Mo═O), 843 (s), 752 (s), 615 (m), 551 (s), 486 (m), 434 (m). MS (EI) (70 eV) *m/z* (%): 736.6 (0.1) $[M]^+$, 706.6 (5.4) $[(M\text{-}NCH_3)\text{-}H]^+$, 691.5 (2.3) $[(M\text{-}N(CH_3)_2)\text{-}H]^+$, 433.2 (31.6) $[M\text{-}C_{19}H_{31}N_2O]^+$, 417.1 (1.6) $[M\text{-}C_{19}H_{31}N_2O_2]^+$, 303.2 (7.2) $[C_{19}H_{31}N_2O]^+$, 58.1 (100.0) $[CH_2N(CH_3)_2]^+$. Anal. Calcd. for $MoO_4N_4C_{38}H_{62}$: C, 62.11; H, 8.50; N, 7.62. Found: C, 62.34; H, 8.30; N, 7.95%.

$[MoO_2(L^4)_2]$ (4). The synthesis of complex **4** followed the general procedure described above. A solution of the ligand HL^4 (0.14 g, 0.63 mmol) in toluene was slowly added to a solution of $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$ (0.15 g, 0.31 mmol) in toluene. After purification, compound **4** was obtained as a light brown solid. Yield: 0.11 g (63%).

^{1}H NMR (300 MHz, chloroform-*d*, 298 K) δ 2.11 (s, 6H, $N(CH_3)_2$), 2.26 (s, 3H, Ar−CH_3), 2.27 (s, 3H, Ar−CH_3), 2.58 (m, 2H, $N(CH_2)_2N(CH_3)_2$), 3.45 (m, 2H, $N(CH_2)_2N(CH_3)_2$), 6.98 (s, 1H, Ar-*H*), 7.14 (s, 1H, Ar-*H*), 8.18 (s, 1H, Ar−*CH*N). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K) δ 16.63 (Ar-CH_3), 20.52 (Ar-CH_3), 45.76 ($N(CH_3)_2$), 59.01 ($N(CH_2)_2N(CH_3)_2$), 60.21 ($N(CH_2)_2N(CH_3)_2$), 120.71 (*Ar*), 127.99 (*Ar*), 129.46 (*Ar*), 130.96 (*Ar*), 131.50 (*Ar*-H), 136.88 (*Ar*-H), 159.12 (*Ar*-O), 167.29 (Ar-CHN). IR (ATR, cm^{-1}): 1625 (s, C═N), 1571 (w), 1454 (w), 1259 (s), 1227 (m), 1171 (w), 1028 (w), 926 (s, Mo═O), 900 (s, br, Mo═O), 867 (m), 846 (s), 823 (s), 781 (w), 749 (m), 611 (m), 549 (m), 514 (m), 417 (m). MS (EI) (70 eV) *m/z* (%): 568.3 (0.1) $[M]^+$, 523.2 (2.9) $[(M\text{-}N(CH_3)_2)\text{-}H]^+$, 482.2 (7.6) $[M\text{-}N(CH_2)_2N(CH_3)_2]^+$, 349.1 (35.5) $[M\text{-}(C_{13}H_{19}N_2O)]^+$, 219.1 (9.3) $[C_{13}H_{19}N_2O]^+$, 72.1 (15.3) $[(CH_2)_2N(CH_3)_2]^+$, 58.2 (100.0) $[CH_2N(CH_3)_2]^+$. Anal. Calcd. for $MoO_4N_4C_{38}H_{62}$: C, 55.12, H, 6.76; N, 9.89. Found: C, 54.93; H, 6.51; N, 10.28%.

$[MoO_2(L^5)_2]$ (5). The synthesis of complex **5** followed the general procedure described above. A solution of the ligand HL^5 (0.18 g, 0.63 mmol) in toluene was slowly added to a solution of $[MoO_2(\eta^2\text{-}t\text{Bu}_2\text{pz})_2]$ (0.15 g, 0.31 mmol) in toluene. After purification, compound **5** was obtained as a yellow solid. Yield: 0.12 g (54%).

^{1}H NMR (300 MHz, chloroform-*d*, 298 K, major isomer A) δ 0.75 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, $N(CH_2)_3CH_3$), 1.13 (m, 2H, $N(CH_2)_3CH_3$), 1.31 (s, 9H, $C(CH_3)_3$), 1.44 (s, 9H, $C(CH_3)_3$), 1.52 (m, 1H, $N(CH_2)_3CH_3$), 1.76 (m, 1H, $N(CH_2)_3CH_3$), 3.46 (m, 2H, $N(CH_2)_3CH_3$), 7.16 (s, $^4J_{H-H}$ = 2.4 Hz, 1H, Ar-*H*), 7.53 (s, $^4J_{H-H}$ = 2.4 Hz, 1H, Ar-*H*), 8.26 (s, 1H, Ar−*CH*N). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K) δ 13.8 ($N(CH_2)_3CH_3$), 20.54 ($N(CH_2)_3CH_3$), 30.21 ($C(CH_3)_3$), 31.65 ($C(CH_3)_3$), 33.58 ($N(CH_2)_3CH_3$), 34.51 ($C(CH_3)_3$), 35.41 ($C(CH_3)_3$), 60.06 ($N(CH_2)_3CH_3$), 121. 59 (Ar), 128.18 (*Ar*-H), 129.69 (*Ar*-H), 138.93 (Ar), 142.35 (Ar), 160.43 (*Ar*-O), 167.02 (Ar-CHN). IR (ATR, cm^{-1}): 1628 (s, C═N), 1563 (w), 1439 (m), 1391 (w), 1360 (w), 1270 (m), 1249 (s), 1202 (w), 1180 (w), 917 (m, Mo═O), 904 (s, Mo═O), 844 (s), 772 (w), 754 (m), 551 (m), 432 (m). MS (EI) (70 eV) *m/z* (%): 706.6 (9.9) $[M]^+$, 690.6 (5.9) $[M\text{-}O]^+$, 623.5 (100.0) $[M\text{-}(CHN(CH_2)_3CH_3)+H]^+$, 57.2 (61.4) $[C_4H_9]^+$. Anal. Calcd. for $MoO_4N_2C_{38}H_{60}$: C, 64.75, H, 8.58; N, 3.97. Found: C, 65.03; H, 8.50; N, 3.97%.

Epoxidation. In a typical epoxidation reaction, catalyst (7.05×10^{-3} mmol, 0.5 mol %), the corresponding alkene (1.41 mmol, 1 equiv), and

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internal standard (1.41 mmol, 1 equiv) were combined in dry chloroform (5 mL). After stirring the mixture for 5 min, the epoxide reaction was started with the addition of TBHP (0.5 mL of a 5.5 M solution in decane, 2.82 mmol, 2 equiv). The reactions were monitored quantitatively by GC/MS (cyclooctene, cyclohexene, styrene, 4-phenyl-1-butene, α-terpineol, R-(+)-limonene), HPLC (*cis*-stilbene, *trans*-stilbene), or ^{1}H NMR (1-octene and 2-propenol) analyses. At fixed intervals samples were taken, and residual TBHP traces were quenched with MnO_2. After centrifuge, sample aliquots were diluted with ethyl acetate (for GC/MS) or acetonitrile (for HPLC). Mesitylene was used as internal standard for GC/MS and HPLC measurements. ^{1}H NMR spectra were measured in chloroform-*d* using dichloroethane as internal standard.

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed at 100 K using graphite monochromated MoK_α radiation (λ = 0.71073 Å) with a BRUKER-AXS SMART APEX II diffractometer equipped with a CCD detector. The data for all compounds were reduced to F_o^2 and corrected for absorption and polarization using SAINT[43] and SADABS[44] programs, respectively. The structures were solved by direct methods (SHELXS-97[45] or SIR92[46]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97[47]). If not otherwise stated, all non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 50% probability thermal ellipsoids, and all H atoms were omitted for clarity. For complex **1** the C15 atom was split and modeled as two-site disorder with 0.6/0.4 occupancy. The crystals for complex **3** were all heavily twinned; data set was collected from a crystal which seemed to be the best from the orientation matrix. For complex **3** the N1 atom was kept isotropic during the refinement as neither ISOR nor DELU constraints could prevent it from going NPD. The high residual electron density (+ 4.4 e Å^{-3}) is located close to the Mo1 atom. Crystallographic data (excluding structure factors) for the structures of compounds **1** and **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Center [CCDC 837295 (**1**) and 837296 (**3**)]. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: (international) +44−1223/336−033; e-mail: deposit@ccdc.cam.ac.uk].

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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