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Oxidorhenium(V) Complexes with Oxazolinylmethoxido Ligands – Structure and Catalytic Epoxidation

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Reaction of $[ReOCl_3(PPh_3)_2]$ with (4,5-dihydrooxazol-2-yl)methanol and three methyl-substituted derivatives thereof (**2a**–**2d**) in boiling acetone or tetrahydrofuran gave oxidorhenium(V) complexes of the type $[ReOCl_2(PPh_3)$(**2a**–**2d**)] (**3a**–**3d**) as blue crystalline materials in good yields. The complexes were characterized by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy, mass spectrometry, elemental analysis and single-crystal X-ray diffraction analysis. All the complexes showed distorted octahedral geometries and were found to contain only one oxazolyl ligand displacing one PPh_3 molecule and one chloride ion from the precursor complex $[ReOCl_3(PPh_3)_2]$. The complexes were tested as catalysts for the epoxidation of cyclooctene with 3 equiv. of *tert*-butyl hydroperoxide (TBHP). Complex **3a** containing (4,5-dihydrooxazol-2-yl)methanol showed the highest yield of epoxide (79 %), whereas the complex with the tetramethyl-substituted ligand **3d** exhibited the lowest catalytic activity.

Introduction

Oxazoline derivatives are known in a wide variety as ligands in transition metal complexes.[1] Upon coordination they are highly robust under many reaction conditions. Furthermore, they are synthetically accessible by convenient organic reactions. Many examples are known including bi-, tri- and polydentate ligands and chiral versions.[1,2] An extensively investigated ligand is 2-(2′-hydroxyphenyl)-2-oxazoline, in particular coordinated to rhenium centres in high oxidation states.[3–7] Abu-Omar et al. demonstrated that oxidorhenium(V) complexes containing 2-(2′-hydroxyphenyl)-2-oxazoline exhibit interesting catalytic behaviour for oxygen atom transfer reactions.[4,8,9] Most interestingly, they were found to successfully catalyze the reduction of perchlorate (ClO_4^-) to chloride ions,[4,8] a reaction that is environmentally interesting (waste water cleaning) but kinetically hindered.[10]

The success of oxazoline ligands as stabilizing agents in catalysis as well as our ongoing interest in rhenium-catalyzed epoxidations[11–15] prompted us to investigate a largely unexplored oxazoline ligand in oxidorhenium(V) chemistry. We were surprised to find that 2-(hydroxymethyl)-2-oxazoline and derivatives thereof have, in general, limited used in coordination chemistry. Thus, with (4,5-dihydrooxazol-2-yl)methanol only a few Cr^{III},[16] Ni^{II},[17,18] Zr^{IV}[19] and Hf^{IV}[20] complexes have been reported. No rhenium complexes with 2-(2′-hydroxymethyl)-2-oxazoline-type ligands have as yet been described in the literature.

Rhenium(VII) compounds are known to be highly active epoxidation catalysts,[21–23] methyltrioxidorhenium being the most prominent among them.[24] However, a pronounced sensitivity towards hydrolysis sometimes decreases turnover numbers.[25] Rhenium(V) complexes are usually less prone towards hydrolysis, which explains the recent investigations of oxidorhenium(V) complexes as catalysts in epoxidation reactions of olefins.[12–14,26–30] However, all the systems reported do not yet reach the activity of rhenium(VII) compounds as they usually suffer from oxidative degradation. For this reason it is a worthwhile goal to further investigate oxidorhenium(V) complexes with ligands exhibiting higher stability towards oxidation, such as (4,5-dihydrooxazol-2-yl)methanol.

Therefore, we report the synthesis and structural characterization of oxidorhenium(V) complexes with several (4,5-dihydrooxazol-2-yl)methanol-type ligands and their catalytic applications in the epoxidation of cyclooctene.

Results and Discussion

Synthesis of Ligands

The 2-oxazoline ligands were obtained according to literature procedures[17,31,32] in a two-step method. Amides were formed in the first step from the respective organic acid and β-amino alcohols by heating neat melts or by re-

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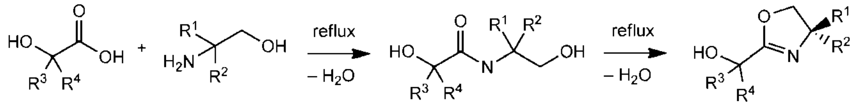


1a: R^1–R^4 = H
1b: $R^1 = R^2$ = Me, $R^3 = R^4$ = H
1c: $R^1 = R^2 = R^3$ = Me, R^4 = H
1d: R^1–R^4 = Me

2a: R^1–R^4 = H
2b: $R^1 = R^2$ = Me, $R^3 = R^4$ = H
2c: $R^1 = R^2 = R^3$ = Me, R^4 = H
2d: R^1–R^4 = Me

Scheme 1. Synthesis of the 2-oxazoline ligands **2a**–**2d**.

fluxing in a suitable high-boiling solvent. Subsequent sublimation of the resulting amides under high vacuum yielded the respective oxazoline (Scheme 1).

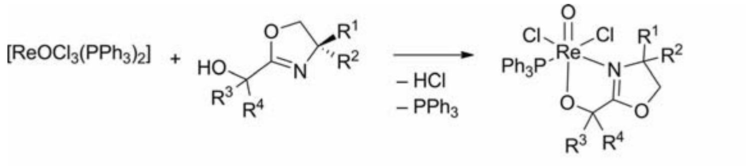
Synthesis of Oxidorhenium(V) Complexes

The desired complexes of the type [$ReOCl_2(PPh_3)$(**2**)] (**3a**–**3d**) were prepared by metathesis reactions between 1 equiv. of [$ReOCl_3(PPh_3)_2$] and the respective ligand **2a**–**2d** (Scheme 2). Interestingly, even when 2 equiv. of the ligands were used, only the monosubstituted complexes were obtained. Use of NEt_3 as a base to accept the proton removed from the oxazoline resulted in decomposition of the starting material. Stronger bases such as NaH also resulted in decomposition. As a result, all attempts to obtain disubstituted rhenium complexes of the type [ReOCl(**2**)$_2$] were not successful. In all cases, stable [$ReOCl_2(PPh_3)$(**2**)] complexes were obtained in agreement with similar work reported in the literature.[33]

Complexes **3a**–**3d** are air-stable, blue solids. They are moderately soluble in strongly polar solvents such as thf, acetonitrile, acetone, chloroform, methanol and ethanol, and are completely insoluble in medium polar (toluene, diethyl ether) and apolar solvents (benzene, hexane). Analytically pure samples were obtained at the end of the synthesis upon cooling of the boiling thf solution, from which **3a**–**3d** precipitated as blue powders. Further concentration and cooling of the solution increased the yield.

The oxidorhenium complexes **3a**–**3d** were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. However, **3a** was not soluble enough for the recording of a meaningful ^{13}C NMR spectrum. All spectra show respective resonances in the aromatic region for phenyl protons and carbon atoms, consistent with the coordination of one molecule of PPh_3 in the complexes. Particularly characteristic for coordinated ligands **2b**–**2d** are the two methyl groups at the ring carbon atom adjacent to the nitrogen atom. The six protons appear as one singlet resonance in the ^1H NMR spectra of the free ligands, whereas two resonances are observed upon coordination due to the different chemical environments. The same is true for the resonance of the two ring protons, the signal of which splits into two characteristic doublets upon coordination. NMR spectra of **3c** reveal the existence of two isomers in solution in contrast to **3a**, **3b** and **3d**, which were found to be isomerically pure. Ligand **2c** contains a chiral centre at the alcoholic carbon atom. Thus, upon coordination of the racemic mixture, two diastereomers are formed as **3c** contains an additional chiral centre at the rhenium atom. The isolated material showed the two isomers in a ratio of 2:1 evidenced by the ^1H NMR spectrum, which displays two sets of resonances in this ratio as indicated in the Experimental Section. The ^{13}C NMR spectrum showed one set of resonances for a coordinated ligand and, unfortunately, the second set was barely visible due to background noise. Extended measurement times did not improve the quality of the spectrum. However, consistent with two isomers, the ^{31}P NMR spectrum of **3c** in $CDCl_3$ revealed two resonances for a coordinated PPh_3 molecule at $\delta = -16.20$ and -17.30 ppm, which is diagnostic of triphenylphosphane in the coordination sphere of Re^V.[15,34–37]

The IR spectra of **3a**–**3d** exhibit characteristic ν(Re=O) bands at 965.00 (**3a**), 974.62 (**3b**), 973.43 (**3c**) and 965.72 cm^{-1} (**3d**), which are in good agreement with those of similar oxidorhenium compounds.[8,15,34,36] The bands at 1670.05 (**3a**), 1644.63 (**3b**), 1644.59 (**3c**) and 1648.17 cm^{-1} (**3d**) are assigned to the ν(C=N) mode of the oxazoline ring, which represents a shift of 4–25 cm^{-1} to a lower frequency compared to the free ligands, indicating that the imine nitrogen atom of the oxazoline ring is strongly coordinated to the metal centre.[8,38]



3a: R^1–R^4 = H
3b: $R^1 = R^2$ = Me, $R^3 = R^4$ = H
3c: $R^1 = R^2 = R^3$ = Me, R^4 = H
3d: R^1–R^4 = Me

Scheme 2. Synthesis of **3a**–**3d**.

Molecular Structures of the Complexes

The structures of **3a**, **3b** and **3d** were determined by single-crystal X-ray diffraction analysis. The high residual density for **3b** is located in close proximity to the Re atom. For **3c** the crystal quality from several crystallization experiments was not high enough, so only a low-quality data set was obtained that could not be refined satisfactorily. Nevertheless, it proves the connectivity of **3c** (see Supporting Information). The perspective molecular views of the complexes are shown in Figures 1, 2 and 3; crystallographic data are presented in Table 1, and selected bond lengths and angles are given in Table 2.

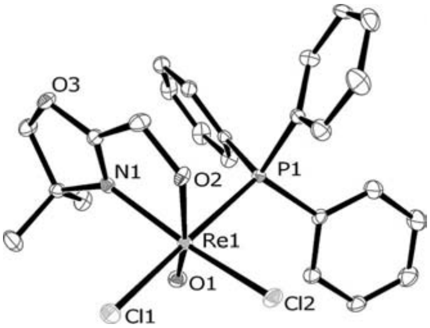


Figure 2. Molecular view of **3b** with selected atom numbering. Hydrogen atoms and a molecule of lattice MeCN are omitted for clarity.

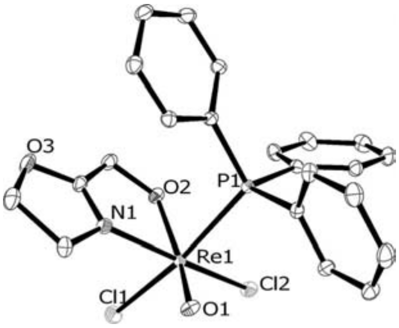


Figure 1. Molecular view of **3a** with selected atom numbering. Hydrogen atoms are omitted for clarity.

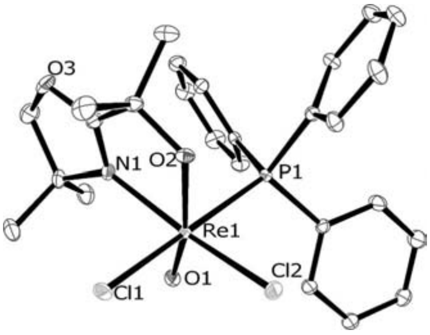


Figure 3. Molecular view of **3d** with selected atom numbering. Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic data for **3a**, **3b** and **3d**.

	[ReOCl$_2$PPh$_3$(**2a**)] (**3a**)	[ReOCl$_2$PPh$_3$(**2b**)] (**3b**)	[ReOCl$_2$PPh$_3$(**2d**)] (**3d**)
Empirical formula	$C_{22}H_{21}Cl_2NO_3PRe$	$C_{24}H_{25}Cl_2NO_3PRe\cdot CH_3CN$	$C_{26}H_{29}Cl_2NO_3PRe$
Formula mass	635.47	704.57	691.57
Color/habit	blue/column	blue/tablet	blue/tablet
Crystal size [mm]	0.17 × 0.80 × 0.13	0.71 × 0.60 × 0.13	0.51 × 0.22 × 0.05
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	7.4525(3)	9.3914(7)	14.5598(8)
b [Å]	7.9206(3)	11.7438(9)	9.4533(5)
c [Å]	18.6652(8)	10.6840(10)	19.5256(10)
α [°]	96.4690(10)	95.886(2)	90
β [°]	91.715(2)	96.464(2)	95.729(2)
γ [°]	93.9960(10)	98.804(2)	90
V [Å^3]	1091.30(8)	1363.43(18)	2674.0(2)
Z	2	2	4
T [K]	100(2)	100(2)	100(2)
$D_{calcd.}$ [d cm^{-3}]	1.934	1.716	1.718
μ [mm^{-1}]	5.910	4.741	4.832
F(000)	616	692	1360
θ range [°]	2.45–30.06	2.55–31.40	2.39–36.92
Limiting indices	$-10 \le h \le 10$	$-13 \le h \le 13$	$-23 \le h \le 23$
	$-11 \le k \le 11$	$-17 \le k \le 17$	$-15 \le k \le 15$
	$-26 \le l \le 26$	$-18 \le l \le 18$	$-32 \le l \le 32$
No. refections collected	46059	30071	53707
No. independent reflections, R_{int}	6345, 0.0329	8726, 0.0481	11568, 0.0573
No. observed reflections [$F > 4\sigma(F)$]	6182	8219	9990
No. data/restraints/parameters	6345/0/271	8726/0/314	11568/0/312
R_F/wR_{F2} [$F \geq 4\sigma(F)$]	0.0159/0.0405	0.0413/0.1219	0.0393/0.0969
R_F/wR_{F2} (all data)[a]	0.0167/0.0408	0.0434/0.1229	0.0448/0.1061
GOF (on F^2)[a]	1.182	1.099	1.044
Largest difference peak/hole [e Å^{-3}]	1.084/–1.310	4.931/–4.514	3.576/– 4.396

[a] $R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. GOF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for **3a**, **3b** and **3d**.

	3a	**3b**	**3d**
Re1–O1	1.6878(16)	1.690(3)	1.694(2)
Re1–O2	1.9751(15)	1.963(3)	1.953(2)
Re1–N1	2.1216(18)	2.141(3)	2.147(2)
Re1–Cl2	2.3438(5)	2.3486(10)	2.3497(7)
Re1–Cl1	2.4230(5)	2.4202(10)	2.4255(7)
Re1–P1	2.4449(5)	2.4599(10)	2.4703(7)
O1–Re1–O2	161.37(7)	163.34(14)	163.5(1)
O1–Re1–N1	88.35(7)	90.20(14)	88.9(1)
O2–Re1–N1	74.67(7)	74.90(13)	75.25(9)
O1–Re1–Cl2	101.25(6)	103.95(11)	102.96(8)
O2–Re1–Cl2	96.29(5)	91.28(9)	93.11(6)
N1–Re1–Cl2	169.59(5)	165.72(10)	167.87(6)
O1–Re1–Cl1	98.96(6)	97.21(11)	96.30(8)
O2–Re1–Cl1	87.36(5)	89.97(9)	87.87(7)
N1–Re1–Cl1	85.04(5)	88.60(9)	88.14(7)
Cl2–Re1–Cl1	89.47(2)	87.78(4)	87.99(3)
O1–Re1–P1	93.76(6)	87.80(11)	88.99(8)
O2–Re1–P1	80.33(5)	85.87(9)	87.74(7)
N1–Re1–P1	94.79(5)	93.95(9)	94.50(7)
Cl2–Re1–P1	88.62(2)1	88.54(4)	88.36(2)
Cl1–Re1–P1	167.27(2)	174.38(3)	174.14(2)

Isostructural **3a** and **3b** are triclinic and crystallize in the space group $P\bar{1}$, whereas **3c** and **3d** are monoclinic and crystallize in $P2_1/c$ and $P2_1/n$, respectively.

The X-ray structures show that in each complex, the rhenium centre is coordinated in an octahedral coordination sphere to one oxido ligand, two chlorido ligands, a phosphorus atom from PPh_3 and a nitrogen and an oxygen atom from the oxazoline ligand. The oxido (Re^V=O) ligand along the axial direction lies *trans* to the oxazolinylmethoxido oxygen atom (O2). This is due to a strong *trans* effect of the oxido group, forcing the harder oxygen atom of the N,O ligand into a *trans* position.[12,13] The high electron density along the Re–O axis strongly influences the positions of the adjacent halogen atoms, which are pushed away.[39] The nitrogen atom in the heterocyclic oxazoline ring is *trans* to one of the *cis*-chloride ions, and the second chloride ion is *trans* to the phosphorus atom. The two *cis*-chloride ions, the nitrogen atom of the oxazoline ring and the phosphorus atom occupy the equatorial plane.

The complexes show Re=O bond lengths between 1.688(6) and 1.694(2) Å, which are in the expected range for monooxidorhenium(V) complexes;[3,14,34,40,41] Re1–O2 distances are 1.953(2)–1.9751(15) Å, which are longer than that of Re^V=O as expected. The Re1–N1 distances are 2.1216(18)–2.147(2) Å, which are within the normal range of Re–N single bonds for oxidorhenium(V) complexes (2.11–2.18 Å). The Re1–Cl1 bond *trans* to the PPh_3 phosphorus atom at 2.4202(10)–2.4255(7) Å is slightly longer than the Re1–Cl2 bond [2.3438(5)–2.3497(7) Å], *trans* to the oxazoline ring nitrogen atom. This seems to be due to the *trans* influence of the phosphorus atom.

The O1–Re1–O2 angles [161.37(7)–163.5(1)°] deviate from 180° for an ideal octahedral structure. The Re^V=O linkage significantly expands the angles to the equatorial chloride ions; the O1–Re1–Cl1 [96.30(8)–98.96(6)°] and O1–Re1–Cl2 [101.25(6)–103.95(11)°] angles deviate significantly from 90°.

Epoxidation of Cyclooctene

Compounds **3a**–**3d** were examined as catalysts for the epoxidation of cyclooctene with TBHP as an oxidant. Typically 1 mol-% of catalyst and 3 equiv. of TBHP were used. Details of the catalytic reaction are given in the Experimental Section. Blank reactions showed that no significant amounts of epoxide are formed in the absence of the catalyst.

All four catalysts **3a**–**3d** showed activity in the epoxidation of cyclooctene with TBHP with similar reactivity patterns (Figures 4 and 5). Furthermore, all four catalysts reached their maximum conversion of cyclooctene after 5 h. The best yield obtained was 79.3% for **3a**, and the lowest was 46.8% for **3d** (Figure 5). However, complete conversion to cyclooctene epoxide was not observed with any of the catalysts. In the case of **3a** at prolonged reaction times, complete consumption of the substrate cyclooctene was observed with concomitant consumption of the product, cyclooctene epoxide, to yet unidentified products. This could be due to further oxidation or hydrolysis of the epoxide. In

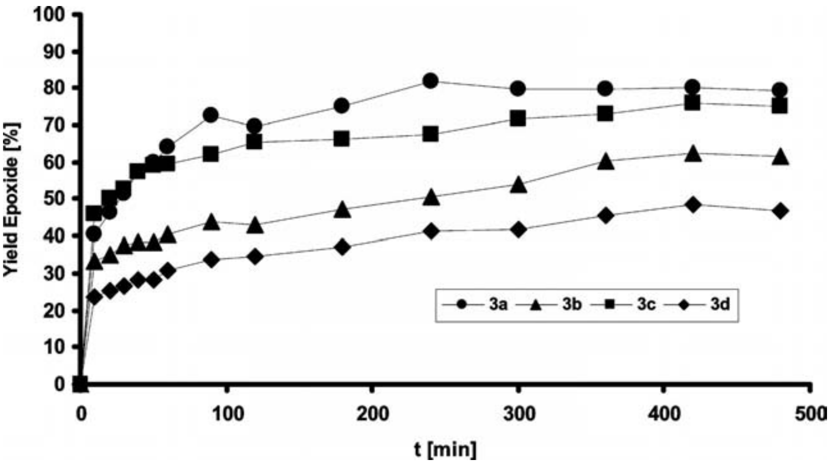


Figure 4. Reaction progress in the epoxidation of cyclooctene by using catalysts **3a**–**3d**.

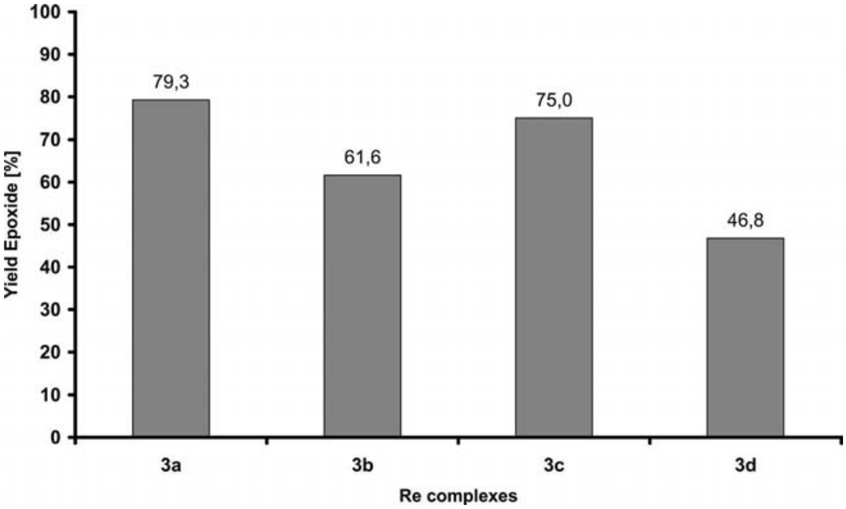


Figure 5. Comparative catalytic conversion of cyclooctene to cyclooctene oxide by catalysts **3a**–**3d**.

the case of **3d** there were no side products observed during the reaction, but reaction progress stalled after 5 h, and neither a significant consumption of substrate nor product was observed. We attribute this to a possible decomposition or inhibition of the catalyst. Further investigations to clarify these issues are needed. We were also interested in how the introduction of electron-donating substituents such as methyl groups affects the catalytic activity. However, there was no clear trend observed regarding the degree of methylation and catalytic activity. For example, **3a** bearing the parent oxazoline ligand with no methyl groups showed the highest catalytic activity of all four complexes, and **3d** bearing four methyl groups showed the lowest catalytic activity. However, the trend is reversed for **3b** with two methyl groups and chiral **3c** with three methyl groups (Figure 5), where **3c** was more active than **3b**.

The average performance of complexes **3a**–**d** in the epoxidation of cyclooctene has also been observed with other oxidorhenium(V) systems.[12,13,29,42] The structure of the active species is as yet unidentified. One possible deactivation of the catalyst could be an irreversible oxidation to a colourless perrhenate(VII) ion, which has been observed in other epoxidation reactions.[29] Another possible inhibition of catalysis is the formation of *tert*-butyl alcohol, the reduction product of TBHP, which could compete with TBHP for empty coordination sites on the Re centre.

Conclusions

Oxidorhenium complexes of 2-(hydroxymethyl)-2-oxazoline-based ligands have been prepared and characterized. The crystal structures of the rhenium complexes show that one oxazoline ligand displaces one PPh_3 and one chlorido ligand in the precursor. The complexes show catalytic activities in the epoxidation of cyclooctene.

Experimental Section

Materials: All chemicals were purchased from commercial sources and were used without further purification. (4,5-Dihydrooxazol-2-yl)methanol (**2a**),[31] (4,4-dimethyl-4,5-dihydrooxazol-2-yl)methanol (**2b**),[17,32] 1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)ethanol (**2c**),[32] 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propan-2-ol (**2d**)[17] and $[ReOCl_3(PPh_3)_2]$[43,44] were prepared according to previously published methods.

Instrumentation: ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 300, 75 and 121 MHz, respectively, with a Bruker AC300 instrument. Chemical shifts are reported in ppm and referenced to residual solvent peaks. ^{31}P NMR shifts are referenced against external H_3PO_4. EI mass spectra were measured with an Agilent 5973 MSD direct-probe. Elemental analysis was carried out by using a Heraeus Vario Elemental Automatic Analyzer. IR spectra were recorded with a Bruker Alpha FTIR spectrometer in the range of 4000–400 cm^{-1}. Melting points were recorded in glass capillary tubes with a Büchi Melting Point B-540 apparatus and are uncorrected. Single-crystal X-ray measurements were performed by using Mo-K_α (λ = 0.71073 Å) radiation with a Bruker SMART APEX II diffractometer equipped with a CCD area detector at 100(2) K. The APEX II program[45] was used for collecting frames of data, indexing reflections and determinations of lattice parameters; datasets were integrated and scaled with SAINT[46] and corrected for absorption and Lp effects with SADABS.[47] Structures were solved either by Patterson synthesis (SHELXL-97)[48] or direct methods (SIR-92)[49] using the WinGX suite of programs.[50] The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares analysis on F^2. Hydrogen atoms were fixed in calculated positions with a riding model (U_{iso} = 1.5 U_{iso} of the parent carbon atom). Graphical plots of the structures were made by using ORTEP-3.[51] CCDC-826465 (for **3a**), -826464 (for **3b**) and -826466 (for **3d**) 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.

Synthesis of Oxidorhenium(V) Complexes

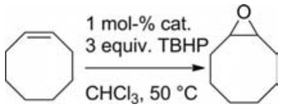
$[ReOCl_2(PPh_3)(2a)]$ (3a): To a greenish-yellow suspension of $[ReOCl_3(PPh_3)_2]$ (0.833 g, 1 mmol) in acetone (300 mL) was added **2a** (0.202 g, 2 mmol) dropwise with vigorous stirring. The resulting deep blue solution was heated to reflux for 24 h. Blue needle-shaped crystals were obtained by slow evaporation of the solvent at room temperature. Collection by filtration and washing with methanol and diethyl ether afforded **3a** (0.43 g, 71 %). Blue single crystals suitable for X-ray diffraction were grown by slow solvent evaporation from a concentrated acetonitrile solution. M.p. 220.0 °C (dec.). ^{1}H NMR (CD$_3$CN): δ = 3.44 (m, 1 H), 3.80 (m, 1 H), 4.19 (m, 2 H), 4.57 (m, 1 H), 4.98 (m, 1 H), 7.55–7.71 (m, 15 H) ppm. ^{31}P NMR (CD$_3$CN): δ = –15.79 ppm. IR: $\tilde{\nu}$ = 3052.39 (w, ν_{C-H}), 2888.00 (w, ν_{C-H}), 1670.05 (s, $\nu_{C=N}$), 1480.70 ($\nu_{C=C}$), 1425.89 ($\nu_{C=C}$), 1251.65, 1202.77, 1185.71, 1099.90, 1077.44, 1065.42, 1025.55, 998.07, 964.86 ($\nu_{Re=O}$), 952.69, 906.02, 757.28, 743.45, 700.85, 689.60 (s), 530.41, 501.75 (s) cm^{-1}. EI-MS: *m/z* = 373.0 [M$^+$ – PPh$_3$], 262.1 [PPh$_3$]. C$_{22}$H$_{26}$Cl$_2$NO$_3$PRe (640.28): cacld. C 41.58, H 3.33, N 2.20; found C 41.59, H 3.28, N 2.18.

[ReOCl$_2$(PPh$_3$)(2b)] (3b): A suspension of [ReOCl$_3$(PPh$_3$)$_2$] (0.416 g, 0.5 mmol) in THF (50 mL) was slowly added to a solution of **2b** (0.129 g, 1 mmol) in THF (20 mL) with vigorous stirring to give a purple solution, which changed to brown on heating to 55 °C and finally to blue after heating to reflux for 9 h. Slow evaporation of the solvent yielded blue crystalline material of **3b**, which was recrystallized from dichloromethane to give blue blocks suitable for X-ray analysis. M.p. 138.0 °C (dec.). ^{1}H NMR ([D$_6$]acetone): δ = 0.61 (s, 3 H), 1.58 (s, 3 H), 4.34 (dd, *J* = 19.2, 3.8 Hz, 1 H), 4.41 (d, *J* = 8.8 Hz, 1 H), 4.67 (dd, *J* = 19.2, 3.8 Hz, 1 H), 4.81 (d, *J* = 8.8 Hz, 1 H), 7.53–7.68 (m, 15 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 23.3 (CH$_3$), 28.9 (CH$_3$), 68.1 (CH$_2$ORe), 70.1 (*C*Me$_2$), 87.2 (ring CH$_2$), 130.0–135.9 (C's of PPh$_3$), 174.1 (C=N) ppm. ^{31}P NMR ([D$_6$]acetone): δ = –18.95 ppm. IR: $\tilde{\nu}$ = 3055.83, 2985.80, 2929.03, 1644.63, 1433.73, 1107.18, 1092.32, 974.62, 959.21, 933.50, 916.14, 744.68, 690.79, 561.69, 529.92 cm^{-1}. EI-MS: *m/z* = 400.9 [M$^+$ – PPh$_3$], 277.1 [OPPh$_3$], 262.1 [PPh$_3$]. C$_{24}$H$_{25}$Cl$_2$NO$_3$PRe (663.27): calcd. C 43.44, H 3.80, N 2.11; found C 43.83, H 4.24, N 2.25.

[ReOCl$_2$(PPh$_3$)(2c)] (3c): A suspension of [ReOCl$_3$(PPh$_3$)$_2$] (0.833 g, 1.0 mmol) in THF (50 mL) was slowly added to a solution of **2c** (0.286 g, 2 mmol) in THF (10 mL). The mixture was heated to reflux for 48 h to yield a deep blue solution. Slow evaporation of the solvent yielded a blue precipitate, which was washed with methanol (4 × 3 mL) and dried under vacuo to afford **3c** (408 mg, 71.4 %). Single crystals suitable for X-ray crystallography were obtained from a concentrated solution of dichloromethane and ethanol (3:1) at room temperature. M.p. 190.0 °C (dec.). ^{1}H NMR [CDCl$_3$, two diastereomers A and B (2:1)]: δ = 0.49 (s, 3 H, minor isomer B), 0.53 (s, 3 H, major isomer A), 0.70 (d, 3 H, B), 1.25 (d, 3 H, B), 1.59 (s, 3 H, B), 1.61 (s, 3 H, A), 4.22 (d, 1 H, A), 4.32 (m, overlap A + B), 4.56 (d, 1 H, A), 4.59 (d, 1 H, B), 4.66–4.77 (m, overlap A + B), 7.40–7.75 (m, 15 H) ppm. ^{13}C NMR (CDCl$_3$, only resonances of the major diastereomer A are distinguishable from noise): δ = 18.8 (CH$_3$) 22.6 (CH$_3$), 28.9 (CH$_3$), 69.2 (*C*HMe), 73.8 (*C*Me$_2$), 85.1 (ring CH$_2$), 128.8–134.9 (C atoms of PPh$_3$), 173.2 (C=N) ppm. ^{31}P NMR (CDCl$_3$): δ = –16.20, –17.30 ppm. IR: $\tilde{\nu}$ = 3184.16, 2968.11, 1664.42, 1463.25, 1366.91, 1259.34, 1195.27, 1123.05, 1075.70, 970.33, 944.02, 919.27, 822.97, 655.56, 506.67 cm^{-1}. EI-MS: *m/z* = 429.1 [M$^+$ – PPh$_3$], 262.1 [PPh$_3$]. C$_{25}$H$_{27}$Cl$_2$NO$_3$PRe (677.29): calcd. C 44.32, H 4.02, N 2.07; found C 43.97, H 4.13, N 2.50.

[ReOCl$_2$(PPh$_3$)(2d)] (3d): A suspension of [ReOCl$_3$(PPh$_3$)$_2$] (0.833 g, 1.0 mmol) in THF (60 mL) was slowly added to a solution of **2d** (0.33 g, 2 mmol) in THF (10 mL) and heated to reflux for 48 h. The resulting deep blue solution was concentrated to give a blue precipitate of **3d**. The material was recrystallized from CH$_2$Cl$_2$ to give blue crystals (300 mg, 43.4 %). Single crystals suitable for X-ray crystallography were obtained by slow solvent evaporation of a concentrated acetonitrile solution. M.p. 196.0 °C (dec.). ^{1}H NMR (CDCl$_3$): δ = 0.43 (s, 3 H), 0.60 (s, 3 H), 1.41 (s, 3 H), 1.60 (s, 3 H), 4.29 (d, *J* = 8.4 Hz, 1 H), 4.57 (d, *J* = 8.4 Hz, 1 H), 7.41–7.71 (m, 15 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.6 (CH$_3$) 24.5 (CH$_3$), 25.0 (CH$_3$), 26.1 (CH$_3$), 69.4 (*C*Me$_2$), 80.6 (O*C*Me$_2$), 85.7 (ring CH$_2$), 128.3–135.1 (C atoms of PPh$_3$), 174.7 (C=N) ppm. ^{31}P NMR (CDCl$_3$, 121 MHz): δ = –17.96 ppm. IR: $\tilde{\nu}$ = 3062.36, 2987.16, 2962.78, 1648.17, 1433.22, 1371.98, 1359.38, 1259.47, 1092.17, 1016.19, 989.09, 965.72, 952.00, 936.23, 795.56, 757.54, 742.62, 691.16, 658.15, 524.21, 501.98 cm^{-1}. EI-MS: *m/z* = 692.1 [M$^+$]. C$_{26}$H$_{29}$Cl$_2$NO$_3$PRe (691.30): calcd. C 45.15, H 4.23, N 2.03; found C 42.79, H 4.48, N 1.74.

Catalytic Reactions: In a typical experiment, cyclooctene (100 mg, 0.91 mmol, 1 equiv.), TBHP (246.03 mg, 2.73 mmol, 3 equiv.) and chloroform (1.5 mL) were heated to 50 °C, and the respective oxidorhenium(V) complexes (1 mol-%) were added (Scheme 3). Samples for GC–MS (10 µL) from each mixture were withdrawn every 10 min with a micropipette over 8 h, and the last sample was taken after stirring at the same temperature for 12 h, diluted with HPLC grade ethyl acetate. The reaction products were analyzed by using GC–MS (Agilent Technologies 7890 GC System), and the epoxide produced from each reaction mixture was quantified vs. *n*-decane as the internal standard.



Scheme 3. Epoxidation of cyclooctene.

Supporting Information (see footnote on the first page of this article): Non-refinable crystal structure of complex **3c** proving the correct connectivity.

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