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Oxidorhenium(V) Complexes with Tridentate and Tetradentate Phenol-Based Ligands

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The synthesis of oxidorhenium(V) complexes with tridentate and potentially tetradentate ligands of the type $[ReOX_2(L)]$ {X = Cl or Br; L = 2-[$CH_2N(Me)CH_2CH_2OCH_3$]-4,6-di-*t*Bu-phenolate, 2-[$CH_2N(Me)CH_2CH_2SCH_2CH_3$]-4,6-di-*t*Bu-phenolate, 2-[$CH_2N(Me)CH_2CH_2N(CH_3)_2$]-4,6-di-*t*Bu-phenolate, 2-[$CH_2N(Me)CH_2CH_2N(CH_2CH_3)_2$]-4,6-di-*t*Bu-phenolate, 2-[$CH_2N(CH_2CH_2OCH_3)_2$]-4,6-di-*t*Bu-phenolate, 2-[$CH_2N(CH_2CH_2SCH_2CH_3)_2$]-4,6-di-*t*Bu-phenolate, 2-[$CH_2N\{CH_2CH_2N(CH_2CH_3)_2\}_2$]-4,6-di-*t*Bu-phenolate} **1**–**14** is reported. All complexes were spectroscopically characterized and shown to be isomerically pure. Compounds **1**, **2**, **9**, and **11** were crystallographically characterized and show similar octahedral geometries with *trans* O=Re–O and *cis* O=Re–Cl bonds. All synthesized complexes **1**–**14** are catalyst precursors for the epoxidation of cyclooctene with *tert*-butyl hydrogenperoxide (TBHP). Yields of the formed epoxide were up to 55 % with all precursors.

Introduction

Oxidorhenium(V) complexes that contain polydentate ligands have attracted considerable interest in recent years due to their application as catalysts in oxygen atom-transfer reactions (OAT).[1–9] Mechanistic aspects were thoroughly investigated by Espenson and co-workers to reveal the two most prominent requirements for a given rhenium(V) compound to be an active catalyst: the active site must allow coordination of the oxygen atom donor such as pyridine *N*-oxide, dimethyl sulfoxide, or *tert*-butyl hydroperoxide (TBHP),[10] and the breaking of the O–X bond within the oxygen donor (e.g., in Py–O) is facilitated by nucleophiles.[3] Rhenium(V) compounds were particularly well studied, because they are easily prepared and are usually moisture- and air-stable. Also, high-oxidation-state rhenium(VII) compounds were investigated and, for example, methyltrioxidorhenium(VII) (MTO) and derivatives thereof proved to be successful catalysts for various oxidations including epoxidation reactions.[11–15] However, the sensitivity of MTO towards water sometimes hampers high yields. For this reason, more stable oxidorhenium(V) complexes were also investigated as catalysts in epoxidations albeit as yet with limited success.[16–20] The rhenium(V) systems investigated so far show significantly lower activity or productivity than rhenium(VII) systems. In contrast to applications in oxidation reactions, oxidorhenium(V) compounds were recently found to be catalysts in several other reactions. Toste and co-workers discovered the rhenium(V)-catalyzed transformation of unsaturated organic substrates by hydrosilylation reactions.[21,22] Subsequently, several rhenium(V) catalysts for the reduction of various substrates were developed.[23] The scope of these transformations has only begun to be explored. Last but not least, due to the water stability and the occurrence of the radioactive isotopes $^{186/188}Re$, oxidorhenium(V) compounds have been applied in therapeutic nuclear medicine.[24]

Phenolate-based ligands have enjoyed much success in the stabilization of metal compounds, which are used in various chemical transformations.[25–28] These ligand types range from simple mono-phenoxide systems to bis-phenoxide systems, many of which are easily obtained by means of Schiff base or Mannich condensation reactions. The mono-phenoxide systems are found as tri- or tetradentate ligands depending on the substituents at the nitrogen atom of the methyleneamine close to the aromatic system (Scheme 1). In 2003, Tolman and co-workers used the chelating tridentate ligand ONNMe for the preparation of highly active zinc catalysts in the polymerization of lactide with good control and high rate.[29] Tetradentate mono-phenoxido ligands remained largely unexplored until Kol and co-workers used the chelating tetradentate ligand ONOO for the preparation of zirconium and titanium alkoxide compounds $[M(\kappa^3\text{-ONNOO})(O\textit{t}Bu)_3]$.[30] Both complexes reveal octahedral geometries with a facial coordination of the ligand in a tridentate fashion and a dangling donor arm that coordinates upon formation of cationic compounds $[M(\kappa^4\text{-ONOO})(O\textit{t}Bu)_2]^+$. In 2006, Gibson and co-workers pre-

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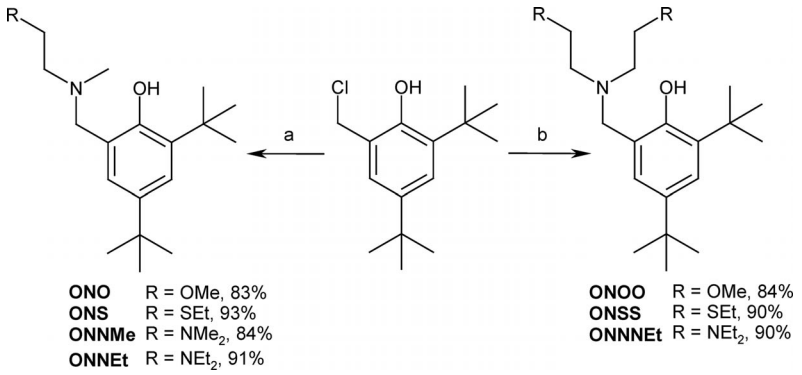


Scheme 1. (a) According to known procedures:[33] amine [(2-methoxyethyl)(methyl)amine for ONO; (2-ethylthioethyl)(methyl)amine for ONS; *N*,*N*,*N*′-trimethylethylenediamine for ONNMe; *N*,*N*-diethyl-*N*′-methylethylenediamine for ONNEt], Et_3N, dioxane, overnight. (b) amine [bis(2-methoxyethyl)amine for ONOO; bis(2-ethylthioethyl)amine for ONSS; *N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine for ONNNEt], Et_3N, dioxane, overnight.

pared a series of metal complexes with potentially tetradentate phenolate ligands (ONNNEt, ONOO; Scheme 1) and found the denticity of the ligands to depend on the coordination requirement of the metal center.[31] Bidentate (Al), tridentate (Mg, Ca, Zn), and tetradentate (K, Cr, Fe, Co) binding modes have been established by X-ray diffraction analysis. Furthermore, NMR spectroscopic studies in solution of the zinc compounds with the ligands ONNNEt and ONOO indicate a dynamic exchange of both donor arms. The remarkable diversity of the binding capability found with this type of ligands as well as the potential to obtain potentially cationic rhenium(V) complexes led us to explore the coordination chemistry of rhenium(V) complexes. We were interested as to whether such a change of denticity on demand can be applied in epoxidation reactions to obtain more active catalytic systems. Here we report the preparation of a series of oxidorhenium(V) complexes with tridentate (ONO, ONS, ONNMe, ONNEt) and tetradentate (ONOO, ONSS, ONNNEt) phenol-based ligands and tested their catalytic properties in the epoxidation of cyclooctene.

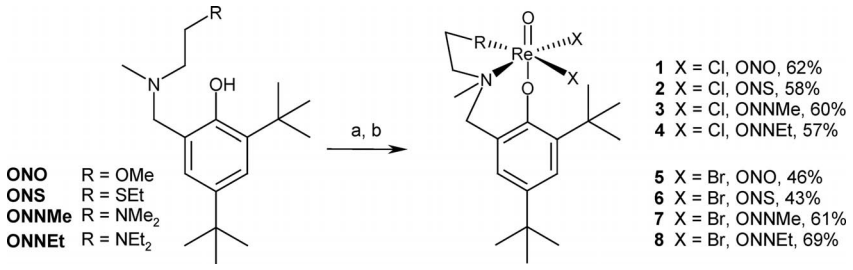
Results and Discussion

Synthesis of Compounds with Tri- and Tetradentate Ligands

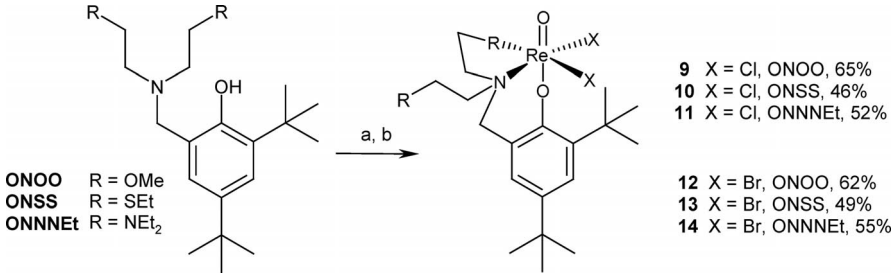
Two procedures for the formation of the tridentate ligands ONO, ONS, ONNMe, and ONNEt and the tetradentate ligands ONOO and ONNEt are readily available from the literature.[29–33] The synthetic strategy reported by Judmaier et al.[33] for the synthesis of tridentate ligands was adopted for the already known tetradentate ligands ONOO and ONNNEt to give more consistent and higher yields. Thus, the ligand syntheses followed a three-step procedure that started from 2,4-di-*tert*-butylphenol, which was converted into 2-hydroxy-3,5-di-*tert*-butylbenzyl chloride.[34] Subsequent treatment of the obtained chloride with the corresponding secondary amines gave the desired ligands in excellent yields and were used without further purification. In the same way, the new ligand ONSS was obtained in a 90% yield (Scheme 1). All ligands were characterized by NMR spectroscopy and elemental analyses. Prior to coordination to the metal atom, all ligands were converted into their potassium salt by the use of potassium hydride in THF.

The desired complexes **1**–**8** were obtained by the use of the rhenium precursors $[ReOX_3(OPPh_3)(SMe_2)]$ (X = Cl or Br) (for **1**–**4**, **7**, **8**) or $[ReOBr_3(PPh_3)_2]$ (for **5** and **6**) in the presence of the corresponding potassium salt of the ligands ONO, ONS, ONNMe, and ONNEt in toluene heated at reflux (Scheme 2).[20] The metal precursors $[ReOX_3(OPPh_3)(SMe_2)]$[35,36] (X = Cl or Br) and $[ReOBr_3(PPh_3)_2]$[37] were prepared essentially according to known procedures.

Analogously, complexes **9**–**14** were obtained on treatment of the potassium salts of ONOO, ONSS, ONNNME, and ONNNEt with $[ReOX_3(OPPh_3)(SMe_2)]$ (X = Cl or Br) in toluene heated at reflux (Scheme 3).



Scheme 2. (a) KH, THF, crude. (b) $[ReOX_3(OPPh_3)(SMe_2)]$ or $[ReOX_3(PPh_3)_2]$ (X = Cl or Br), toluene, reflux, 2 h.



Scheme 3. (a) KH, THF, crude. (b) $[ReOX_3(OPPh_3)(SMe_2)]$ (X = Cl or Br), toluene, reflux, 2 h.

Removal of the solvent and recrystallization of the obtained residue from a mixture of chloroform/heptane gave the desired complexes **1**–**14** in 43–69% yields. All complexes show high air and moisture stability.

Complexes **1**–**14** were characterized by NMR and IR spectroscopy and elemental analyses. For compounds **1**, **2**, **9**, and **11** single-crystal X-ray diffraction analyses were performed. The IR spectra of the complexes gave a characteristic stretching frequency for the Re=O moiety, and elemental analyses confirmed the basic formula of $[ReOX_2L]$ (X = Cl or Br; L = ligand) for all compounds.

Formation of compounds **1**–**8** with tridentate ligands can in principle form isomers with the ligand to be coordinated in a meridional or facial fashion with the oxygen atom of the phenol moiety in a *trans* position towards the oxygen or chlorine atom of the rhenium moiety. NMR spectra of all compounds confirmed the occurrence of only one isomer in solution, which was shown to contain a facially coordinated ligand towards the rhenium atom and a *trans* coordination of the phenol oxygen atom towards the oxido group at the rhenium atom as confirmed by X-ray diffraction analysis (vide infra). In ^{1}H NMR spectroscopy, the methylene groups present in the ligand gave a characteristic splitting for the diastereotopic protons. The protons of the methylene fragment attached to the aromatic ring gave two doublets at $\delta \approx 3.5$ and 5.5 ppm, which is indicative of complex formation. The formation of only one isomer of complexes **1**–**8** by using ONO, ONS, ONNMe, and ONNEt is in contrast to reported oxidomolybdenum compounds $[MoO_2Cl(L)]$ in which two isomers were found in solution for complexes that contained ONNMe and ONNEt ligands.[33]

Compared to the tridentate ligands, the tetradentate derivatives consist of an additional donor atom. This type of ligands was previously shown to coordinate in a tetradentate fashion and form a cationic complex with a chloride counterion.[30] This encouraged us to investigate tetradentate ligands and their coordination mode towards the rhenium moiety. A possible formation of a rhenium complex of the type $[ReOCl(L)]^+Cl^-$ may form a reactive species useful in catalytic applications.[2,38,39] Analogously to complexes **1**–**8**, NMR spectroscopic analyses of complexes **9**–**14** indicated the formation of only one isomer of the type $[ReOCl_2L]$ with a dangling donor arm. The ^{1}H NMR spectra of complexes **9** and **12** gave chemical shifts for OCH_3 of δ = 3.42, 4.47 ppm (**9**) and 3.43, 4.54 ppm (**12**), respectively, in which the downfield resonance can be assigned to the protons of coordinated OMe groups as also found in complexes **1** and **5** (δ = 4.45 and 4.53 ppm for OMe). The upfield-shifted singlet points to a noncoordinated OMe group whose signal is in the same range as that found for the free ligand. For complexes **10**, **11**, **13**, and **14**, ^{1}H NMR spectroscopic analyses also indicated that the additional side arm was not coordinated, which was confirmed by single-crystal structure analyses of **9** and **11** (vide infra).

Molecular Structures of $[ReOCl_2(ONO)]$ (1), $[ReOCl_2(ONS)]$ (2), $[ReOCl_2(ONOO)]$ (9), and $[ReOCl_2(ONNNEt)]$ (11)

Structures of compounds **1**, **2**, **9**, and **11** were determined by X-ray diffraction analyses after crystallization from a chloroform/heptane mixture. Molecular views are shown in Figure 1, crystallographic data are presented in Table 2, and selected bond lengths and angles are given in Table 1. All complexes show a six-coordinate rhenium atom with distorted octahedral geometries and *trans* O–Re=O and *cis* Cl–Re=O bonds. The Re–N bond [Re(1)–N(2) 2.209(4) Å for **1**; 2.235(3) Å for **2**; Re(1)–N(1) 2.230(8) Å for **9**; and Re(2)–N(1) 2.195(5) Å, Re(2)–N(2) 2.228 Å for **11**] is significantly longer than the Re–O bond [Re(1)–O(1) 1.904(3) Å for **1**; Re(1)–O(2) 1.913(2) Å for **2**; Re(1)–O(2) 1.907(6) Å for **9**; and Re(1)–O(1) 1.916(5) Å for **11**]. The *trans* coordination of the ligand oxygen atom towards the oxygen atom attached to the rhenium atom is well documented in the literature.[7,18,40–42] For distorted octahedral Re^VO complexes with oxygen-containing bidentate ligands, it is suggested that O–Re=O corresponds to a minimum of *trans* weakening caused by the Re=O multiple bond. In addition, the repulsion exerted by the Re=O atom causes a compression field that tends to increase the mean O=Re–L_{cis} angle beyond 90°.[43] All complexes show a facial coordination of the ligand towards the rhenium moiety. The equatorial plane of the complexes consists of the two halide atoms, the nitrogen atom, and the chalcogen atom (compounds **1**, **2**, **9**) or an additional nitrogen atom (compound **11**) from the ligand. All complexes gave bond lengths for Re=O

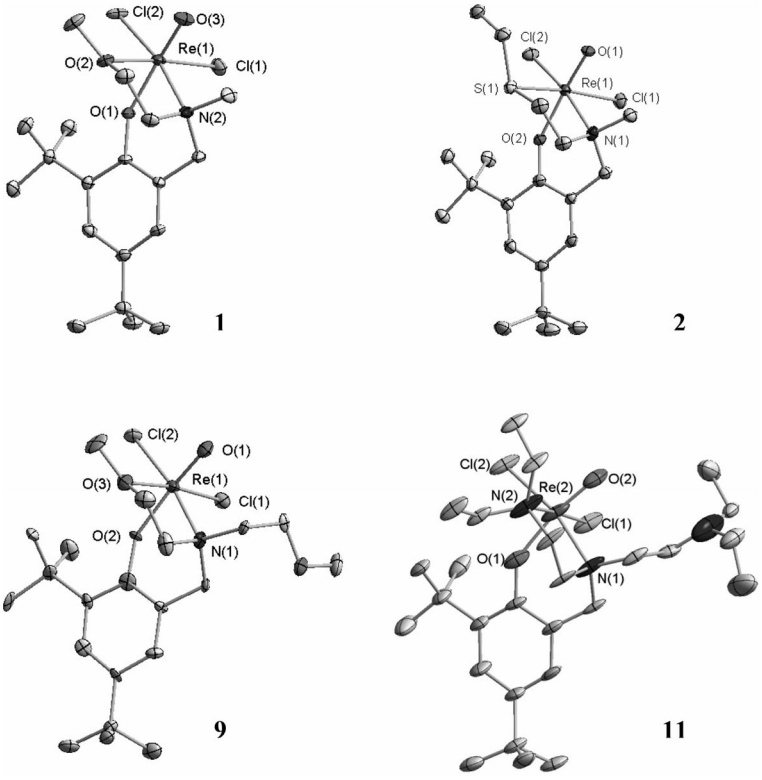


Figure 1. Molecular views of compounds **1**, **2**, **9**, and **11** with selected atom numbering. Hydrogen atoms are omitted for clarity. Ellipsoids for compound **11** are given at the 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for [ReOCl$_2$(ONO)] (**1**), [ReOCl$_2$(ONS)] (**2**), [ReOCl$_2$(ONOO)] (**9**), and [ReOCl$_2$(ONNNEt)] (**11**).

Compound **1**		Compound **2**	
Re(1)–O(3)	1.696(3)	Re(1)–O(1)	1.692(2)
Re(1)–O(1)	1.904(3)	Re(1)–O(2)	1.913(2)
Re(1)–Cl(1)	2.381(1)	Re(1)–Cl(1)	2.410(1)
Re(1)–Cl(2)	2.377(1)	Re(1)–Cl(2)	2.370(1)
Re(1)–O(2)	2.144(3)	Re(1)–S(1)	2.421(1)
Re(1)–N(2)	2.209(4)	Re(1)–N(1)	2.235(3)
O(3)–Re(1)O(1)	167.4(2)	O(1)–Re(1)–O(2)	168.8(1)
Cl(2)–Re(1)–N(2)	169.6(1)	Cl(2)–Re(1)–N(1)	169.63(8)
Cl(1)–Re(1)–O(2)	174.36(9)	Cl(1)–Re(1)–S(1)	173.39(3)
O(2)–Re(1)–N(2)	79.8(1)	S(1)–Re(1)–N(1)	83.26(8)
O(3)–Re(1)–Cl(1)	95.9(1)	O(1)–Re(1)–Cl(1)	94.22(9)
O(3)–Re(1)–Cl(2)	99.90(1)	O(1)–Re(1)–Cl(2)	101.00(9)
Cl(1)–Re(1)–Cl(2)	89.56(5)	Cl(1)–Re(1)–Cl(2)	88.21(4)
O(1)–Re(1)–N(2)	80.6(1)	O(2)–Re(1)–N(1)	80.35(10)
Compound **9**		Compound **11**	
Re(1)–O(1)	1.682(7)	Re(2)–O(2)	1.676(5)
Re(1)–O(2)	1.907(6)	Re(2)–O(1)	1.916(5)
Re(1)–Cl(2)	2.365(3)	Re(2)–Cl(1)	2.409(1)
Re(1)–Cl(1)	2.357(3)	Re(2)–Cl(2)	2.377(2)
Re(1)–N(1)	2.230(8)	Re(2)–N(2)	2.228(6)
Re(1)–O(3)	2.136(7)	Re(2)–N(1)	2.195(5)
O(1)–Re(1)–O(2)	166.6(3)	O(2)–Re(2)–O(1)	169.9(2)
N(1)–Re(1)–Cl(2)	171.1(2)	Cl(2)–Re(2)–N(1)	167.2(2)
O(3)–Re(1)–Cl(1)	172.8(2)	Cl(1)–Re(2)–N(2)	176.8(2)
O(3)–Re(1)–N(1)	79.8(3)	N(1)–Re(2)–N(2)	82.3(2)
O(1)–Re(1)–Cl(1)	97.9(2)	O(2)–Re(2)–Cl(1)	91.7(2)
O(1)–Re(1)–Cl(2)	99.6(3)	O(2)–Re(2)–Cl(2)	102.8(2)
Cl(1)–Re(1)–Cl(2)	88.2(1)	Cl(1)–Re(2)–Cl(2)	88.52(6)
O(2)–Re(1)–N(1)	81.3(3)	O(1)–Re(2)–N(1)	80.5(2)

[1.696(3) Å (**1**), 1.692(2) Å (**2**), 1.682(7) Å (**9**), 1.676(5) Å (**11**)] and Re–Cl [2.3807(13) and 2.3765(12) Å (**1**), 2.4100(10) and 2.3704(10) Å (**2**), 2.365(3) and 2.357(3) Å (**9**), 2.4090(18) and 2.3770(17) Å (**11**)] within the expected range for other [ReOCl$_2$L] structures.[18,20,44]

In complex **1**, the chlorine atoms Cl(1) and Cl(2) are coordinated in *cis* position to each other with comparable bond lengths of Re(1)–Cl(1) [2.3807(13) Å] and Re(1)–Cl(2) [2.3765(12) Å] including an angle Cl(1)–Re(1)–Cl(2) of 89.56(5)°. The nitrogen atom N(2) is in *trans* position to the chlorine atom Cl(2) with an angle of N(2)–Re(1)–Cl(2) 169.56(10)°, and the oxygen atom O(2) is in *trans* position to the chlorine atom Cl(1) with an angle of Cl(1)–Re(1)–O(2) 174.36(9)°. The facially coordinated ligand shows a *trans* coordination of the phenol oxygen atom towards the Re=O unit with an angle O(1)–Re(1)–O(3) of 167.35(16), whereas donor atoms of the ligand coordinate in *cis* position to each other including angles O(1)–Re(1)–N(2) of 80.60(14)°, N(2)–Re(1)-(O2) of 79.84(14)°, and O(1)–Re(1)–O(2) of 84.43(13)°. The coordinated atoms N(2) and O(2) of the side arm in the phenolate ring form a five-membered ring that includes C(23), C(24), and the rhenium atom Re(1), in which C(24) is 0.665 Å out of the plane and oriented in the same direction as O(3).

In complex **2**, the distance Re(1)–S(1) of 2.4215(10) Å is longer than that in complex **1**, in which an oxygen atom [OMe, O(2)] coordinates with an Re(1)–O(2) bond length of 2.144(3) Å. This indicates that an oxygen atom is a better ligand than a sulfur atom. The chlorine atoms Cl(1) and

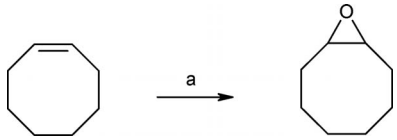
Cl(2) are coordinated in a *cis* position to each other with comparable bond lengths of Re(1)–Cl(1) [2.4100(10) Å] and Re(1)–Cl(2) [2.3704(12) Å] including an angle Cl(1)–Re(1)–Cl(2) of 88.21(4)°. The nitrogen atom N(1) is in *trans* position to the chlorine atom Cl(2) with an angle N(1)–Re(1)–Cl(2) of 169.63(8)°, and the sulfur atom S(1) is in *trans* position to the chlorine atom Cl(1) with an angle Cl(1)–Re(1)–S(2) of 173.39(3)°. The facially coordinated ligand shows a *trans* coordination of the phenol oxygen atom towards the Re=O unit with an angle O(1)–Re(1)–O(2) of 168.81(10), whereas donor atoms of the ligand coordinate in *cis* position to each other including angles N(1)–Re(1)–S(1) of 83.26(8)°, O(2)–Re(1)–N(1) of 80.35(10)°, and O(2)–Re(1)–S(1) of 89.13(9)°. The coordinated atoms N(1) and S(1) of the side arm in the phenolate ring form a five-membered ring that includes C(17), C(18), and the rhenium atom Re(1), in which C(18) is 0.734 Å out of the plane and oriented in the same directions as O(1).

In complex **9**, the chlorine atoms Cl(1) and Cl(2) are coordinated in *cis* position to each other with comparable bond lengths Re(1)–Cl(1) of 2.357(3) Å and Re(1)–Cl(2) of 2.365(3) Å including an angle Cl(1)–Re(1)–Cl(2) of 88.24(10)°. The nitrogen atom N(1) is in *trans* position to the chlorine atom Cl(2) with an angle N(1)–Re(1)–Cl(2) of 171.1(2)°, and the oxygen atom O(3) is in *trans* position to the chlorine atom Cl(1) with an angle Cl(1)–Re(1)–O(3) of 172.8(2)°. The facially coordinated ligand shows a *trans* coordination of the phenol oxygen atom towards the Re=O unit with an angle O(1)–Re(1)–O(2) of 166.6(3), whereas donor atoms of the ligand coordinate in *cis* position to each other and include angles N(1)–Re(1)–O(3) of 79.8(3)°, O(2)–Re(1)–N(1) of 81.3(3)°, and O(2)–Re(1)–O(3) of 83.3(3)°. The coordinated atoms N(1) and O(3) of the side arm in the phenolate ring form a five-membered ring that includes C(16), C(17), and the rhenium atom Re(1), in which C(17) is 0.643 Å out of the plane and oriented in the same direction as O(1). The additional side arm is oriented in the same direction as O(1).

In complex **11**, the chlorine atoms Cl(1) and Cl(2) are coordinated in *cis* position to each other with comparable bond lengths Re(2)–Cl(1) of 2.4090(18) Å and Re(2)–Cl(2) of 2.3770(17) Å, including an angle Cl(1)–Re(2)–Cl(2) of 88.52(6)°. The nitrogen atom N(1) is in *trans* position to the chlorine atom Cl(2) with an angle N(1)–Re(2)–Cl(2) of 167.2(2)°, and the nitrogen atom N(2) is in *trans* position to the chlorine atom Cl(1) with an angle Cl(1)–Re(2)–N(2) of 176.75(15)°. The facially coordinated ligand shows a *trans* coordination of the phenol oxygen atom towards the Re=O unit with an angle O(1)–Re(2)–O(2) of 169.9(2), whereas donor atoms of the ligand coordinate in *cis* position to each other and include angles N(1)–Re(2)–N(2) of 82.3(2)°, O(1)–Re(1)–N(1) of 80.5(2)°, and O(1)–Re(1)–N(2) of 91.2(2)°. The coordinated atoms N(1) and N(2) of the side arm in the phenolate ring form a five-membered ring that includes C(16), C(17), and the rhenium atom Re(1), in which C(17) is 0.645 Å out of the plane and oriented in the opposite direction as O(2). The additional side arm is oriented in the same direction as O(2).

Catalytic Epoxidations

Few oxidorhenium(V) complexes are known to show catalytic activity in epoxidation reactions.[16,17,19,41,45] Recently, we investigated complexes of the type [ReOCl_2(L)(PPh_3)] and [Re$OCl(L)_2$] (L = oxo iminato ligands) in the reaction of cyclooctene with TBHP in which a conversion to the epoxide of 55% was observed.[18,20] To explore the influence of additional donors in the catalyst on the catalytic activity, we tested rhenium complexes **1** to **14** in the model reaction shown in Scheme 4.



Scheme 4. (a) TBHP, Re^V (2 mol-%), $CHCl_3$, 50 °C.

The catalytic reactions were performed in chloroform at 50 °C by the use of 2 mol-% of the corresponding catalyst and a threefold excess amount of the peroxide (Scheme 4). The conversion to the epoxide was monitored by GC–MS analyses, and complexes **1**–**14** were tested for their catalytic activity by using *tert*-butyl hydrogenperoxide (TBHP) as the oxidant. However, all complexes gave comparable conversion of the alkene into the epoxide with a yield in the range of 50–55%. A representative epoxidation reaction monitored by GC–MS when using compound **2** as the catalyst is shown in Figure 2.

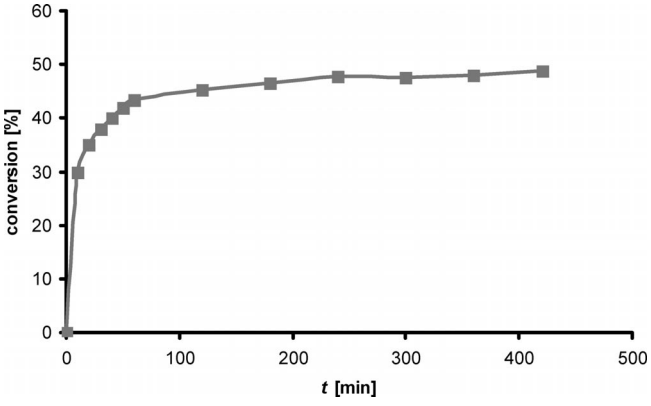


Figure 2. Epoxidation of cyclooctene by using catalyst [ReOCl_2(ONS)] (**2**).

The catalytic activity is fast within the first 60 min without the occurrence of an induction period. No significant increase in yield was obtained beyond 60 min. Apparently, the catalytically active species is quickly formed but is only stable for approximately 1 h. Furthermore, is seems to be independent of the ligand at the rhenium atom, because identical yields were obtained. Relative to our previous results with bidentate ligands,[20] additional donors in the ligand system did not improve the stability of the complexes in the catalytic reaction. We ruled out perrhenate to be the active species, because we tested sodium perrhenate as a

catalyst in the epoxidation reaction under analogous conditions and found a 27 mol-% yield of the corresponding epoxide. As the active species, an oxidized form of our compounds with a dioxidorhenium(VII) core is conceivable since the Re^{VII} complex of the type $[ReO_2(hoz)_2]^+$ with the (hydroxyphenyl)oxazoline ligand (hoz) has been crystallographically characterized.[46] However, the identification of the active catalyst has so far remained elusive. Attempts to use H_2O_2 instead of TBHB as the oxidant gave no conversion to the epoxide. Other olefins proved to be unreactive towards epoxidation when complexes **1**–**14** were used as catalysts.

Conclusion

Oxidorhenium(V) complexes of the type $[ReOX_2L]$ (X = Cl or Br) **1**–**14** that contain tridentate and potentially tetradentate ligands {L = 2-$[CH_2N(Me)CH_2CH_2OCH_3]$-4,6-di-*t*Bu-phenolate, 2-$[CH_2N(Me)CH_2CH_2SCH_2CH_3]$-4,6-di-*t*Bu-phenolate, 2-$[CH_2N(Me)CH_2CH_2N(CH_3)_2]$-4,6-di-*t*Bu-phenolate, 2-$[CH_2N(Me)CH_2CH_2N(CH_2CH_3)_2]$-4,6-di-*t*Bu-phenolate, 2-$[CH_2N(CH_2CH_2OCH_3)_2]$-4,6-di-*t*Bu-phenolate, 2-$[CH_2N(CH_2CH_2SCH_2CH_3)_2]$-4,6-di-*t*Bu-phenolate, 2-$[CH_2N\{CH_2CH_2N(CH_2CH_3)_2\}_2]$-4,6-di-*t*Bu-phenolate} were prepared and characterized. Despite the fact that several isomers can be formed on reaction of the ligands with rhenium precursors, all complexes were obtained in isomerically pure form. The prepared ligands formed complexes with facial coordination around the metal center. The tetradentate ligands coordinate in a tridentate fashion with a dangling arm. Compounds **1**–**14** proved to be catalytic precursors for the epoxidation of cyclooctene with TBHP to give yields of the formed epoxide up to 55%.

Experimental Section

General: Syntheses were performed under argon by using common Schlenk techniques with subsequent workup under ambient conditions. The metal precursors[35–37] $[ReOCl_3(OPPh_3)(SMe_2)]$, $[ReOBr_3(OPPh_3)(SMe_2)]$, and $[ReOBr_3(PPh_3)_2]$, as well as the ligands ONO, ONS, ONNMe, and ONNEt[29,32,33] were prepared according to known procedures. Chemicals were purchased from commercial sources and were used without further purification. Solvents were purified with a Pure Solv Solvent Purification System. NMR spectra were recorded with a Bruker (300 MHz) instrument. Chemical shifts (δ) are given in ppm and are referenced to partially protonated solvent or internal standard. Signals are described as s (singlet), d (doublet), dd (double doublet), t (triplet), dt (double triplet), or m (multiplet), and coupling constants (J) are given in Hertz (Hz). Elemental analyses were carried out with a Heraeus Vario Elementar automatic analyzer. Mass spectra were recorded with an Agilent 5973 MSD Direct Probe by using the EI ionization technique. Samples for IR spectroscopy were prepared as KBr pellets and measured with a Perkin–Elmer FTIR 1725X spectrometer. GC–MS measurements were performed with an Agilent 7890A with an Agilent 19091J-433 column coupled to an Agilent 5975C mass spectrometer.

X-ray Structural Determination: For X-ray structural analyses, the crystals were mounted onto the tip of glass fibers, and data collection was performed at low temperature by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with a Bruker-AXS SMART APEX CCD diffractometer. The data were reduced to F_o^2 and corrected for absorption effects with SAINT[47] and SADABS,[48] or an empirical absorption correction[49] was applied. The structures were solved by direct methods or by Patterson superposition procedures when direct methods failed, and refined by full-matrix least-squares method (SHELXL97).[50] For structures **9** and **11**, restraints were applied to model the disordered ethyl and/or *tert*-butyl groups. 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. Common isotropic displacement parameters were refined for the hydrogen atoms bonded to the same C atom or to the same phenyl ring. All diagrams were drawn with 50% probability thermal ellipsoids and all hydrogen atoms were omitted for clarity. A summary of the crystallographic data is listed in Table 2. CCDC-783689 (**1**), -784006 (**2**), -783932 (**9**), and -783931 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Preparation of the Ligands: Triethylamine (Et_3N) was added to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzyl chloride[34] and the respective amine in dioxane. The reaction mixture was stirred overnight and filtered through a plug of Celite. The filtrate was concentrated in vacuo to give the corresponding ligand as an oil, which was used without further purification.

Synthesis of ONOO: The ligand was prepared by the reaction of 3,5-di-*tert*-butyl-2-hydroxybenzyl chloride (3.40 g, 13.4 mmol), bis(2-methoxyethyl)amine (1.78 g, 13.4 mmol), and Et_3N (2.7 g, 27 mmol) in dioxane (70 mL) to give ONOO (3.97 g, 84%) as a yellow viscous oil. The data for NMR spectroscopy and elemental analysis are consistent with those reported in the literature.[30,31]

Synthesis of ONNNEt: The ligand was prepared by the reaction of 3,5-di-*tert*-butyl-2-hydroxybenzyl chloride (3.25 g, 12.7 mmol), *N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine (2.75 g, 12.7 mmol), and Et_3N (2.6 g, 26 mmol) in dioxane (70 mL) to give ONNNEt (4.98 g, 90%) as a light brown oil. The data for NMR spectroscopy and elemental analysis are in good agreement with those reported in the literature.[31]

Synthesis of ONSS: The ligand was prepared by the reaction of 3,5-di-*tert*-butyl-2-hydroxybenzyl chloride (4.39 g, 17.2 mmol), bis(2-ethylthioethyl)amine[51] (3.33 g, 17.2 mmol), and Et_3N (3.5 g, 35 mmol) in dioxane (100 mL) to give ONSS (6.30 g, 90%) as a brown oil. ^1H NMR (C_6D_6): δ = 0.97 (t, J = 7.4 Hz, 6 H, CH_3), 1.35 (s, 9 H, CH_3), 1.69 (s, 9 H, CH_3), 2.14 (q, J = 7.4 Hz, 4 H, CH_2), 2.38 (t, J = 7.8 Hz, 4 H, CH_2), 2.49 (t, J = 7.7 Hz, 4 H, CH_2), 3.38 (s, 2 H, CH_2), 6.88 (d, J = 2.31 Hz, 1 H, Ar), 7.48 (d, J = 2.4 Hz, 1 H, Ar), 10.54 (br. s, 1 H, OH) ppm. $C_{23}H_{41}NOS_2$ (411.70): calcd. C 67.10, H 10.04, N 3.40; found C 66.59, H 9.83, N 3.93. IR (KBr): $\tilde{\nu}$ = 2958, 2868, 1482, 1458, 1390, 1362, 1300, 1236, 1202, 1164, 1100, 876 cm^{-1}. EI-MS: *m*/*z* (%) = 411 (13) [M^+].

General Procedure for the Preparation of Rhenium Complexes 1–14: The respective potassium salt of the ligand (KONO, KONS, KONNMe, KONNEt) in toluene was added to a suspension of the precursor $[ReOX_3(OPPh_3)(SMe_2)]$ or $[ReOX_3(PPh_3)_2]$ (X = Cl or Br) in toluene. A color change from brown to green indicated the start of the reaction after 5 min of stirring at room temperature. Heating to reflux for 2 h gave a dark green solution with a dark

Table 2. Crystallographic data for [$ReOCl_2(ONO)$] (**1**), [$ReOCl_2(ONS)$] (**2**), [$ReOCl_2(ONOO)$] (**9**), and [$ReOCl_2(ONNNEt)$] (**11**).

	Compound **1**	Compound **2**	Compound **9**	Compound **11**
Empirical formula	$C_{20}H_{33}Cl_5NO_3Re$	$C_{28}H_{50}Cl_2NO_4ReS$	$C_{42}H_{72}Cl_4N_2O_8Re_2$	$C_{27}H_{50}Cl_2N_3O_2Re$
M_r [g mol]	698.92	753.85	1247.22	705.8
Color, habit	green, block	green, needle	green, needle	green, block
Crystal size [mm]	$0.20\times0.20\times0.16$	$0.20\times0.10\times0.10$	$0.38\times0.22\times0.20$	$0.36\times0.24\times0.14$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	Pc	$P2_1/c$
a [Å]	7.933(1)	10.226(2)	7.7956(16)	7.768(2)
b [Å]	28.874(3)	11.167(2)	31.144(6)	25.606(5)
c [Å]	11.844(2)	28.792(6)	12.319(4)	17.686(5)
α [°]	90	90	90	90
β [°]	100.01(1)	98.61(3)	124.19(2)	115.60(3)
γ [°]	90	90	90	90
V [Å^3]	2671.8(7)	3250.8(1)	2474.0(1)	3172.7(1)
Z	4	4	2	4
T [K]	95	100(2)	100(2)	100(2)
$D_{calcd.}$ [g cm^{-3}]	1.738	1.540	1.674	1.478
μ [mm^{-1}]	5.069	9.670	5.153	4.025
$F(000)$	1376	1528	1240	1432
θ range [°]	2.70–26.00	2.12–29.51	1.96–26.37	2.04–26.38
Limiting indices	$-9\le h\le9$ $-1\le k\le35$ $-1\le l\le14$	$-11\le h\le11$ $-12\le k\le12$ $-31\le l\le32$	$-9\le h\le9$ $-38\le k\le38$ $-15\le l\le15$	$-9\le h\le9$ $-32\le k\le31$ $-22\le l\le22$
Reflections collected	6241	33326	19467	24803
Independent reflections, R_{int}	5229, 0.0347	4640, 0.0426	9910, 0.0558	6480, 0.0626
Observed reflections [$I>2\sigma(I)$]	4713	4122	8270	4550
Data/restraints/parameters	5229/0/289	4640/0/342	9910/44/540	6480/74/368
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0337, 0.0838	0.0258, 0.0603	0.0486, 0.0981	0.0501, 0.0976
R_1, wR_2 (all data)[a]	0.0390, 0.0872	0.0307, 0.0627	0.0612, 0.1028	0.0811, 0.1080
GoF (on F^2)[a]	1.080	1.087	1.032	1.112
Flack parameter			0.02(1)	
Largest diff peak/hole [e Å^{-3}]	1.226/–1.448	1.104/–0.817	2.544/–2.426	1.365/–2.991

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. GoF = $\{\Sigma[w(F_o^2 - F_c^2)(n-p)]\}^{1/2}$.

precipitate. After hot filtration and rinsing with hot toluene, the solvent was removed in vacuo. Recrystallization of the green solid from a mixture of chloroform/heptane gave the dark green products in 43–69% yields.

Synthesis of [$ReOCl_2(ONO)$] (1): The compound was prepared according to the general procedure by employing KONO (39 mg, 0.10 mmol) in toluene (20 mL) and [$ReOCl_3(OPPh_3)(SMe_2)$] (67 mg, 0.10 mmol) in toluene (30 mL) to give **1** (36 mg, 62%). ^{1}H NMR ($CDCl_3$): δ = 1.26 (s, 18 H, CH_3), 2.54 (d, J = 13.7 Hz, 1 H, CH_2), 3.27 (m, 1 H, CH_2), 3.33 (s, 3 H, CH_3), 3.53 (s, J = 13.9 Hz, 1 H, CH_2), 4.33 (dd, J = 9.6, 3.5 Hz, 1 H, CH_2), 4.45 (s, 3 H, CH_3), 4.50 (m, 1 H, CH_2), 5.11 (d, J = 13.8 Hz, 1 H, CH_2), 6.89 (d, J = 1.8 Hz, 1 H, Ar), 7.27 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.3, 31.4, 34.6, 34.8, 56.0, 62.5, 66.3, 70.5, 85.6 (CH_2, CH_3, CMe_3), 121.6, 124.4, 124.9, 138.6, 144.0, 152.1 (Ar) ppm. $C_{19}H_{32}Cl_2NO_3Re$ (579.57): calcd. C 39.38, H 5.56, N 2.42; found C 39.20, H 5.57, N 2.21. IR (KBr): $\tilde{\nu}$ = 2948, 2864, 1474, 1262, 958, 914, 864 cm^{-1}. EI-MS: m/z (%) = 579 (71) [M$^+$].

Synthesis of [$ReOCl_2(ONS)$] (2): The compound was prepared according to the general procedure by employing KONS (37 mg, 0.10 mmol) in toluene (20 mL) and [$ReOCl_3(OPPh_3)(SMe_2)$] (67 mg, 0.10 mmol) in toluene (30 mL) to give **2** (35 mg, 58%). ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 9 H, CH_3), 1.24 (s, 9 H, CH_3), 1.57 (t, J = 7.5 Hz, 3 H, CH_3), 2.87 (dt, J = 11.8, 4.6 Hz, 1 H, CH_2), 3.12 (q, J = 7.3 Hz, 2 H, CH_2), 3.20 (m, 1 H, CH_2), 3.45 (s, 3 H, CH_3), 3.48 (m, 1 H, CH_2), 3.55 (d, J = 13.9 Hz, 1 H, CH_2), 3.73 (d, J = 12.2 Hz, 1 H, CH_2), 5.32 (d, J = 13.7 Hz, 1 H, CH_2), 6.89 (s, 1 H, Ar), 7.22 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.3, 29.7, 31.4, 34.5, 34.7, 40.0, 47.9, 56.4, 66.2, 66.3 (CH_2, CH_3, CMe_3), 122.9, 124.4, 124.7, 139.2, 144.3, 151.4 (Ar) ppm. $C_{20}H_{34}Cl_2NO_2ReS$ (609.66): calcd. C 39.40, H 5.62, N 2.30; found C 39.43, H 5.47, N 2.19. IR (KBr): $\tilde{\nu}$ = 2952, 2866, 1456, 1256, 956, 914, 854 cm^{-1}. EI-MS: m/z (%) = 609 (38) [M$^+$].

Synthesis of [$ReOCl_2(ONNMe)$] (3): The compound was prepared according to the general procedure by employing KONNMe (59 mg, 0.16 mmol) in toluene (20 mL) and [$ReOCl_3(OPPh_3)(SMe_2)$] (113 mg, 0.17 mmol) in toluene (30 mL) to give **3** (63 mg, 60%). ^{1}H NMR ($CDCl_3$): δ = 1.25 (s, 9 H, CH_3), 1.26 (s, 9 H, CH_3), 2.52 (s, 3 H, CH_3), 2.97 (m, 1 H, CH_2), 3.21 (s, 3 H, CH_3), 3.30 (m, 2 H, CH_2), 3.51 (d, J = 13.6 Hz, 1 H, CH_2), 3.54 (s, 3 H, CH_3), 3.55 (m, 1 H, CH_2), 5.20 (d, J = 14.1 Hz, 1 H, CH_2), 6.83 (d, J = 1.8 Hz, 1 H, Ar), 7.24 (d, J = 2.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.3, 31.4, 34.5, 35.0, 51.3, 55.6, 61.7, 65.3, 66.8, 74.1 (CH_2, CH_3, CMe_3), 121.1, 124.3, 125.0, 138.8, 143.7, 151.7 (Ar) ppm. $C_{20}H_{35}Cl_2N_2O_2Re\cdot0.15\ OPPh_3$ (634.36): calcd. C 42.98, H 5.92, N 4.42; found C 43.05, H 5.79, N 3.72. IR (KBr): $\tilde{\nu}$ = 2948, 1458, 1250, 972, 914, 862 cm^{-1}. EI-MS: m/z (%) = 592 (43) [M$^+$].

Synthesis of [$ReOCl_2(ONNEt)$] (4): The compound was prepared according to the general procedure by employing KONNEt (61 mg, 0.16 mmol) in toluene (20 mL) and [$ReOCl_3(OPPh_3)(SMe_2)$] (107 mg, 0.17 mmol) in toluene (30 mL) to give **4** (60 mg, 57%). ^{1}H NMR ($CDCl_3$): δ = 1.26 (s, 9 H, CH_3), 1.29 (s, 9 H, CH_3), 1.29 (m, overlapped by s, 3 H, CH_3), 1.45 (t, J = 6.5 Hz, 3 H, CH_3), 2.64 (m, 1 H, CH_2), 3.12 (m, 1 H, CH_2), 3.25 (s, 3 H, CH_3), 3.35 (m, 5 H, CH_2), 3.47 (m, 1 H, CH_2), 3.87 (m, 1 H, CH_2), 5.23 (d, J

= 14.0 Hz, 1 H, CH_2), 6.81 (s, 1 H, Ar), 7.27 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.09, 10.6, 30.6, 31.4, 34.4, 35.1, 52.2, 56.3, 61.0, 66.8, 66.9, 68.0 (CH_2, CH_3, CMe_3), 121.4, 123.8, 125.3, 139.0, 143.3, 152.4 (Ar) ppm. $C_{22}H_{39}Cl_2N_2O_2Re$ (620.67): calcd. C 42.57, H 6.33, N 4.51; found C 42.60, H 4.60, N 2.10. IR (KBr): $\tilde{\nu}$ = 2946, 1472, 1250, 964, 918, 852 cm^{-1}. EI-MS: *m*/*z* (%) = 620 (32) [M^+].

Synthesis of [$ReOBr_2(ONO)$] (5): The compound was prepared according to the general procedure by employing KONO (69 mg, 0.20 mmol) in toluene (20 mL) and [$ReOBr_3(PPh_3)_2$] (193 mg, 0.25 mmol) in toluene (30 mL) to give **5** (62 mg, 46%). ^1H NMR ($CDCl_3$): δ = 1.27 (s, 18 H, CH_3), 2.39 (m, 1 H, CH_2), 3.34 (m, 4 H, CH_3, CH_2), 3.48 (d, *J* = 14.0 Hz, 1 H, CH_2), 4.20 (m, 1 H, CH_2), 4.48 (m, 1 H, CH_2), 4.53 (s, 3 H, CH_3), 5.38 (d, *J* = 15.3 Hz, 1 H, CH_2), 6.87 (s, 1 H, Ar), 7.27 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.6, 31.6, 34.8, 35.1, 55.9, 62.4, 66.7, 70.4, 84.4 (CH_2, CH_3, CMe_3), 121.5, 124.5, 125.3, 139.2, 144.4, 152.3 (Ar) ppm. $C_{19}H_{32}Br_2NO_3Re$ (668.48): calcd. C 34.14, H 4.82, N 2.10; found C 33.90, H 4.63, N 2.12. IR (KBr): $\tilde{\nu}$ = 2962, 2864, 1474, 1436, 1262, 1020, 968, 918, 864 cm^{-1}. EI-MS: *m*/*z* (%) = 669 (27) [M^+].

Synthesis of [$ReOBr_2(ONS)$] (6): The compound was prepared according to the general procedure by employing KONS (75 mg, 0.20 mmol) in toluene (20 mL) and [$ReOBr_3(PPh_3)_2$] (193 mg, 0.25 mmol) in toluene (30 mL) to give **6** (60 mg, 43%). ^1H NMR ($CDCl_3$): δ = 1.21 (s, 9 H, CH_3), 1.25 (s, 9 H, CH_3), 1.27 (m, 3 H, CH_3), 2.83 (dt, *J* = 11.3, 3.1 Hz, 1 H, CH_2), 2.99 (m, 2 H, CH_2), 3.17 (dt, *J* = 11.5, 2.2 Hz, 1 H, CH_2), 3.25 (s, 3 H, CH_3), 3.49 (d, *J* = 13.9 Hz, 1 H, CH_2), 3.70 (m, 2 H, CH_2), 5.62 (d, *J* = 13.8 Hz, 1 H, CH_2), 6.84 (s, 1 H, Ar), 7.21 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.5, 29.7, 31.4, 34.5, 34.8, 47.1, 57.4, 58.1, 65.2, 66.7 (CH_2, CH_3, CMe_3), 122.5, 124.5, 124.8, 139.5, 144.5, 151.0 (Ar) ppm. $C_{20}H_{34}Br_2NO_2ReS$ (698.56): calcd. C 34.39, H 4.91, N 2.01; found C 34.61, H 4.97, N 1.91. IR (KBr): $\tilde{\nu}$ = 2960, 1442, 1244, 968, 914, 854 cm^{-1}. EI-MS: *m*/*z* (%) = 699 (46) [M^+].

Synthesis of [$ReOBr_2(ONNMe)$] (7): The compound was prepared according to the general procedure by employing KONNMe (51 mg, 0.15 mmol) in toluene (20 mL) and [$ReOBr_3(OPPh_3)(SMe_2)$] (118 mg, 0.15 mmol) in toluene (30 mL) to give **7** 62 mg (61%). ^1H NMR ($CDCl_3$): δ = 1.24 (s, 9 H, CH_3), 1.26 (s, 9 H, CH_3), 2.51 (s, 3 H, CH_3), 2.93 (d, *J* = 12.5 Hz, 1 H, CH_2), 3.19 (s, 3 H, CH_3), 3.30 (m, 2 H, CH_2), 3.52 (d, *J* = 14.5 Hz, 1 H, CH_2), 3.57 (s, 3 H, CH_3), 3.57 (s, 1 H, CH_2), 5.40 (d, *J* = 14.2 Hz, 1 H, CH_2), 6.84 (s, 1 H, Ar), 7.23 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.3, 31.4, 34.5, 35.0, 51.1, 55.4, 61.5, 64.5, 66.8, 73.2 (CH_2, CH_3, CMe_3), 121.1, 124.5, 125.0, 138.9, 143.9, 151.3 (Ar) ppm. $C_{20}H_{35}Br_2N_2O_2Re{\cdot}0.09OPPh_3$ (706.56): calcd. C 36.75, H 5.19, N 3.96; found C 36.83, H 4.71, N 2.98. IR (KBr): $\tilde{\nu}$ = 2948, 1472, 1248, 1116, 962, 862, 856 cm^{-1}. EI-MS: *m*/*z* (%) = 682 (29) [M^+].

Synthesis of [$ReOBr_2(ONNEt)$] (8): The compound was prepared according to the general procedure by employing KONNEt (53 mg, 0.14 mmol) in toluene (20 mL) and [$ReOBr_3(OPPh_3)(SMe_2)$] (113 mg, 0.14 mmol) in toluene (30 mL) to give **8** (68 mg, 69%). ^1H NMR (CD_2Cl_2): δ = 1.24 (s, 9 H, CH_3), 1.27 (s, 9 H, CH_3), 1.27 (m, overlapped by s, 3 H, CH_3), 1.43 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.61 (m, 1 H, CH_2), 3.05 (m, 1 H, CH_2), 3.17 (s, 3 H, CH_3), 3.37 (m, 6 H, CH_2), 3.94 (m, 1 H, CH_2), 5.35 (d, *J* = 14.3 Hz, 1 H, CH_2), 6.86 (s, 1 H, Ar), 7.28 (s, 1 H, Ar) ppm. ^{13}C NMR (CD_2Cl_2): δ = 10.1, 11.5, 30.8, 31.7, 34.6, 35.5, 53.2, 56.5, 61.5, 66.5, 67.3, 67.4 (CH_2, CH_3, CMe_3), 122.1, 124.9, 125.7, 139.5, 144.7, 152.2 (Ar) ppm. $C_{22}H_{39}Br_2N_2O_2Re$ (709.57): calcd. C 37.24, H 5.54, N 3.95; found C 37.00, H 5.06, N 3.85. IR (KBr): $\tilde{\nu}$ = 2952, 2898, 1444, 1238, 974, 914, 854 cm^{-1}. EI-MS: *m*/*z* (%) = 710 (17) [M^+].

Synthesis of [$ReOCl_2(ONOO)$] (9): The compound was prepared according to the general procedure by employing KONOO (59 mg, 0.15 mmol) in toluene (20 mL) and [$ReOCl_3(OPPh_3)(SMe_2)$] (104 mg, 0.16 mmol) in toluene (20 mL) to give **9** (61 mg, 65%). ^1H NMR ($CDCl_3$): δ = 1.28 (s, 18 H, CH_3), 2.84 (d, *J* = 14.0 Hz, 1 H, CH_2), 3.19 (m, 1 H, CH_2), 3.42 (s, 3 H, CH_3), 3.45 (m, 1 H, CH_2), 3.75 (m, 2 H, CH_2), 3.89 (m, 1 H, CH_2), 4.28 (m, 2 H, CH_2), 4.45 (m, 1 H, CH_2), 4.47 (s, 3 H, CH_3), 5.09 (d, *J* = 14.0 Hz, 1 H, CH_2), 6.88 (d, *J* = 1.4 Hz, 1 H, Ar), 7.27 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.3, 31.4, 34.6, 34.8, 58.9, 61.0, 62.5, 64.9, 69.1, 70.1, 85.4 (CH_2, CH_3, CMe_3), 121.7, 124.3, 124.8, 144.0, 152.1, 157.4 (Ar) ppm. $C_{21}H_{36}Cl_2NO_4Re$ (623.63): calcd. C 40.45, H 5.82, N 2.25; found C 40.12, H 5.53, N 2.17. IR (KBr): $\tilde{\nu}$ = 2942, 1468, 1440, 1266, 958, 918, 858 cm^{-1}. EI-MS: *m*/*z* (%) = 623 (14) [M^+].

Synthesis of [$ReOCl_2(ONSS)$] (10): The compound was prepared according to the general procedure by employing KONSS (63 mg, 0.14 mmol) in toluene (20 mL) and [$ReOCl_3(OPPh_3)(SMe_2)$] (94 mg, 0.14 mmol) in toluene (20 mL) to give **10** (44 mg, 46%). ^1H NMR ($CDCl_3$): δ = 1.22 (s, 9 H, CH_3), 1.25 (s, 9 H, CH_3), 1.29 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.59 (t, *J* = 7.4 Hz, 3 H, CH_3), 2.60 (q, *J* = 7.3 Hz, 2 H, CH_2), 2.88 (t, *J* = 12.0 Hz, 1 H, CH_2), 3.12 (m, 3 H, CH_2), 3.25 (m, 2 H, CH_2), 3.53 (m, 2 H, CH_2), 3.66 (d, *J* = 13.6 Hz, 1 H, CH_2), 3.75 (d, *J* = 11.7 Hz, 1 H, CH_2), 4.05 (dt, *J* = 10.8, 4.7 Hz, 1 H, CH_2), 5.42 (d, *J* = 13.4 Hz, 1 H, CH_2), 6.88 (d, *J* = 1.8 Hz, 1 H, Ar), 7.22 (d, *J* = 2.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1, 15.2, 26.9, 27.4, 29.7, 30.3, 34.6, 34.8, 41.1, 50.1, 62.3, 66.5, 66.9 (CH_2, CH_3, CMe_3), 122.6, 124.6, 124.7, 139.3, 144.4, 151.0 (Ar) ppm. $C_{23}H_{40}Cl_2NO_2ReS_2$ (683.80): calcd. C 40.40, H 5.90, N 2.05; found C 40.84, H 5.89, N 2.06. IR (KBr): $\tilde{\nu}$ = 2926, 1448, 1254, 960, 900, 856 cm^{-1}. EI-MS: *m*/*z* (%) = 683 (1) [M^+].

Synthesis of [$ReOCl_2(ONNNEt)$] (11): The compound was prepared according to the general procedure by employing KONNNEt (64 mg, 0.14 mmol) in toluene (20 mL) and [$ReOCl_3(OPPh_3)(SMe_2)$] (92 mg, 0.14 mmol) in toluene (30 mL) to give **11** (51 mg, 52%). ^1H NMR ($CDCl_3$): δ = 1.25 (s, 18 H, CH_3), 1.25 (m, 12 H, CH_3), 2.65 (m, 1 H, CH_2), 2.95 (m, 4 H, CH_2), 3.68 (m, 8 H, CH_2), 3.62 (d, *J* = 13.9 Hz, 1 H, CH_2), 3.83 (m, 1 H, CH_2), 3.90 (m, 1 H, CH_2), 3.96 (m, 1 H, CH_2), 5.14 (d, *J* = 13.8 Hz, 1 H, CH_2), 6.87 (d, *J* = 2.0 Hz, 1 H, Ar), 7.25 (d, *J* = 2.1 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.43, 10.5, 10.7, 30.5, 31.4, 34.5, 35.0, 48.3, 48.5, 52.5, 62.2, 62.7, 65.9, 67.8 (CH_2, CH_3, CMe_3), 121.4, 124.5, 125.1, 138.8, 144.1, 152.3 (Ar) ppm. $C_{27}H_{50}Cl_2N_3O_2Re$ (705.82): calcd. C 45.95, H 7.14, N 5.95; found C 44.99, H 7.02, N 5.59. IR (KBr): $\tilde{\nu}$ = 2938, 1468, 1248, 968, 914, 852 cm^{-1}. EI-MS: *m*/*z* (%) = 705 (3) [M^+].

Synthesis of [$ReOBr_2(ONOO)$] (12): The compound was prepared according to the general procedure by employing KONOO (52 mg, 0.13 mmol) in toluene (20 mL) and [$ReOBr_3(OPPh_3)(SMe_2)$] (110 mg, 0.14 mmol) in toluene (20 mL) to give **12** (57 mg, 62%). ^1H NMR ($CDCl_3$): δ = 1.27 (s, 9 H, CH_3), 1.28 (s, 9 H, CH_3), 2.90 (m, 1 H, CH_2), 3.14 (m, 1 H, CH_2), 3.43 (s, 3 H, CH_3), 3.61 (m, 4 H, CH_2), 3.96 (d, *J* = 13.8 Hz, 1 H, CH_2), 4.21 (m, 1 H, CH_2), 4.29 (m, 1 H, CH_2), 4.54 (s, 3 H, CH_3), 5.24 (d, *J* = 13.7 Hz, 1 H, CH_2), 6.88 (s, 1 H, Ar), 7.26 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.4, 31.4, 34.4, 34.5, 59.1, 59.5, 62.2, 64.0, 69.1, 70.2, 85.0 (CH_2, CH_3, CMe_3), 122.0, 124.6, 124.8, 138.6, 144.2, 152.4 (Ar) ppm. $C_{21}H_{36}Br_2NO_4Re$ (712.53): calcd. C 35.40, H 5.09, N 1.97; found C 35.50, H 4.96, N 1.96. IR (KBr): $\tilde{\nu}$ = 2947, 1452, 1263, 960, 856 cm^{-1}. EI-MS: *m*/*z* (%) = 713 (12) [M^+].

Synthesis of [$ReOBr_2$(ONSS)] (13): The compound was prepared according to the general procedure by employing KONSS (55 mg, 0.12 mmol) in toluene (20 mL) and [$ReOBr_3(OPPh_3)(SMe_2)$] (101 mg, 0.13 mmol) in toluene (20 mL) to give **13** (42 mg, 49%). ^{1}H NMR ($CDCl_3$): δ = 1.20 (s, 9 H, CH_3), 1.25 (s, 9 H, CH_3), 1.28 (m, 3 H, CH_3), 1.58 (t, J = 7.4 Hz, 3 H, CH_3), 2.60 (q, J = 7.4 Hz, 2 H, CH_2), 2.91 (t, J = 12.3 Hz, 1 H, CH_2), 3.03 (m, 2 H, CH_2), 3.22 (m, 3 H, CH_2), 3.52 (m, 1 H, CH_2), 3.72 (m, 2 H, CH_2), 3.74 (d, J = 13.6 Hz, 1 H, CH_2), 4.12 (m, 1 H, CH_2), 5.63 (d, J = 13.7 Hz, 1 H, CH_2), 6.87 (d, J = 1.8 Hz, 1 H, Ar), 7.22 (d, J = 2.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1, 15.2, 26.9, 27.4, 29.0, 29.7, 30.3, 31.5, 34.6, 40.6, 47.8, 62.4, 65.8 (CH_2, CH_3, CMe_3), 122.4, 124.7, 124.8, 139.5, 144.6, 150.7 (Ar) ppm. $C_{23}H_{40}Br_2NO_2ReS_2$ (772.70): calcd. C 35.75, H 5.22, N 1.81; found C 36.03, H 5.23, N 1.81. IR (KBr): $\tilde{\nu}$ = 2922, 1438, 1238, 958, 910, 856 cm^{-1}.

Synthesis of [$ReOBr_2$(ONNNEt)] (14): The compound was prepared according to the general procedure by employing KONNNEt (56 mg, 0.12 mmol) in toluene (20 mL) and [$ReOBr_3(OPPh_3)$-(SMe_2)] (99 mg, 0.13 mmol) in toluene (20 mL) to give **14** (51 mg, 55%). ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 9 H, CH_3), 1.25 (s, 9 H, CH_3), 1.42 (t, J = 6.7 Hz, 12 H, CH_3), 2.64 (m, 1 H, CH_2), 3.12 (m, 2 H, CH_2), 3.33 (m, 8 H, CH_2), 3.41 (m, 1 H, CH_2), 3.70 (d, J = 13.5 Hz, 1 H, CH_2), 3.73 (m, 1 H, CH_2), 4.04 (m, 2 H, CH_2), 4.42 (dt, J = 10.0 Hz, 1 H, CH_2), 5.35 (d, J = 13.6 Hz, 1 H, CH_2), 6.92 (s, 1 H, Ar), 7.26 (d, J = 2.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.90, 8.91, 10.2, 11.2, 30.5, 31.3, 34.6, 35.0, 48.5, 53.3, 59.4, 62.1, 62.5, 65.1, 66.0 (CH_2, CH_3, CMe_3), 120.9, 124.8, 125.2, 139.1, 144.8, 151.0 (Ar) ppm. $C_{27}H_{50}Br_2N_3O_2Re$ (794.72): calcd. C 40.81, H 6.34, N 5.29; found C 40.20, H 6.23, N 4.78. IR (KBr): $\tilde{\nu}$ = 2946, 1456, 1236, 962, 910, 854 cm^{-1}. EI-MS: m/z (%) = 795 (1) [M^+].

Catalytic Epoxidation Reaction: The reactions were carried out under an inert gas. Cyclooctene (0.30 g, 2.72 mmol), dibutyl ether (0.30 g, 2.30 mmol), and the respective rhenium(V) catalyst (2 mol-%) were dissolved in chloroform (20 mL). The reaction mixture was heated to 50 °C, whereupon TBHP (1.5 mL, 5.5 M solution in decane, 8.2 mmol) was added. Prior to GC–MS analyses, aliquot samples were quenched with MnO_2 with subsequent dilution.

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