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Oxidorhenium(V) Complexes with Phenolate- and Carboxylate-Based Ligands: Structure and Catalytic Epoxidation

Barbara Machura,*[a] Mariusz Wolff,[a] Dominik Tabak,[b] Jörg A. Schachner,[c] and Nadia C. Mösch-Zanetti[c]

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Several oxidorhenium(V) complexes with phenolate- and carboxylate-based ligands were synthesized: $[ReOCl(hpbi)_2]\cdot THF$, $[ReOCl(hmpbta)_2]$, $[ReOBr(hmpbta)_2]$, $[ReOCl(hpbo)_2]$, $[ReOCl(hpbt)_2]\cdot 2MeCN$, $[ReO(OMe)(quin)_2]$, $[ReO(OMe)(pic)_2]$, $[ReO(OMe)(2,5\text{-}dipic)_2]\cdot C_5H_5N$, $[ReOCl(pic)_2]$, and $[ReOCl(3\text{-}ind)_2]$ [in which Hhpbi = 2-(2-hydroxyphenyl)-1*H*-benzimidazole, Hhmpbta = 2-(2-hydroxy-5-methylphenyl)-benzotriazole, Hhpbo = 2-(2-hydroxyphenyl)-2-benzoxazole, Hhpbt = 2-(2-hydroxyphenyl)benzothiazole, Hquin = quinaldic acid, picH = picolinic acid, 2,5-dipicH = 2,5-pyridinedicarboxylic acid, and 3-indH = indazole-3-carboxylic acid]. The compounds were characterized by spectroscopic methods and single-crystal X-ray diffraction analysis. Interestingly, the complex $[ReO(OMe)(quin)_2]$ is a rare *trans*-N,N and *trans*-O,O isomer of $[ReOX(N\text{–}O)_2]$ with two chelating quinoline-2-carboxylate ligands in the equatorial plane and a linear axial [O=Re–OMe] unit. The other disubstituted compounds were found to be the most common *cis*-N,N structure of $[ReOX(N\text{-}O)_2]$ with the oxygen atom of one of the chelating ligands in a *trans* position to the oxido ligand. All the complexes were tested in the epoxidation of cyclooctene with *tert*-butyl hydroperoxide (3 equiv.). The lowest conversion of only 3 % has been confirmed for $[ReOCl(hpbi)_2]$. All other complexes reached yields of cyclooctane oxide between 58 and 75 %.

Introduction

The widespread contemporary interest in the coordination chemistry of rhenium arises mainly from the introduction of β^--emitting isotopes ^{188}Re and ^{186}Re in radiotherapy and its similarity with technetium, the metastable γ-emitting isotope ^{99m}Tc, which plays an important role in diagnostic nuclear medicine. Thus, there is still a need for basic knowledge about the structural and spectroscopic properties, redox activities, and mechanism of ligand-substitution reactions to develop new and improved Re radiopharmaceuticals.[1–4]

Another area of growing interest for rhenium–oxido compounds is their application as catalysts, particularly in oxidation and oxygen-atom-transfer (OAT) reactions. This field is clearly highlighted by methyltrioxidorhenium(VII), one of the most versatile and highly efficient transition-metal catalysts known to date.[5–7]

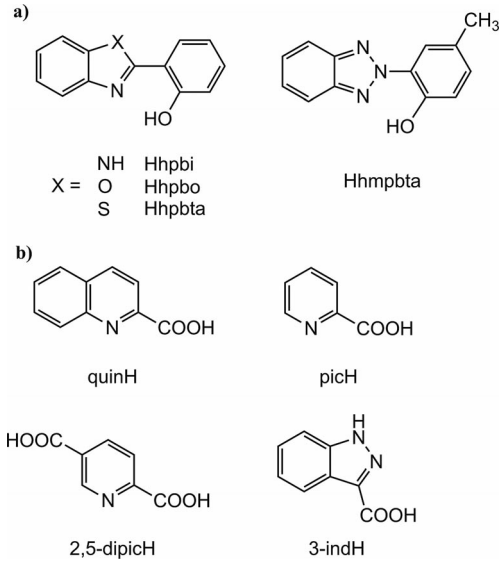
Oxidorhenium(V) compounds have been far less explored, although straightforward preparation and high stability towards hydrolysis make them attractive options as catalysts. For this reason, some effort has been recently devoted to the investigation of Re^V complexes as catalysts in epoxidation reactions of olefins. Detailed studies have been performed for monosubstituded or disubstituted complexes of the type $[ReOX_2\mathbf{L}(PPh_3)]$ and $[ReOX\mathbf{L}_2]$ with β-ketiminate ligands, pyrazole phenolate and naphtholate ligands, acetylacetone-derived Schiff bases, and oxazolinylmethoxido ligands, as well as for $[ReOX_2\mathbf{L}]$ and $[ReOX\mathbf{L}]$ with tridentate or tetradentate Schiff bases or pyridazine phenolate ligands. However, only limited success has been attained as the reported Re^V complexes showed lower activity or productivity than rhenium(VII) systems.[8–16] Therefore, there is a need for further investigations on furnishing novel rhenium(V) complexes with ligands that exhibit higher stability towards oxidation.

However, oxidorhenium(V) complexes were found to be highly successful in OAT reactions. Espenson and co-workers reported some rhenium(V) complexes to be efficient catalysts of oxygen-atom transfer from pyridine *N*-oxide to phosphanes.[17,18] Abu-Omar and co-workers developed a new class of molecular rhenium(V) oxotransferases that incorporate oxazoline-derivatized phenolates, which efficiently catalyze the reduction of perchlorate to chloride ions, one of the most challenging reactions due to its kinetic hindrance and environmental importance.[19–21]

The recent success of the rhenium(V) complexes and the need for novel catalytically active species prompted us to

[a] Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland
E-mail: basia@ich.us.edu.pl
[b] Department of Organic Chemistry, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland
[c] Institute of Chemistry, Karl-Franzens-University Graz, Stremayrgasse 16, 8010 Graz, Austria
E-mail: nadia.moesch@uni-graz.at

synthesize a set of oxo compounds of the general formula $[ReOX(N–O)_2]$ and investigate their potential as catalysts in oxidation reactions. Depending on the type of chelating ligand, compounds investigated herein can be divided into two groups: those that incorporate ligands structurally related to oxazoline-derivatized phenolates investigated by Abu-Omar et al.,[19–21] namely, 2-(2-hydroxyphenyl)-1*H*-benzimidazole (Hhpbi), 2-(2-hydroxy-5-methylphenyl)benzotriazole (Hhmpbta), 2-(2-hydroxyphenyl)-2-benzoxazole (Hhpbo), and 2-(2-hydroxyphenyl)benzothiazole (Hhpbt), and those that include bidentate ligands based on an aromatic heterocycle and a carboxylic acid as second and charge-neutralizing coordinating functionality [quinaldic acid (quinH), picolinic acid (picH), 2,5-pyridinedicarboxylic acid (2,5-dipicH), and indazole-3-carboxylic acid (3-indH)]. Phenolate- and carboxylate-based ligands employed in this study are shown in Scheme 1. The use of various chelating ligands that incorporate different heterocycle rings and O-donor groups allows us to expect unusual electronic influences on the coordinating capability as well as on the catalytic activity.



Scheme 1. (a) Phenolate- and (b) carboxylate-based ligands employed in this study.

Results and Discussion

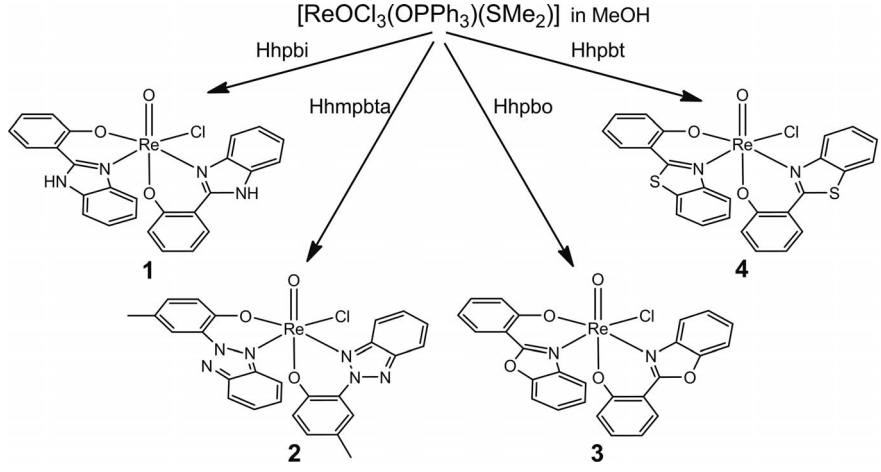
Synthesis

Phenolate-disubstituted oxidorhenium(V) complexes $[ReOCl(N–O)_2]$ (**1**–**4**) were obtained by treatment of $[ReOCl_3(OPPh_3)(SMe_2)]$ with the corresponding ligand (2 equiv.) 2-(2-hydroxyphenyl)-1*H*-benzimidazole (Hhpbi), 2-(2-hydroxy-5-methylphenyl)benzotriazole (Hhmpbta), 2-(2-hydroxyphenyl)-2-benzoxazole (Hhpbo), and 2-(2-hydroxyphenyl)benzothiazole (Hhpbt) (Scheme 2).

To investigate the effect of the halide ion, the reaction of $[ReOBr_3(OPPh_3)(SMe_2)]$ with 2-(2-hydroxy-5-methylphenyl)benzotriazole was also examined and $[ReOBr(hmpbta)_2]$ (**5**) was isolated.

As expected, the metal precursors $[ReOX_3(OPPh_3)(SMe_2)]$ turned out to be an excellent starting material for preparation of these complexes. The yields obtained were comparable with those reported for alternative metal precursor $[NBu_4][ReOX_4]$[22] and significantly higher than $[ReOX_3(PPh_3)_2]$, which gave only minor amounts of $[ReOX_2(N–O)_2]$.[23] Complexes **1**–**5** show high stability toward air and moisture both in the solid state and in solution for several months at ambient temperature. They exhibit moderate solubility in strong polar solvents such as thf, acetonitrile, acetone, chloroform, methanol, and ethanol, and are insoluble in medium polar and apolar solvents.

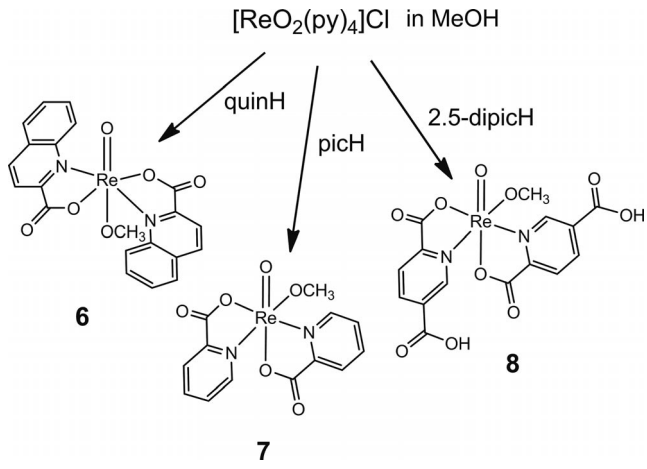
The ^1H NMR spectra of these complexes confirmed the occurrence of only one isomer in solution, which was shown to contain nonequivalent N–O ligands. Particularly characteristic are protons of the N–H group of the imidazole ring in **1** and methyl groups attached to the phenolate ring in **2** and **5**, which gave nonequivalent chemical shifts (δ = 13.80 and 13.64 ppm for **1**, δ = 2.58 and 2.05 ppm for **2**, and δ = 2.58 and 2.04 ppm for **5**).



Scheme 2.

The IR spectra were characterized by strong absorptions at approximately 960 cm^{-1} that were assigned to the Re=O stretching frequencies. This value is in the range typical of neutral six-coordinate mono-oxidorhenium(V) complexes with an anionic phenolate oxygen coordinated *trans* to the oxo group.[13,14,24] The absorptions in the region 1630–1520 cm^{-1} were assigned to the ν(C=N) modes of the chelating ligands.

To synthesize carboxylate-disubstituted oxidorhenium(V) complexes, two metal precursors $[ReOCl_3(OPPh_3)(SMe_2)]$ and $[ReO_2(py)_4]Cl$ were used. The better results were achieved in the case of synthetic strategy based on the reaction of $[ReO_2(py)_4]Cl$ with carboxylic acids, which yielded the compounds $[ReO(OMe)(N–O)_2]$ (**6**–**8**; Scheme 3).

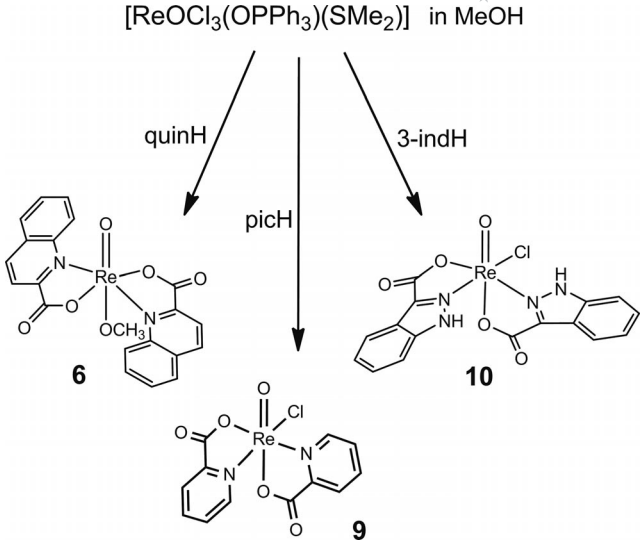


Scheme 3.

Apart from its high yield, this procedure has another important advantage: the desired complexes precipitate directly from the reaction mixture under prolonged reflux conditions and are easily isolated by simple filtration. Treatment of the alternative metal precursor $[ReOCl_3(OPPh_3)(SMe_2)]$ with the corresponding carboxylic acid (2 equiv.) in MeOH heated at reflux led to the disubstituted complexes $[ReOCl(N–O)_2]$ (**9**, **10**; Scheme 4), but the yields obtained were lower than $[ReO_2(py)_4]Cl$.

Most interestingly, the choice of metal precursor turned out to be crucial in the synthesis of the carboxylate-disubstituted rhenium(V) complexes. Attempts to synthesize the disubstituted rhenium complex of indazole-3-carboxylate ligand by employing $[ReO_2(py)_4]Cl$ failed. They yielded an insoluble pink powder, which prevented its further characterization. The desired complex $[ReOCl(3\text{-ind})_2]$ (**10**) was obtained by using $[ReOCl_3(OPPh_3)(SMe_2)]$.

In contrast, treatment of $[ReO_2(py)_4]Cl$ with 2,5-pyrazinedicarboxylic acid led to $[ReO(OMe)(2,5\text{-dipic})_2]$, whereas a synthetic procedure with $[ReOCl_3(OPPh_3)(SMe_2)]$ resulted in the formation of an unidentified reaction mixture as revealed by ^1H NMR spectroscopy. Pyridine-2-carboxylic and quinoline-2-carboxylic acids reacted with both metal precursors to give disubstituted Re^V–oxido complexes $[ReO(OMe)(N–O)_2]$ or $[ReOCl(N–O)_2]$.

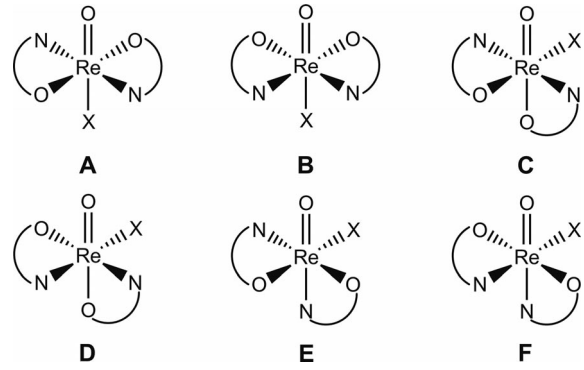


Scheme 4.

All carboxylate–rhenium(V)–oxido complexes **6**–**10** show high stability toward air and moisture both in the solid state and in solution, but compounds **7**, **8**, and **10** exhibit limited solubility in most common solvents, which prevented the recording of their ^{13}C NMR spectra.

The ^1H NMR spectrum of **6** revealed only one set of ligand resonances, thus indicating a higher symmetric species in contrast to complexes **7**–**10** with two sets of signals in the ^1H NMR spectra for the attached ligands.

In principle, there are several different possible orientations for the ligands in complexes of general formula $[ReOX(N–O)_2]$, as shown in Scheme 5.



Scheme 5. Possible ligand orientations for $[ReOX(N–O)_2]$ complexes.

Generally, they can be divided into two subgroups: (i) with the X ligand coordinated *trans* to the Re=O group (types A and B), and (ii) with the X ligand *cis* to the Re=O moiety (types C–F). Moreover, five of the possible constitution isomers (types B–F) exist as a pair of enantiomers.

Unambiguous determination of the ligand arrangement around the metal center in **6**–**10** was possible by single-crystal X-ray diffraction, and structural studies are in good agreement with the NMR spectroscopic results. Complexes **7**–**10** adopt the most common structure of type D and dis-

play two sets of ^{1}H NMR spectroscopic signals for the attached ligands, which is in accordance with their nonequivalent coordination geometry. The ligands of **6** are arranged around the Re center as in isomer A, and two equivalent N–O ligands revealed only one set of ligand resonances in the NMR spectra.

For each carboxylato-rhenium(V) complex, IR spectroscopy confirmed the presence of an Re=O fragment. The strong Re=O stretching mode was found at 955 cm^{-1} for **6** and approximately 985 cm^{-1} for **7**–**10**. The bathochromic shift of this vibration in complex **6**, which incorporates a *trans*-[ReO(OMe)]$^{2+}$ unit, is normal and results from the competition of the methoxide group for π bonding with the dπ orbitals of the metal, thereby leading to the weakness of the Re=O bond.[25] A higher wavenumber of **7**–**10** indicates that the Re–carboxylate bond *trans* to the oxido ligand is not very strong and does not compete effectively for the d_{Re} orbitals. Coordination of the carboxylate group was confirmed by absorptions in the regions 1730–1660 and 1330–1280 cm^{-1}, which are assigned to the asymmetric and symmetric stretching vibration of the COO$^-$ group, respectively.

Molecular Structures of the Complexes [ReOX(N–O)$_2$]

The molecular structures of compounds **1** and **3**–**10** were determined by single-crystal X-ray diffraction analysis. The perspective molecular views of the complexes are shown in Figures 1, 2, and 3. Crystallographic data are presented in Tables 1 and 2, and selected bond lengths and angles are given in Tables 3, 4, and 5. The molecular structure of **2** was discussed in our previous paper.[23]

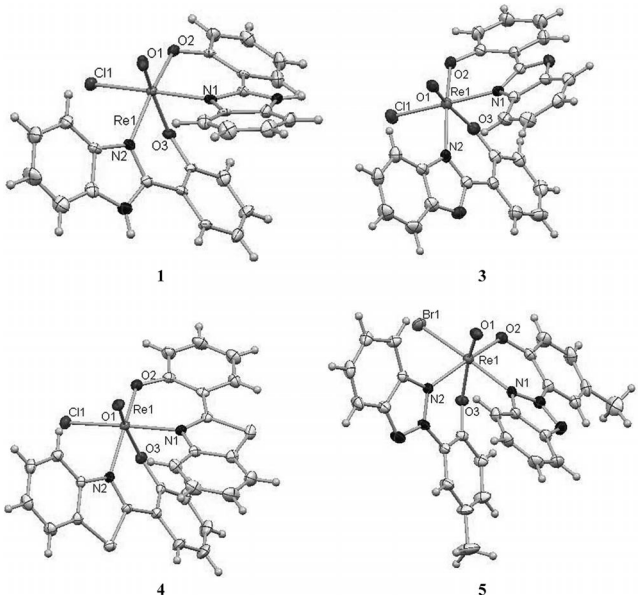


Figure 1. Molecular views of phenolate disubstituted compounds [ReOCl(N–O)$_2$] with selected atom numbering.

All examined complexes show a six-coordinate rhenium atom with distorted octahedral geometries. Each phenolate or carboxylate ligand chelates to the oxidorhenium core through N and O atoms. In complex **6**, two quinoline-2-carboxylate ligands are situated in an equatorial plane with a *trans*-N,N *trans*-O,O arrangement, and the coordination site *trans* to the oxido ligand is occupied by the methoxy group. Such ligand arrangement around the central ion makes complex **6** a very rare example of [ReOX(N–O)$_2$] complexes.

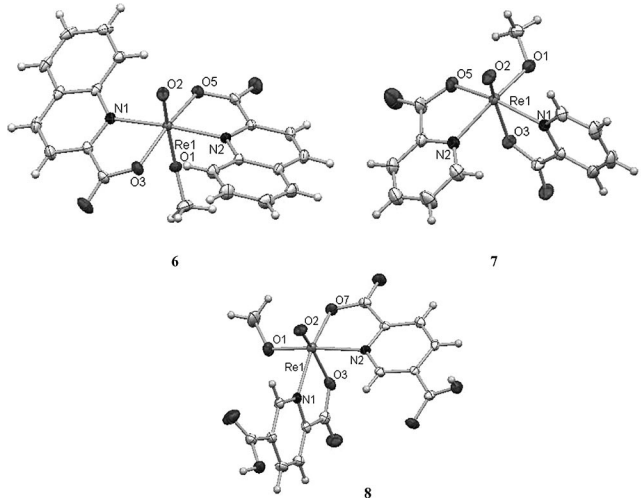


Figure 2. Molecular views of carboxylate disubstituted compounds [ReO(OMe)(N–O)$_2$] with selected atom numbering.

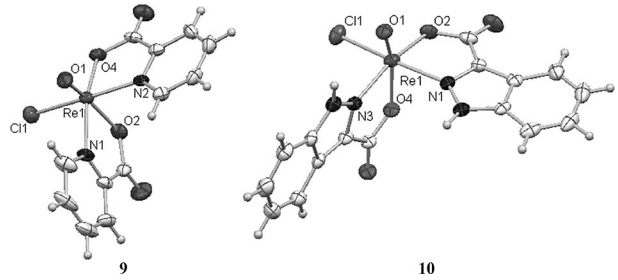


Figure 3. Molecular views of carboxylate disubstituted compounds [ReOCl(N–O)$_2$] with selected atom numbering.

A related [ReOCl(N–O)$_2$] compound with two symmetrically coordinated salen ligands in the equatorial plane and a linear [O=Re–X] moiety was isolated by Herrmann and co-workers in 2007 as a side product in the reaction of [NBu$_4$][ReOCl$_4$] with the bis(alkyl/aryl)-2-pyridylalcoholate ligand.[8] A *trans* O=Re–X conformation has also been confirmed in a few other [ReOX**L**$_2$] compounds, namely, [ReOCl(*o*-C$_6$O$_2$Cl$_4$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)],[25] [ReOCl(NH$_2$-CH$_2$CH$_2$S)$_2$],[26] [ReOCl{NH(*o*-C$_6$H$_4$)SCH$_3$}$_2$],[27] and [ReOCl(OPhsal){P(CH$_3$)$_2$Ph}] [OPhsal = *N*-(2-oxidophenyl)salicylideneiminate].[28]

Complexes **1**–**5** and **7**–**10** were found to be the *cis*-N,N isomer of type D (Scheme 1). The equatorial plane of these compounds consists of the two nitrogen atoms, an oxygen atom from the chelating ligand, and the halide atom or methoxy group. The oxido ligand along the axial direction is *trans* to the phenol or carboxylic oxygen atom. This is due to a strong *trans* influence of the oxido group, which forces the harder oxygen atom of the N–O ligand into a *trans* position. Such stereochemistry is well documented in

Table 1. Crystal data and structure refinement for complexes **1**, **3**, **4**, and **5**.

	1	**3**	**4**	**5**
Empirical formula	$C_{30}H_{26}ClN_4O_4Re$	$C_{26}H_{16}ClN_2O_5Re$	$C_{30}H_{22}ClN_4O_3S_2Re$	$C_{26}H_{20}BrN_6O_3Re$
Formula weight	728.20	658.06	772.29	730.59
T [K]	293.0(2)	293.0(2)	293.0(2)	293.0(2)
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$Pbca$
a [Å]	12.9021(10)	9.2556(13)	13.3205(4)	15.8338(6)
b [Å]	13.6136(8)	14.5250(3)	15.9693(5)	15.8517(8)
c [Å]	15.9407(16)	17.5280(2)	13.4978(4)	19.9989(9)
α [°]	90	90	90	90
β [°]	110.716(10)	104.320(12)	94.374(3)	90
γ [°]	90	90	90	90
V [Å^3]	2618.9(4)	2283.2(3)	2862.88(15)	5019.6(4)
Z	4	4	4	8
$\rho_{calcd.}$ [g cm^{-3}]	1.847	1.914	1.792	1.934
μ [mm^{-1}]	4.788	5.482	4.524	6.475
$F(000)$	1432	1272	1512	2816
Crystal size [mm]	0.851 × 0.203 × 0.011	0.158 × 0.054 × 0.028	1.318 × 0.504 × 0.424	0.346 × 0.092 × 0.086
θ range for data collection [°]	3.38 to 25.00	3.61 to 25.00	3.72 to 25.00	3.52 to 25.00
Reflections collected	23034	9935	14038	22712
Independent reflections	4568 (R_{int} = 0.0652)	3997 (R_{int} = 0.0593)	4980 (R_{int} = 0.0268)	4403 (R_{int} = 0.0437)
Completeness to 2θ = 25° [%]	99.1	99.7	98.8	99.7
Min. and max. transmission	0.511 to 1.000	0.505 to 1.000	0.362 to 1.000	0.475 to 1.000
Data / restraints / parameters	4568 / 0 / 361	3997 / 0 / 316	4980 / 0 / 372	4403 / 0 / 336
Goodness-of-fit on F_2	1.138	1.010	0.952	0.975
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0343	R_1 = 0.0541	R_1 = 0.0221	R_1 = 0.0207
	wR_2 = 0.1083	wR_2 = 0.1313	wR_2 = 0.0505	wR_2 = 0.0555
R indices (all data)	R_1 = 0.0498	R_1 = 0.0738	R_1 = 0.0331	R_1 = 0.0339
	wR_2 = 0.1507	wR_2 = 0.1422	wR_2 = 0.0521	wR_2 = 0.0572
Largest diff. peak / hole [e Å^{-3}]	1.568 and –1.650	3.835 and –1.976	0.744 and –0.809	0.700 and –0.539

Table 2. Crystal data and structure refinement for complexes **6**, **7**, **8**, **9**, and **10**.

	6	**7**	**8**	**9**	**10**
Empirical formula	$C_{21}H_{15}N_2O_6Re$	$C_{13}H_{11}N_2O_6Re$	$C_{20}H_{16}N_3O_{10}Re$	$C_{12}H_8ClN_2O_5Re$	$C_{17}H_{14}ClN_4O_6Re$
Formula weight	577.55	477.44	644.56	481.85	591.97
T [K]	293.0(2)	293.0(2)	293(2)	293.0(2)	293.0(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	Cc	$P\bar{1}$
a [Å]	7.6615(15)	14.3597(6)	13.1896(5)	7.7249(3)	7.2256(7)
b [Å]	7.9952(16)	7.5279(2)	7.2002(2)	12.0684(5)	8.6703(8)
c [Å]	17.5095(4)	14.3971(6)	22.2021(8)	15.1121(6)	16.4617(16)
α [°]	83.332(4)	90	90	90	94.924(8)
β [°]	84.009(4)	113.328(5)	99.129(3)	99.368(4)	93.370(8)
γ [°]	61.519(6)	90	90	90	110.372(9)
V [Å^3]	934.89(8)	1429.08(9)	2081.78(12)	1390.07(10)	958.87(16)
Z	2	4	4	4	2
$\rho_{calcd.}$ [g cm^{-3}]	2.052	2.219	2.057	2.302	2.050
μ [mm^{-1}]	6.543	8.534	5.903	8.956	6.519
$F(000)$	556	904	1248	904	568
Crystal size [mm]	0.099 × 0.098 × 0.056	0.402 × 0.279 × 0.031	0.218 × 0.132 × 0.065	0.162 × 0.110 × 0.108	0.145 × 0.122 × 0.014
θ range for data collection [°]	3.41 to 25.00	3.39 to 25.00	3.38 to 25.00	3.38 to 25.00	3.73 to 25.00
Reflections collected	17400	25290	14891	10106	17532
Independent reflections	3279 (R_{int} = 0.0582)	2502 (R_{int} = 0.0878)	3668 (R_{int} = 0.0353)	2438 (R_{int} = 0.0359)	3374 (R_{int} = 0.0552)
Completeness to 2θ = 25° [%]	99.7	99.7	99.8	99.8	99.6
Min. and max. transmission	0.462 to 1.000	0.108 to 1.000	0.545 to 1.000	0.481 to 1.000	0.397 to 1.000
Data / restraints / parameters	3279 / 0 / 266	2502 / 0 / 200	3668 / 0 / 308	2438 / 2 / 190	3374 / 0 / 264
Goodness-of-fit on F_2	1.094	1.100	1.313	1.027	1.057
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0225	R_1 = 0.0334	R_1 = 0.0342	R_1 = 0.0201	R_1 = 0.0329
	wR_2 = 0.0525	wR_2 = 0.0881	wR_2 = 0.0824	wR_2 = 0.0384	wR_2 = 0.0826
R indices (all data)	R_1 = 0.0261	R_1 = 0.0397	R_1 = 0.0387	R_1 = 0.0221	R_1 = 0.0389
	wR_2 = 0.0537	wR_2 = 0.0918	wR_2 = 0.0836	wR_2 = 0.0390	wR_2 = 0.0843
Largest diff. peak / hole [e Å^{-3}]	0.548 and –1.216	0.916 and –1.295	1.129 and –0.905	0.624 and –0.413	2.259 and –0.794

Table 3. Selected bond lengths [Å] and angles [°] of compounds **1**, **3**, **4**, and **5**.

	1	3	4	5
Re1–O1	1.682(6)	1.654(7)	1.673(2)	1.685(3)
Re1–O2	1.982(6)	1.977(6)	1.966(2)	1.968(3)
Re1–O3	2.019(6)	1.986(6)	1.984(2)	1.976(2)
Re1–N1	2.083(6)	2.111(7)	2.133(3)	2.112(3)
Re1–N2	2.109(7)	2.127(8)	2.140(3)	2.134(3)
Re1–X1	2.359(2)	2.353(3)	2.3633(9)	2.4856(5)
O1–Re1–O2	103.0(3)	105.2(3)	103.69(11)	102.71(13)
O1–Re1–O3	166.0(3)	165.6(3)	165.33(11)	162.33(12)
O2–Re1–O3	86.4(2)	82.7(3)	85.40(10)	88.49(11)
O1–Re1–N1	88.0(3)	85.1(3)	87.01(11)	86.64(13)
O2–Re1–N1	87.8(2)	88.3(3)	90.25(10)	87.63(12)
O3–Re1–N1	82.0(2)	83.0(3)	81.39(10)	80.14(12)
O1–Re1–N2	92.1(3)	91.9(3)	91.04(11)	89.73(13)
O2–Re1–N2	164.7(3)	162.8(3)	164.66(10)	167.41(12)
O3–Re1–N2	79.0(2)	81.2(3)	81.07(10)	79.90(11)
N1–Re1–N2	94.6(2)	95.5(3)	94.81(10)	95.12(12)
O1–Re1–X1	101.9(2)	99.7(2)	100.94(9)	102.10(10)
O2–Re1–X1	85.27(17)	87.27(19)	85.74(8)	87.57(9)
O3–Re1–X1	89.04(17)	92.7(2)	91.09(7)	91.86(8)
N1–Re1–X1	168.98(19)	174.2(2)	171.75(7)	170.77(8)
N2–Re1–X1	89.94(19)	87.7(2)	87.32(7)	87.93(9)

Table 4. Selected bond lengths [Å] and angles [°] of compounds **6**, **7**, and **8**.

	6	7	8
Re1–O2	1.696(3)	1.671(5)	1.683(5)
Re1–O1	1.893(3)	1.937(5)	1.927(5)
Re1–O5	2.037(3)	1.995(5)	–
Re1–O7	–	–	2.006(5)
Re1–O3	2.068(3)	2.081(4)	2.075(5)
Re1–N1	2.131(3)	2.121(5)	2.098(6)
Re1–N2	2.138(3)	2.132(6)	2.139(6)
O1–C1	1.388(5)	1.419(9)	1.409(10)
O2–Re1–O1	170.59(13)	104.4(3)	102.9(3)
O2–Re1–O5	99.94(14)	109.7(2)	–
O1–Re1–O5	86.15(13)	89.9(2)	–
O2–Re1–O7	–	–	108.6(3)
O1–Re1–O7	–	–	93.7(2)
O2–Re1–O3	91.38(14)	159.0(2)	160.9(2)
O1–Re1–O3	82.63(13)	86.1(2)	86.4(2)
O5–Re1–O3	168.69(12)	88.1(2)	–
O5–Re1–N1	100.64(12)	162.2(2)	–
O2–Re1–N1	95.86(14)	88.1(2)	89.6(3)
O1–Re1–N1	90.00(13)	85.8(2)	84.7(2)
O7–Re1–O3	–	–	87.1(2)
O7–Re1–N1	–	–	161.6(2)
O3–Re1–N1	77.96(12)	74.3(2)	74.5(2)
O2–Re1–N2	90.64(13)	94.7(3)	93.1(2)
O1–Re1–N2	83.51(12)	160.1(2)	163.8(2)
O5–Re1–N2	78.52(12)	78.5(2)	–
O7–Re1–N2	–	–	78.3(2)
O3–Re1–N2	101.57(12)	77.5(2)	79.1(2)
N1–Re1–N2	173.49(12)	100.3(2)	98.4(2)
C1–O1–Re1	141.2(3)	122.1(5)	123.0(6)

the literature and seems to be the most common structure type for [ReOX(N–O)$_2$] complexes.[12,14,22,23,29] There is no clear explanation for the different ligand orientation of complex **6** relative to compounds **7**–**10**. The studies have shown that even small changes in the steric and electronic properties of the ligand can have a significant impact on the stereochemistry of the resulting compounds.

Table 5. Selected bond lengths [Å] and angles [°] of compounds **9** and **10**.

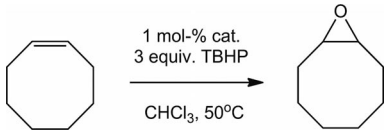
	9	10
Re1–O1	1.674(4)	1.681(4)
Re1–O4	1.986(6)	1.999(5)
Re1–O2	2.007(5)	2.059(4)
Re1–N2	2.092(5)	–
Re1–N3	–	2.076(5)
Re1–N1	2.120(7)	2.107(5)
Re1–Cl1	2.3482(18)	2.3711(18)
O1–Re1–O4	109.8(2)	109.9(2)
O1–Re1–O2	162.2(2)	159.8(2)
O4–Re1–O2	85.6(2)	89.84(18)
O1–Re1–N2	91.4(2)	–
O4–Re1–N2	79.93(19)	–
O2–Re1–N2	82.5(2)	–
O1–Re1–N3	–	96.2(2)
O4–Re1–N3	–	78.53(19)
O2–Re1–N3	–	83.44(18)
O1–Re1–N1	89.5(2)	86.7(2)
O4–Re1–N1	160.5(2)	163.26(19)
O2–Re1–N1	74.9(2)	73.42(17)
N2–Re1–N1	97.8(2)	–
N3–Re1–N1	–	99.0(2)
O1–Re1–Cl1	98.97(16)	97.42(17)
O4–Re1–Cl1	90.21(15)	87.74(15)
O2–Re1–Cl1	89.42(14)	87.12(13)
N2–Re1–Cl1	167.66(15)	–
N3–Re1–Cl1	–	163.30(14)
N1–Re1–Cl1	89.03(18)	91.46(15)

All compounds give bond lengths for Re=O [1.654(7)–1.996(3) Å; Tables 2, 3, and 4] within the expected range for six-coordinate monooxidorhenium(V) complexes.[8,12–16,22–28] The Re=O distance of **6** [1.696(3) Å] is slightly longer than Re=O bond lengths in **7** [1.671(5) Å] and in **8** [1.683(5) Å]. This elongation of Re=O in **6** is accompanied by a small shortening of the Re–O(methoxy) distance [1.893(3) Å in **6**, 1.937(5) Å in **7**, and 1.927(5) Å in **8**]. It seems to be a consequence of the competition of the methoxide with the oxido group in the interaction with the dπ orbitals of the metal and is a typical feature of complexes that incorporate a linear core $[O{=}Re{-}OR]^{2+}$.[29,30] However, the weakening of the Re=O bond in **6** is better illustrated by a significant bathochromic shift for ν(Re=O) in **6** discussed above. In all reported complexes, the O=Re–O_{trans} angles are significantly below the ideal of 180° for an octahedral complex, and the interatomic distances between the rhenium atom and phenolate or carboxylate oxygen atom in a *trans* position to the terminal oxido ligand are longer than the corresponding Re–O bonds in the equatorial plane, which seems to be a typical feature of *cis*-N,N isomers of [ReOX(N–O)$_2$] of type D.

The nitrogen atoms of **6** are coordinated in a *trans* position to each other with comparable bond lengths of 2.131(3) and 2.138(3) Å. In compounds [ReOCl(N–O)$_2$], the Re–N bond *trans* to the chloride ion is shorter than the Re–N bond *trans* to the oxygen atom of the chelating ligand. It seems to be due to the stronger π donation of the chloride ion. For all reported complexes the Re–N bonds are significantly longer than the Re–O distances.

Catalytic Epoxidation Experiments

All ten oxidorhenium(V) complexes **1**–**10** were tested in the epoxidation of cyclooctene (cyOct). Epoxidation experiments were done with 1 mol-% of the respective complex at 50 °C in $CHCl_3$ using *tert*-butyl hydrogenperoxide (TBHP; 3 equiv.) for a time between 20–27 h (Scheme 6).



Scheme 6. Epoxidation of cyclooctene.

Out of the 10 complexes, **1**, which is equipped with benzimidazole ligands, showed the lowest conversion of only 3%, respectively, with a very long induction period (>3 h). All other complexes **2**–**10** reached yields of cyclooctane oxide (cyOxid) between 58 and 75% (Table 6).

Table 6. Catalytic performance of complexes **2**–**10** in the epoxidation of cyclooctene.

Cat.	*t* [h]	cyOxid [%]	Selectivity of epoxide [%]	Side product [%]
2	5	61	84	5[a]
	21	50		11[b]
3	0.5	16	97	3[a]
	3	36		
	20	62		
	27	74		
4	1	4	96	4[a]
	3	22		
	7.5	59		
	23	75		
5	1	16	95	5[a]
	4	33		
	24	61		
6	1	33	>99	–
	2.75	56		
	19	69		
	25	68		
7	0.5	4	>99	–
	5	26		
	21	62		
8	3	13	>99	–
	22	55		
9	0.5	4	98	2[a]
	5	21		
	21	58		
10	0.5	22	98	2[a]
	5	41		
	21	59		

[a] Side product: cyclooctane-1,2-diole (cyDiole). [b] Side product: *tert*-butoxycyclooctane (cyO*t*Bu).

The catalytic performances of the oxidorhenium(V) complexes that incorporate phenolate ligands were found to be strongly influenced by the heterocycle ring, most likely because of the different electronic properties. The carboxylate oxidorhenium(V) complexes gave comparable conversion of the alkene into the epoxide with a yield only slightly lower than the complexes that incorporate benzoxazole and the benzothiazole ligand (**3** and **4**), for which the best yield was observed. The highest selectivity (>99%) in catalytic epoxidation experiments was found with **7** and **8**, for which no side products could be detected (below the threshold of the GC–MS integration routine). Slightly higher catalytic performance with regard to substrate conversion was shown by **7** with a yield of cyOxide of 62% after 21 h in comparison to **8** with 55%. Furthermore, with catalyst **8**, an induction period was observed. All other complexes (**2**–**6**, **9**, and **10**) revealed variable amounts of side products (2–15%), usually the ring-opened product by water, cyclooctane-1,2-diole (cyDiole). Only with complex **2**, which contained a benzotriazole ligand, could the formation of an additional side product be observed (11% cyO*t*Bu after 21 h). Its mass spectrum is consistent with *tert*-butoxycyclooctane, presumably formed through a ring-opening by *tert*-butyl alcohol. This is in line with the observed 10% decrease of cyOxide with time (60% after 5 h and 50% after 21 h). In general, all observed yields are in a similar range, thereby impeding a detailed structure/activity correlation. Apparently, the electronic and steric environments imposed by the investigated ligands lead to similar rhenium centers. This is apparent when comparing compounds **7** and **9**, which differ only in one anionic ligand (methoxy versus chloro). However, the two complexes **2** and **6** display a superior initial activity (61% after 5 h for **2** and 56% after 2.75 h for **6**). It is worth noting that **2** is the only compound among the phenoxide group with an additional methyl substituent, and **6** is the only one with a *trans* MeO–Re=O orientation. With the rhenium(V) catalyst, no full conversion has been observed thus far, presumably due to both catalase activity and catalyst deactivation.[8–16] Apparently, the better donor properties of hmpbta in **2** and the *trans* orientation in **6** have a beneficial influence on the catalytic yield. Therefore, future complex design will include *trans*-oriented complexes with ligands that have superior donor properties.

Conclusion

A series of oxidorhenium(V) complexes that incorporate phenolate and carboxylate ligands were synthesized, characterized, and utilized as catalyst in the epoxidation of cyclooctene. The metal precursors $[ReO_2(py)_4]Cl$ turned out to be an excellent starting material for the preparation of $[ReOX(N–O)_2]$ complexes with carboxylate ligands. One of the reported $[ReOX(N–O)_2]$ complexes shows a very rare *trans*-N,N and *trans*-O,O ligand arrangement. Except for **1**, the compounds show good catalytic activity and selectivity in the epoxidation of cyclooctene with *tert*-butyl hydroperoxide. The yield of cyclooctane oxide varies between 58 and 75%, which is comparable to previously reported oxidorhenium(V) systems, but lower than rhenium(VII) compounds. Interestingly, the highest initial activity was displayed by an

unusual *trans*-N,N and *trans*-O,O isomer of $[ReOX(N–O)_2]$, thus indicating that different region isomers might have a significant influence on catalyst activity.

Experimental Section

Materials: All chemicals were purchased from commercial sources and were used without further purification. $[ReOCl_3(OPPh_3)(SMe_2)]$ and $[ReO_2(py)_4]Cl$ were prepared according to previously published methods.[31–33]

Instrumentation: IR spectra were recorded with a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm^{-1} with the samples in the form of KBr pellets. The ^1H and ^{13}C NMR spectra were recorded (295 K) with a Bruker Avance 400 NMR spectrometer at a resonance frequency of 400 MHz for ^1H NMR spectra and 100 MHz for ^{13}C NMR spectra by using $[D_6]DMSO$ or $CDCl_3$ as solvent and TMS as an internal solvent. ESI–MS was performed with a Varian 500-MS IT mass spectrometer ion trap apparatus. The instrument was operating in the positive-ion mode with a capillary voltage of 20 V, needle voltage of 5 kV, and a spray shield voltage of 600 V. The drying gas (N_2) temperature was 150 °C. The single-crystal X-ray diffraction measurement was carried out with a Gemini A Ultra diffractometer equipped with an Atlas CCD detector. Intensities of reflections were measured using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with ω scan mode at room temperature. During the data reduction, Lorentz, polarization, and empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm, were applied.[34] The structures were solved by Patterson synthesis using SHELXS-97[35] and refined on F_2 by full-matrix least-square techniques using the SHELXTL-97[36] program. The non-hydrogen atoms of the complexes were refined with anisotropic temperature parameters. The hydrogen atoms bound to carbon atoms were placed in calculated positions and treated as riding on their parent atoms with d(C–H) = 0.93 Å, U_{iso}(H) = 1.2 U_{eq}(C) (aromtic); and d(C–H) = 0.96 Å, U_{iso}(H) = 1.5 U_{eq}(C) (methyl). The methyl groups were allowed to rotate about their local threefold axis.

CCDC-858621 (for **1**), -858622 (for **3**), -858623 (for **4**), -858624 (for **5**), -858625 (for **6**), -858626 (for **7**), -858627 (for **8**), -858628 (for **9**), and -858629 (for **10**) 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 Epoxidation Procedure: Epoxidation experiments were carried out with 1 mol-% of the respective complex at 50 °C in $CHCl_3$ by using TBHP (3 equiv.) for a time between 20 and 27 h. Progress was analyzed by GC–MS using Mesitylene as internal standard. Yields were calculated in relation to cyclooctene (cyOct) conversion. In a typical experiment, the respective catalyst (1–1.5 mg) was dissolved in $CHCl_3$ (2 mL) in a Mininert vial, and the calculated amount of cyOct (which resulted in 1 mol-% catalyst loading) was added with a syringe, capped, and heated to 50 °C. Then TBHP (3 equiv. with respect to cyOct) was added through the septum and stirred. For GC–MS analysis, samples (10 μL) were withdrawn at different times and diluted to 1 mL with ethyl acetate that contained 50 ppb mesitylene as internal standard. All solvents as well as reagents were used as received. GC–MS measurements were performed with an Agilent 7890 A with an Agilent 19091J–433 column coupled to a mass spectrometer type Agilent 5975 C.

General Procedure for the Preparation of Rhenium Complexes 1–5: $[ReOX_3(OPPh_3)(SMe_2)]$ (0.77 mmol) was suspended in methanol (80 mL) and phenol-based ligand (1.54 mmol) was added. The suspension was stirred at ambient temperature for 48 h and filtered, thus yielding a green solid, which was washed with ethanol and diethyl ether and then recrystallized.

$[ReOCl(hpbi)_2]$·THF (1): The compound was prepared according to the general procedure by employing hpbi (0.32 g, 1.54 mmol) and $[ReOCl_3(OPPh_3)(SMe_2)]$ (0.50 g, 0.77 mmol) to give **1** (0.34 g, 61%). Recrystallization from methanol/tetrahydrofuran. ^1H NMR (400 MHz, $[D_6]DMSO$): δ = 13.80 (s, 1 H), 13.64 (s, 1 H), 8.08–8.00 (m, 2 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.62–7.55 (m, 2 H), 7.49 (t, J = 7.6 Hz, 1 H), 7.42 (dd, J = 7.9, 1.4 Hz, 1 H), 7.35 (d, J = 8.0 Hz, 1 H), 7.24 (d, J = 7.4 Hz, 1 H), 7.07 (t, J = 7.5 Hz, 1 H), 7.04–6.96 (m, 2 H), 6.81 (t, J = 7.5 Hz, 1 H), 6.69 (t, J = 7.1 Hz, 1 H), 6.14 (d, J = 8.3 Hz, 1 H), 6.04 (d, J = 7.5 Hz, 1 H), 3.64–3.58 (m 4 H), 1.79–1.73 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $[D_6]$-DMSO): δ = 167.5, 161.2, 154.3, 141.6, 140.4, 133.8, 133.7, 131.4, 131.3, 130.9, 130.4, 129.0, 128.9, 128.4, 127.7, 125.6, 124.7, 123.8, 123.2, 120.4, 119.6, 119.4, 119.0, 114.9, 112.9, 112.7, 49.08, 21.8 ppm. $C_{30}H_{26}Cl_1N_4O_4Re$ (728.20): calcd. C 49.44, H 3.57, N 7.69; found C 48.32, H 3.03, N 8.24. IR (KBr): $\tilde{\nu}$ = 3190 [ν(N–H)]; 1622, 1603, 1578 and 1538 ν(C=N) and ν(C=C); 960 ν(Re=O) cm^{-1}. ESI^+-MS (MeOH): m/z = 437.62 [{ReO(hpbi)} + Na + 2H]$^+$, 621.57 [{ReO(hpbi)$_2$}]$^+$, 643.63 [{ReO(hpbi)$_2$} + Na]$^+$, 655.65 [{ReOCl(hpbi)$_2$}]$^+$, 675.61 [{ReO(hpbi)$_2$} + Na + MeOH]$^+$, 728.10 [{ReOCl(hpbi)$_2$} + THF]$^+$.

$[ReOCl(hmpbta)_2]$ (2): The compound was prepared according to the general procedure by employing hmpbta (0.35 g, 1.54 mmol) and $[ReOCl_3(OPPh_3)(SMe_2)]$ (0.50 g, 0.77 mmol) to give **2** (0.34 g, 66%). Recrystallization from methanol/acetonitrile. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 8.8 Hz, 1 H), 8.35 (d, J = 1.2 Hz, 1 H), 8.02 (d, J = 8.7 Hz, 1 H), 7.84–7.80 (m, 1 H), 7.76 (d, J = 8.6 Hz, 1 H), 7.60–7.55 (m, 3 H), 7.42–7.37 (m, 1 H), 7.35–7.31 (m, 1 H), 7.14–7.10 (m, 1 H), 6.75 (dd, J = 8.4, 1.6 Hz, 1 H) 6.34 (d, J = 8.8 Hz, 1 H), 6.22 (d, J = 8.4 Hz, 1 H), 2.58 (s, 3 H), 2.05 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 151.4, 146.0, 145.4, 143.3, 142.6, 132.8, 132.8, 132.6, 131.8, 130.7, 130.6, 128.1, 127.8, 127.2, 125.7, 125.2, 121.6, 121.4, 120.1, 119.3, 119.0, 118.6, 114.3, 20.6, 20.5 ppm. $C_{26}H_{20}Cl_1N_6O_3Re$ (686.13): calcd. C 45.47, H 2.91, N 12.24; found C 44.97, H 2.73, N 12.87. IR (KBr): $\tilde{\nu}$ = 1612, 1572 and 1504 ν(C=N) and ν(C=C); 957 ν(Re=O) cm^{-1}. ESI^+-MS (MeOH): m/z = 651.66 [{ReO(hmpbta)$_2$}]$^+$, 675.76 [{ReO(hmpbta)$_2$} + Na + H]$^+$, 709.54 [{ReOCl(hmpbta)$_2$} + Na]$^+$, 1394.16 [{ReOCl(hmpbta)$_2$}$_2$ + Na]$^+$.

$[ReOCl(hpbo)_2]$ (3): The compound was prepared according to the general procedure by employing hpbo (0.33 g, 1.54 mmol) and $[ReOCl_3(OPPh_3)(SMe_2)]$ (0.50 g, 0.77 mmol) to give **3** (0.33 g, 65%). Recrystallization from methanol/acetonitrile. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.32–8.28 (m, 1 H), 8.16 (dd, J = 8.0, 1.6 Hz, 1 H), 7.81 (dd, J = 7.3, 1.5 Hz, 1 H), 7.73–7.66 (m, 3 H), 7.64–7.60 (m, 2 H), 7.44 (d, J = 8.2 Hz, 1 H), 7.25–7.20 (m, 1 H), 7.09–7.00 (m, 3 H), 6.83–6.79 (m, 1 H), 6.55 (d, J = 7.9 Hz, 1 H), 6.49 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 166.8, 164.7, 164.5, 149.2, 149.1, 143.0, 140.2, 137.2, 136.2, 128.9, 128.0, 127.4, 126.9, 126.6, 126.1, 124.6, 121.2, 121.1, 119.1, 118.9, 115.7, 111.5, 111.3, 110.7, 108.9 ppm. $C_{26}H_{16}Cl_1N_2O_5Re$ (658.06): calcd. C 47.41, H 2.43, N 4.25; found C 49.70, H 2.93, N 3.61. IR (KBr): $\tilde{\nu}$ = 1607, 1567 and 1535 ν(C=N) and ν(C=C); 958 ν(Re=O) cm^{-1}. ESI^+-MS (MeOH): m/z = 623.47 [{ReO(hpbo)$_2$}]$^+$, 647.52 [{ReO(hpbo)$_2$} + Na]$^+$, 677.56 [{ReOCl(hpbo)$_2$} + NH_4]$^+$, 681.45 [{ReOCl(hpbo)$_2$} + Na]$^+$, 1333.69 [{ReOCl(hpbo)$_2$}$_2$ + NH_4]$^+$.

[ReOCl(hpbt)$_2$]·2MeCN (4): The compound was prepared according to the general procedure by employing hpbt (0.35 g, 1.54 mmol) and [ReOCl$_3$(OPPh$_3$)(SMe$_2$)] (0.50 g, 0.77 mmol) to give **4** (0.41 g, 68%). Recrystallization from methanol/acetonitrile. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.79 (d, J = 8.1 Hz, 1 H), 7.99 (d, J = 7.8 Hz, 1 H), 7.80–7.68 (m, 3 H), 7.66–7.60 (m, 1 H), 7.57–7.54 (m, 2 H), 7.23–7.16 (m, 2 H), 7.08–7.01 (m, 2 H), 7.00–6.94 (m, 1 H), 6.92–6.87 (m, 1 H), 6.65 (t, J = 7.6 Hz, 1 H), 6.44 (d, J = 8.2 Hz, 1 H), 2.52 (s, 3 H), 2.50 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 171.9, 168.0, 161.5, 155.0, 153.1, 136.0, 135.5, 130.8, 130.1, 129.5, 129.1, 129.0, 127.5, 127.1, 126.8, 126.6, 126.3, 124.9, 121.9, 121.5, 121.4, 120.8, 119.5, 119.3, 118.2, 117.6, 116.4, 114.8, 30.9, 2.1 ppm. $C_{30}H_{22}ClN_4O_3ReS_2$ (772.29): calcd. C 46.61, H 2.85, N 7.25; found C 42.51, H 2.03, N 3.66. IR (KBr): $\tilde{\nu}$ = 1599 and 1557 ν(C=N) and ν(C=C); 960 ν(Re=O) cm^{-1}. ESI$^+$-MS (MeOH): m/z = 655.45 [{ReO(hpbt)$_2$}]$^+$, 679.50 [{ReO(hpbt)$_2$} + Na + H]$^+$, 709.54 [{ReOCl(hpbt)$_2$} + NH$_4$ + H]$^+$, 713.43 [{ReOCl(hpbt)$_2$} + Na]$^+$, 1397.61 [{ReOCl(hpbt)$_2$}$_2$ + NH$_4$]$^+$.

[ReOBr(hmpbta)$_2$] (5): The compound was prepared according to the general procedure by employing hmpbta (0.29 g, 1.28 mmol) and [ReOBr$_3$(OPPh$_3$)(SMe$_2$)] (0.60 g, 0.64 mmol) to give **5** (0.32 g, 57%). Recrystallization from methanol/acetonitrile. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.53 (d, J = 8.8 Hz, 1 H), 8.33 (s, 1 H), 8.00 (d, J = 8.7 Hz, 1 H), 7.85–7.79 (m, 1 H), 7.76 (d, J = 8.6 Hz, 1 H), 7.62–7.52 (m, 3 H), 7.41–7.35 (m, 1 H), 7.35–7.29 (m, 1 H), 7.14–7.07 (m, 1 H), 6.75 (d, J = 8.3 Hz, 1 H), 6.29 (d, J = 8.8 Hz, 1 H), 6.23 (d, J = 8.4 Hz, 1 H), 2.58 (s, 3 H), 2.04 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.9, 151.1, 145.8, 145.6, 143.3, 142.5, 132.8, 132.7, 132.6, 131.8, 130.7, 130.6, 128.1, 127.8, 127.3, 125.6, 125.2, 121.5, 121.5, 120.1, 119.3, 119.1, 119.0, 114.1, 20.6, 20.5 ppm. $C_{26}H_{20}Br_1N_6O_3Re$ (730.59): calcd. C 42.70, H 2.74, N 11.50; found C 42.87, H 2.50, N 11.49. IR (KBr): $\tilde{\nu}$ = 1612, 1571 and 1504 ν(C=N) and ν(C=C); 956 ν(Re=O) cm^{-1}. ESI$^+$-MS (MeOH): m/z = 528.36 [{ReO(hmpbta)} + Na]$^+$, 621.32 [{ReO(hmpbta)$_2$} – 2CH$_3$]$^+$, 675.46 [{ReO(hmpbta)$_2$} + Na]$^+$, 752.21 [{ReOBr(hmpbta)$_2$} + Na]$^+$.

General Procedure for the Preparation of Rhenium Complexes 6–8: A mixture of [ReO$_2$(py)$_4$]Cl (0.90 mmol) and the corresponding carboxylic acid (1.80 mmol) in methanol (80 mL) was heated at reflux for 30 min and allowed to cool to ambient temperature. The resulting dark red suspension was filtered and the reddish-brown microcrystalline precipitate was washed with methanol and diethyl ether.

[ReO(OMe)(quin)$_2$] (6): The compound was prepared according to the general procedure by employing quin (0.31 g, 1.80 mmol) and [ReO$_2$(py)$_4$]Cl (0.50 g, 0.90 mmol) to give **6** (0.38 g, 75%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.76 (d, J = 8.9 Hz, 2 H), 8.83 (d, J = 8.3 Hz, 2 H), 8.73 (d, J = 8.3 Hz, 2 H), 8.27 (ddd, J = 8.6, 6.9, 1.5 Hz, 2 H), 8.12 (d, J = 7.0 Hz, 2 H), 7.99–7.90 (m, 2 H), 3.08 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 182.3, 150.2, 150.0, 144.4, 134.9, 130.7, 130.2, 128.9, 128.4, 121.9, 57.6 ppm. $C_{21}H_{15}N_2O_6Re$ (577.55): calcd. C 43.62, H 2.60, N 4.85; found C 43.37, H 2.26, N 4.71. IR (KBr): $\tilde{\nu}$ = 1683 ν(COO)$_{asym}$; 1617, 1595, 1569 and 1515 ν(C=N) and ν(C=C); 1323 ν(COO)$_{sym}$; 955 ν(Re=O); 512 and 500 ν(Re–OMe) cm^{-1}. ESI$^+$-MS (MeOH): m/z = 428.45 [{ReO(OMe)(quin)} + Na]$^+$, 547.33 [{ReO(quin)$_2$}]$^+$, 571.34 [{ReO(quin)$_2$} + Na + H]$^+$, 601.31 [{ReO(OMe)(quin)$_2$} + Na]$^+$, 1176.69 [{ReO(OMe)(quin)$_2$}$_2$ + Na]$^+$.

[ReO(OMe)(pic)$_2$] (7): The compound was prepared according to the general procedure by employing pic (0.22 g, 1.80 mmol) and [ReO$_2$(py)$_4$]Cl (0.50 g, 0.90 mmol) to give **7** (0.29 g, 68%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.74 (d, J = 5.6 Hz, 1 H), 8.67 (d, J = 5.3 Hz, 1 H), 8.54–8.48 (m, 2 H), 8.24–8.22 (m, 1 H), 8.23 (dd, J = 7.7, 0.7 Hz, 1 H), 8.09–8.05 (m, 1 H), 8.00–7.92 (m, 2 H), 4.55 (s, 3 H) ppm. $C_{13}H_{11}N_2O_6Re$ (477.44): calcd. C 32.67, H 2.30, N 5.86; found C 32.65, H 2.10, N 5.86. IR (KBr): $\tilde{\nu}$ = 1712 and 1676 ν(COO)$_{asym}$; 1609 ν(C=N) and ν(C=C); 1317 and 1287 ν(COO)$_{sym}$; 984 ν(Re=O); 573 ν(Re–OMe) cm^{-1}. ESI$^+$-MS (MeOH): m/z = 447.43 [{ReO(pic)$_2$}]$^+$, 501.36 [{ReO(OMe)(pic)$_2$} + Na]$^+$, 977.49 [{ReO(OMe)(pic)$_2$}$_2$ + Na]$^+$.

[ReO(OMe)(2,5-dipic)$_2$]·C$_5$H$_5$N (8): The compound was prepared according to the general procedure by employing 2,5-dipic (0.30 g, 1.80 mmol) and [ReO$_2$(py)$_4$]Cl (0.50 g, 0.90 mmol) to give **8** (0.42 g, 73%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.15 (dd, J = 2.1, 0.7 Hz, 1 H), 8.74 (d, J = 4.9 Hz, 1 H), 8.43 (dd, J = 8.1, 2.1 Hz, 2 H), 8.15 (dd, J = 8.1, 0.7 Hz, 2 H), 7.74–7.66 (m, 1 H), 2.09 (s, 3 H) ppm. $C_{20}H_{16}N_3O_{10}Re$ (644.56): calcd. C 37.23, H 2.48, N 6.52; found C 36.30, H 2.17, N 6.37. IR (KBr): $\tilde{\nu}$ = 1716 and 1685 ν(COO)$_{asym}$; 1565 ν(C=N) and ν(C=C); 1299 and 1289 ν(COO)$_{sym}$; 980 ν(Re=O); 570 ν(Re–OMe) cm^{-1}. ESI$^+$-MS (MeOH + AcOH): m/z = 415.25 [{ReO(OMe)} + Na + 2C$_5$H$_5$N]$^+$, 437.37 [{ReO(OMe)(py)$_2$} + K]$^+$, 573.23 [{ReO(py)$_2$} + K]$^+$.

General Procedure for the Preparation of Rhenium Complexes 9 and 10: [ReOCl$_3$(OPPh$_3$)(SMe$_2$)] (0.77 mmol) was suspended in methanol or acetonitrile (80 mL) and the corresponding carboxylic acid (1.54 mmol) was added. The suspension was stirred at ambient temperature for 48 h and filtered, thereby yielding a blue solid, which was washed with ethanol and diethyl ether and then recrystallized.

[ReOCl(pic)$_2$] (9): The compound was prepared according to the general procedure by employing pic (0.19 g, 1.54 mmol) and [ReOCl$_3$(OPPh$_3$)(SMe$_2$)] (0.50 g, 0.77 mmol) to give **9** (0.28 g, 77%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.02 (d, J = 5.5 Hz, 1 H), 8.69 (d, J = 5.4 Hz, 1 H), 8.64 (d, J = 3.6 Hz, 2 H), 8.30 (d, J = 7.6 Hz, 1 H), 8.19 (t, J = 6.0 Hz, 1 H), 8.12–8.02 (m, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 180.7, 164.3, 158.2, 151.7, 148.6, 147.2, 146.2, 143.4, 132.4, 129.6, 127.4, 126.1 ppm. $C_{12}H_8ClN_2O_5Re$ (481.85): calcd. C 29.88, H 1.66, N 5.81; found C 29.98, H 1.44, N 5.92. IR (KBr): $\tilde{\nu}$ = 1712 and 1669 ν(COO)$_{asym}$; 1609 and 1570 ν(C=N) and ν(C=C); 1317 and 1287 ν(COO)$_{sym}$; 984 ν(Re=O) cm^{-1}. ESI$^+$-MS (MeOH): m/z = 447.48 [{ReO(pic)$_2$}]$^+$, 501.41 [{ReO(OMe)(pic)$_2$} + Na]$^+$, 977.35 [{ReO(OMe)(pic)$_2$}$_2$ + Na]$^+$.

[ReOCl(3-ind)$_2$]·CH$_3$OH (10): The compound was prepared according to the general procedure by employing pic (0.25 g, 1.54 mmol) and [ReOCl$_3$(OPPh$_3$)(SMe$_2$)] (0.50 g, 0.77 mmol) to give **10** (0.34 g, 74%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.10 (d, J = 8.0 Hz, 1 H), 7.90 (d, J = 7.5 Hz, 1 H), 7.85 (d, J = 7.0 Hz, 1 H), 7.73 (d, J = 8.4 Hz, 1 H), 7.50–7.35 (m, 4 H), 3.62 (s, 1 H), 2.08 (s, 3 H) ppm. $C_{17}H_{14}Cl_1N_4O_6Re$ (591.97): calcd. C 34.46, H 2.36, N 9.46; found C 35.89, H 2.01, N 11.46. IR (KBr): $\tilde{\nu}$ = 3109 ν(N–H); 1725 and 1685 ν(COO)$_{asym}$; 1630 and 1583 ν(C=N) and ν(C=C); 1388 and 1366 ν(COO)$_{sym}$; 990 ν(Re=O) cm^{-1}. ESI$^+$-MS (MeOH + AcOH): m/z = 415.35 [{ReOCl(ind)} + NH$_4$]$^+$, 421.43 [{ReOCl(ind)} + Na]$^+$, 527.41 [{ReO(ind)$_2$}]$^+$.

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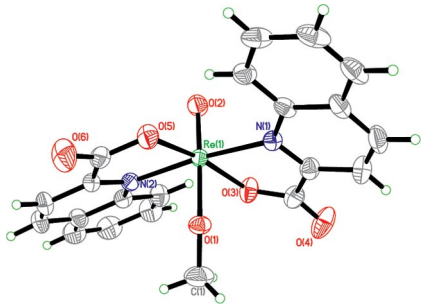
Epoxidation Catalysis

Several oxidorhenium(V) complexes that contain phenolate- and carboxylate-based ligands were synthesized and characterized by spectroscopic means and by X-ray crystal structure analysis. The complexes are air- and moisture-stable and show catalytic activity for the epoxidation of cyclooctene.



Keywords: Rhenium / Phenolate ligands / Carboxylate ligands / Epoxidation

