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Oxorhenium(V) complexes with naphtholate-oxazoline ligands in the catalytic epoxidation of olefins

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ABSTRACT

Four oxorhenium(V) complexes **3a–d** equipped with naphtholate-oxazoline based ligands **2a–d** have been prepared and characterized by NMR, IR and mass spectroscopy as well as elemental analysis. Ligands **2a–d** were prepared in a two-step procedure from commercially available starting materials. Ligands **2a–b** and **2c–d** are regioisomers to each other regarding the position of the –OH group and oxazoline moiety on the naphthol ring. Reaction of **2a–d** with $(NBu_4)[ReOCl_4]$ in methanol under reflux gave oxorhenium(V) complexes **3a–d** of the type $[ReOCl(L)_2]$ as green solids in acceptable to good yields. The molecular structures of complexes **3b** and **3d** have been determined via single crystal X-ray diffraction analysis and both display a distorted octahedral geometry. Complexes **3a–d** are active catalysts for the epoxidation of cyclooctene with tert-butylhydroperoxide (TBHP) showing moderate conversions between 41% and 65%.

1. Introduction

The remarkable ability of oxorhenium(V) complexes to catalyze various oxygen atom transfer (OAT) reactions has spurred intensive research over the last few years. Espenson and coworkers described the OAT reactivity of oxorhenium(V) complexes from various pyridine-*N*-oxides to phosphines [1]. Abu-Omar and coworkers reported an oxorhenium(V) complex employing the phenolate-oxazoline ligand 2-(4,5-dihydrooxazol-2-yl)phenol (Hhoz) which is capable of reducing kinetically stable perchlorate anions to chloride ions via OAT to sulphides [2,3]. Finally, OAT to olefinic substrates resulting in the formation of epoxides employing rhenium catalysts has developed into an important field of research, especially since the advent of the oxorhenium(VII) catalyst methyltrioxorhenium (MTO) [4–6]. MTO is a highly active catalyst for olefin epoxidation, however, with certain substrates unwanted, hydrolytic ring opening of the formed epoxide occurs due to the Brønstedt acidity of MTO [7]. Oxorhenium(V) complexes are usually less prone towards hydrolysis, thereby avoiding the unselective hydrolysis of epoxides. For this reason several oxorhenium(V) complexes have been investigated as epoxidation catalysts by us and other groups over the last years [8–14]. The success of oxazoline ligands as stabilizing motifs in catalysis as well as our ongoing interest in rhenium-catalyzed epoxidations prompted us to further investigate unexplored oxazoline ligands and their oxorhenium(V) chemistry. Within this paper we would like to report on the synthesis and characterization of four naphtholate-oxazoline ligands **2a–d** (Fig. 1) as well as the oxorhenium(V) complexes **3a–d** thereof. Furthermore complexes **3a–d** were tested as potential catalysts in the epoxidation of olefins (see Schemes 1–3).

2. Results and discussion

Ligands **2a–b** (Fig. 1) were synthesized by a two step reaction in analogy to published procedures [15,16] varying in the R-groups adjacent to the nitrogen as well as in the position of the substituents on the naphthole ring. Starting from commercially available 1-hydroxy-2-naphthoic acid and the respective aminoalcohol the amides **1a–b** were obtained by a Steglich condensation. The cyclization to obtain the respective oxazoline ligands **2a–b** was achieved with thionyl chloride [17]. Compounds **2a–b** represent bidentate *O,N*-coordinating ligands, where the hydroxyl group is easily deprotonated by bases like NEt_3, whereby they become mono-anionic.

Since the amides **1c–d** are not directly accessible from 2-hydroxy-3-naphthoic acid, which is in contrast to amides **1a–b**, the methyl ester was first synthesized in situ, which could then be converted to the amides **1c–d** via a Steglich condensation [18].

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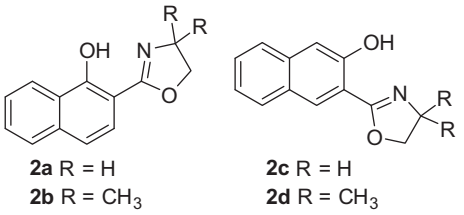


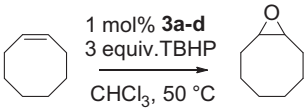
Fig. 1. Ligands **2a–d** used to synthesize oxorhenium(V) complexes.

The synthesis of **1c** had been previously mentioned, but without analytical data [19].

The oxorhenium(V) complexes **3a–d** were obtained by refluxing a mixture of $(NBu_4)[ReOCl_4]$ and two equivalents of the corresponding ligand **2a–d** in the presence of triethylamine in methanol. Upon cooling and concentration of the deep green reaction mixture the respective complexes started to precipitate in analytical pure form as a green–brownish solid.

Interestingly the complexes showed quite different solubilities. Complexes **3a** and **3c** (with R = H) are barely soluble in polar solvents like methanol, ethanol, acetone, dichloromethane (DCM), chloroform, THF or dimethylsulfoxide (DMSO) whereas **3b** and **3d** are quite soluble in these solvents. This is due to the four methyl groups in complexes **3b** and **3d**. ^{1}H NMR spectra of **3a–d** display two different sets of ligand signals indicating the formation of asymmetrically substituted Re(V) complexes. Similar to previously published disubstituted complexes, an asymmetrical coordination of the two bidentate ligands is expected, where one ligand coordinates the Re atom in an all-equatorial fashion and the second ligand in an equatorial-axial fashion [3,12,20,21]. This proposed structure was confirmed by single crystal X-ray diffraction analysis of complex **3b** and **3d** respectively (vide infra). The formation of complexes **3a–d** was also apparent by IR spectroscopy. Upon coordination of the respective ligand **2a–d** a shift to lower wave numbers of the $\nu_{C=N}$ band of the oxazoline moiety is observed as well as the appearance of the diagnostic $\nu_{Re=O}$ band between 900 and 1000 cm^{-1} (Table 1) [2,12].

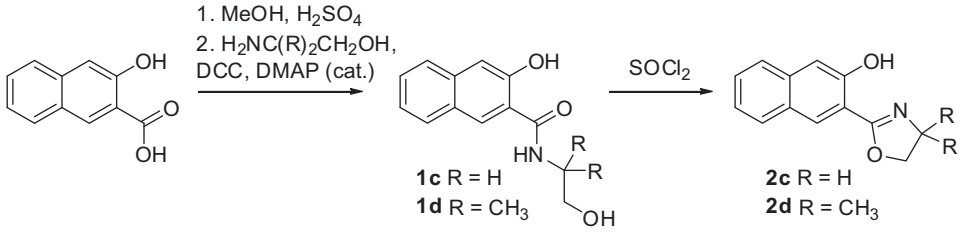
Mass spectroscopy as well as elemental analysis are also consistent with the proposed formulas of oxorhenium(V) complexes **3a–d**. Single crystals of **3b** and **3d** suitable for X-ray crystallography could be grown by slow evaporation of a concentrated solution of the respective complex in acetone (**3b**) or methanol (**3d**). Both **3b** and **3d** adopt an asymmetric conformation in the solid state, where one ligand coordinates in an equatorial fashion and the other ligand in an equatorial-axial fashion. Furthermore, both structures show some disorder, with atoms occupying two different orientations. This disorder however does not change the overall geometry of the complexes. Since both structures are quite similar, only the structure of **3b** will be discussed in detail. In complex **3b** the two oxazoline N atoms N13 and N33 are trans to each other, and the two naphtholate O atoms O21 and O41 are in a cis orientation (Fig. 2). Consequently the remaining oxo (O1) and chloro (Cl1) ligands are also in cis configuration to each other, completing the distorted, octahedral coordination geometry around the Re atom. The rhenium atom as well as the oxo and chloro ligands are disordered resulting in a slight displacement (Re2, O2, Cl2, not labeled in Fig. 2) with a lower occupation factor of 0.4005(10). Nevertheless, the overall geometry of both disordered structures remains the same, with one naphtholate oxygen atom occupying a position trans to the terminal oxo ligand.



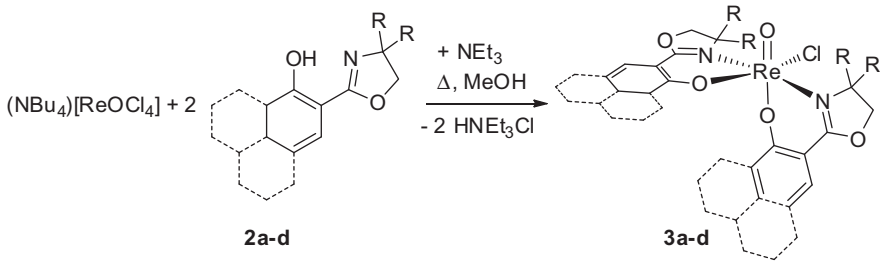
Scheme 3. Epoxidation of cyclooctene.

Table 1
Selected IR bond stretching frequencies of ligands **2a–d** and complexes **3a–d**.

	Bond stretching frequencies, ν (cm^{-1})			
	2a	**2b**	**2c**	**2d**
$\nu_{C=N}$	1626	1620	1651	1650
	3a	**3b**	**3c**	**3d**
$\nu_{C=N}$	1596	1594	1610	1599
$\nu_{Re=O}$	961	956	966	952



Scheme 1. Synthesis of ligands **2c–d** via amides **1c–d**.



Scheme 2. Synthesis of oxorhenium(V) complexes **3a–d**.

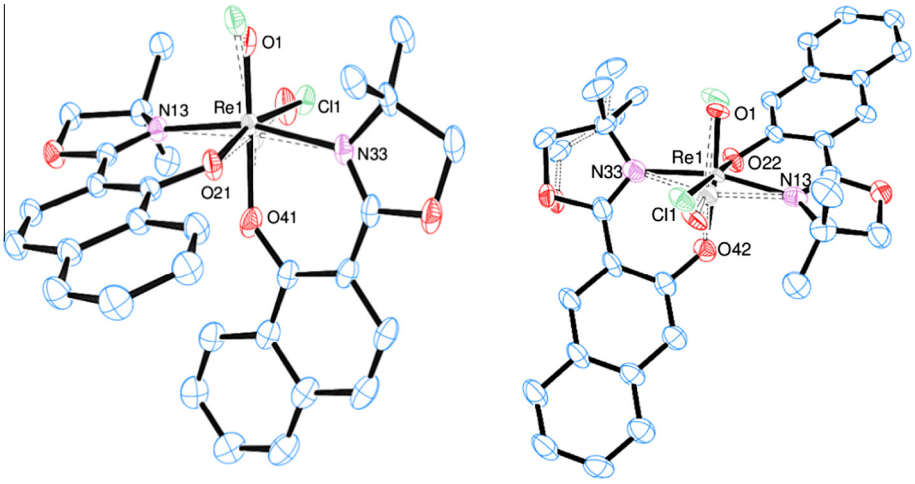


Fig. 2. Molecular views of **3b** (left) and **3d** (right) showing the atomic numbering scheme. Probability ellipsoids are drawn at the 50% level; H atoms are omitted for clarity. Bonds to disordered atoms with lower occupation factors are drawn with dashed lines.

Table 2
Comparison of selected bond distances and angles of **3b** and **3d**.

Bond distances (Å)	**3b**	Bond-distances (Å)	**3d**
Re1–O1	1.672(3)	Re1–O1	1.673(10)
Re1–O21	1.9691(15)	Re1–O22	1.975(5)
Re1–O41	2.0790(18)	Re1–O42	2.003(5)
Re1–N13	2.0921(17)	Re1–N13	2.091(6)
Re1–N33	2.1245(18)	Re1–N33	2.137(6)
Re1–Cl1	2.3845(11)	Re1–Cl1	2.4361(18)
Bond angles (°)	**3b**	**Bond angles (°)**	**3d**
O1–Re1–O41	178.38(14)	O1–Re1–O42	169.8(7)
N13–Re1–N33	163.58(7)	N13–Re1–N33	164.5(2)
O21–Re1–Cl1	167.09(5)	O22–Re1–Cl1	172.65(12)
O21–Re1–N13	88.18(6)	O22–Re1–N13	87.4(2)
O1–Re1–O21	97.18(14)	O1–Re1–O22	100.0(7)
O1–Re1–Cl1	93.21(13)	O1–Re1–Cl1	85.1(7)

All bond lengths and angles in **3b** as well as **3d** fall within the expected range for an octahedral oxorhenium(V) complex (Table 2) [3,12–14,20,22,23]. The Re=O bond distance Re1–O1 is 1.672(3) Å for **3b**, which lies within the typical range of such bonds of 1.688–1.694 Å. The two axial ligands O1 and O41 show almost perfect linear arrangement at 178.38(14)°. The deviation from an ideal octahedron is displayed by the angle of the trans oriented N atoms N13 and N33 of 163.58(7)°, which also reflects the small bite angel of the bidentate ligand **2b**. As mentioned above, the structural parameters of **3b** and **3d** are very similar to each other, with one exception. The bond distance from Re to the naphtholate oxygen trans to the terminal oxo ligand is significant shorter in **3d** (Re1–O42 = 2.003(5) Å) compared to **3b** (Re1–O41 = 2.0790(18) Å) (Table 2). This might be attributed to the difference in p*K*a of the oxygen atom and the reduced steric pressure in **3d**.

Table 3
Results of epoxidation of cyclooctene catalyzed by **3a–d**.

t (h)	Epoxide (%)			
	3a	**3b**	**3c**	**3d**
1	16	27	10	27
2	30	42	21	47
8	54	49	41	65

Cond.: 1 mol% **3a–d**, 3 equiv. TBHP, $CHCl_3$, 50 °C.

3. Epoxidation of cyclooctene

Complexes **3a–d** were tested as catalysts for the epoxidation of cyclooctene with tert-butylhydroperoxide (TBHP) as oxidant. The best conditions were found with 1 mol% of catalyst and 3 equiv. of TBHP in $CHCl_3$ at 50 °C. Under these conditions catalyst **3a** reached 49%, catalyst **3b** 54%, catalyst **3c** 65% and catalyst **3d** 41% conversion of cyclooctene to cyclooctene oxide selectively. Experiments were carried out for eight hours, after which no more conversion to cyclooctene oxide could be detected. Due to their low solubilities, complexes **3a** and **3c** did not fully dissolve initially, in contrast to **3b** and **3d**. We believe that the initial lower conversion rates of **3a** and **3c** after 1 h are mainly due to this lower solubility. At longer reaction times, also complexes **3a** and **3c** dissolved. At the end of the reaction time of 8 h, homogeneous, almost colorless solutions were observed. The discoloration indicates the formation of colorless perrhenate(VII) species in solution, which was also observed for other oxorhenium(V) catalysts after a similar time span [11–14,21,24]. This points to concomitant catalyst decomposition over the reaction time and explains the lack of catalysis after longer reaction times. No induction period for all four complexes could be observed. Due to their pronounced difference in solubility, it is difficult to observe an isomeric effect between complexes **3a** and **3b** or **3c** and **3d** respectively.

Experiments in acetonitrile or methanol only gave small conversions to epoxide, which were mainly due to the uncatalyzed reaction with TBHP. Test reactions without **3a–d** confirmed this finding. Also, if the amount of catalyst loading or oxidant is decreased, the conversion to product drops significantly. Experiments using hydrogenperoxide also resulted in low conversion (>5%). Details of the catalytic reaction are given in the Section 4 (see Table 3).

Complexes **3a–d** are catalytically active in the epoxidation of cyclooctene to cyclooctene oxide. All catalysts show good selectivity towards the epoxide, as no other side products, for example the ring-opened diol, are observed. The overall catalytic activity as well as catalyst stability is comparable to other oxorhenium(V) complexes [11–14,21,24].

4. Conclusions

Within this paper we present the synthesis and characterization of four novel oxorhenium(V) complexes **3a–d** equipped with the bidentate monoanionic naphtholate-oxazoline ligands **2a–d**. All

analytical data is consistent with the formation of asymmetrically disubstituted complexes. Complexes **3b** and **3d** were additionally characterized by single crystal X-ray diffraction analysis. Furthermore the complexes **3a**–**d** were tested in the catalytic epoxidation of cyclooctene where they showed to be active catalysts comparable to other oxorhenium(V) complexes.

4.1. Experimental

4.1. General remarks

Unless otherwise specified, all experiments were performed under atmospheric conditions with standard laboratory equipment at the Institute of Chemistry, University of Graz. The metal precursor $(NBu_4)[ReOCl_4]$ was prepared according to a published procedure. [25] Amides **1c**–**d** as well as ligands **2a**–**b** were synthesized according to a published procedure. [19,16] All other chemicals and solvents were purchased from commercial sources and used as received. 1-Hydroxy-2-naphthoic acid was purchased from Sigma–Aldrich (>97.0%). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Optics Instrument. Chemical shifts are reported in parts per million (ppm) and referenced to residual protons or carbons in the deuterated solvent. Electron impact mass spectroscopy measurements (EI-MS) were recorded with an Agilent 5973 MSD mass spectrometer with Direct Probe. Gas chromatography mass spectroscopy measurements (GC–MS) have been performed with a model Agilent 7890 A (column type Agilent 19091 J-433), coupled to a mass spectrometer type Agilent 5975 C. Samples for infrared spectroscopy were measured on a Bruker Optics ALPHA ATR FT-IR Spectrometer. IR bands are reported with wave number (cm^{-1}). Elemental analyses were measured on a Heraeus Vario Elementar automatic analyzer at the Technische Universität Graz, Department of Inorganic Chemistry.

4.2. Single crystal X-ray diffraction analysis

All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100 K. **3b**: $C_{30}H_{28}ClN_2O_5Re$, M_r 718.19, monoclinic, space group $P\ 2_1/c$, $a = 16.9287(7)$ Å, $b = 12.8952(5)$ Å, $c = 12.4258(5)$ Å, $\beta = 103.114(2)°$, $V = 2641.80(18)$ Å^3, $Z = 4$, $d_{calc} = 1.806$ g cm^{-3}, $\mu = 4.746$ mm^{-1}. A total of 23693 reflections were collected ($\Theta_{max} = 30.00°$), from which 7693 were unique ($R_{int} = 0.0224$), with 6529 having $I > 2\sigma(I)$. For 392 parameters final R indices of $R_1 = 0.0212$ and $wR^2 = 0.0466$ (GOF = 1.069) were obtained. **3d**: $C_{30}H_{28}ClN_2O_5Re$, M_r 718.19, monoclinic, space group $P\ 2_1/c$, $a = 18.8284(8)$ Å, $b = 7.4928(3)$ Å, $c = 20.0590(9)$ Å, $\beta = 103.414(1)°$, $V = 2752.7(2)$ Å^3, $Z = 4$, $d_{calc} = 1.733$ g cm^{-3}, $\mu = 4.554$ mm^{-1}. A total of 21 271 reflections were collected ($\Theta_{max} = 30.0°$), from which 7989 were unique ($R_{int} = 0.0166$), with 7108 having $I > 2\sigma(I)$. For 399 parameters final R indices of $R_1 = 0.0465$ and $wR^2 = 0.1626$ (GOF = 1.587) were obtained. For full details on data collection and refinement refer to the Supporting information.

Synthesis of **2c**. A suspension of **1c** (1.73 g, 7.5 mmol, 1 equiv.) in dichloromethane (70 mL) was cooled to 0 °C. Thionyl chloride (1.78 g, 15 mmol, 2 equiv.) was added slowly under Ar over a period of 15 min. The solution was allowed to slowly warm up to room temperature and stirred overnight after which the solution was concentrated to a small volume. The crude product of **2c**·HCl was precipitated with ether, subjected to aqueous work-up with saturated $NaHCO_3$ and dried in vacuo to yield 1.53 g (7.03 mmol, 93%) of **2b** as white flakes. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.00 (s, 1H), 8.32 (s, 1H), 7.94 (dd, $J = 8.3$, 1.1 Hz, 1H), 7.76 (dd, $J = 8.3$, 1.1 Hz, 1H), 7.50 (ddd, $J = 8.3$, 6.8, 1.1 Hz, 1H), 7.33 (m, 2H), 4.51 (t, $J = 9.5$ Hz, 2H), 4.11 (t, $J = 9.5$ Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.05, 154.70, 136.12, 129.33, 128.81, 128.41, 126.57, 126.01, 123.66, 112.44, 110.21, 67.05, 53.29. Selected ATR frequencies (cm^{-1}): 1651 ($\nu_{C=N}$). MS (EI, m/z): 213.1 [M$^+$]. *Anal.* Calc. for $C_{13}H_{11}NO_2$ (213.23): C, 73.23; H, 5.20; N, 6.57. Found: C, 72.34; H, 5.11; N, 6.41%.

Synthesis of **2d**. A suspension of **1d** (2.0 g, 7.72 mmol, 1 equiv.) in dichloromethane (70 mL) was cooled to 0 °C. Thionyl chloride (1.56 g, 13.12 mmol, 1.5 equiv.) was added slowly under Ar over a period of 15 min. The solution was allowed to slowly warm up to room temperature and stirred overnight after which the solution was concentrated to a small volume. The crude product of **2d**·HCl was precipitated with ether, subjected to aqueous work-up with saturated $NaHCO_3$ and dried in vacuo to yield 1.28 g (5.32 mmol, 69%) of **2b** as light-brown flakes. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.96 (s, 1H), 8.32 (s, 1H), 7.94 (dd, $J = 8.3$, 1.1 Hz, 1H), 7.76 (dd, $J = 8.3$, 1.1 Hz, 1H), 7.50 (ddd, $J = 8.3$, 6.8, 1.1 Hz, 1H), 7.34 (m, 2H), 4.23 (s, 2H), 1.38 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.10, 155.17, 136.59, 129.76, 129.24, 128.85, 127.05, 126.48, 124.11, 113.00, 110.64, 78.33, 67.66, 28.45. Selected ATR frequencies (cm^{-1}): 1650 ($\nu_{C=N}$). MS (EI, m/z): 241.1 [M$^+$]. *Anal.* Calc. for $C_{15}H_{15}NO_2$ (241.29): C, 74.76; H, 6.27; N, 5.81. Found: C, 73.58; H, 6.23; N, 5.58%.

Synthesis of **3a**. To a green solution of $(NBu_4)[ReOCl_4]$ (0.586 g, 1 mmol) in methanol (25 mL), **2a** (0.426 g, 2 mmol) was added with stirring. Triethylamine (0.202 g, 2 mmol) was slowly added to the mixture which resulted in a deep green precipitate. The mixture was refluxed for 3 h, cooled to room temperature and concentrated to ~5 mL of solvent to enforce precipitation of **3a**. After filtration, washing with small amounts of methanol and drying under vacuo analytically pure **3a** was obtained (0.540 g, 0.82 mmol, 82%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.72 (q, $J = 10.5$ Hz, 2H), 4.16 (dt, $J = 25.0$, 9.0 Hz, 2H), 4.71 (m, 2H), 5.10 (m, 2H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.31 (m, 1H), 7.43 (m, 4H), 7.69 (m, 2H), 7.83 (m, 2H), 7.97 (m, 1H), 8.86 (d, $J = 8.0$ Hz, 2H). Due to the low solubility of **3a** no ^{13}C NMR spectrum could be obtained. Selected ATR IR frequencies (cm^{-1}): 1599 ($\nu_{C=N}$), 959 ($\nu_{Re=O}$). EI-MS (m/z): = 662.3 [M$^+$], 627.4 [M$^+$– Cl]. *Anal.* Calc. for $C_{26}H_{20}ClN_2O_5Re$ (662.11): C, 47.16; H, 3.04; N, 4.23. Found: C, 46.29; H, 2.99; N 3.99%.

Synthesis of **3b**. To a green solution of $(NBu_4)[ReOCl_4]$ (0.586 g, 1 mmol) in methanol (20 mL) **2b** (0.482 g, 2 mmol) was added with stirring. Triethylamine (0.202 g, 2 mmol) was slowly added to the mixture which resulted in a deep green solution. The mixture was refluxed for 3 h, cooled to room temperature and concentrated to ~2 mL of solvent to enforce precipitation of **3b**. The product obtained was filtered, washed with small amounts of methanol and dried in vacuo to yield 0.52 g of **3b** (0.72 mmol, 72%) as a yellowish green powder. Dark brown prisms of single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **3b** in acetone. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.07 (s, 3H), 4.49 (d, $J = 8.3$ Hz, 1H), 4.75 (m, 2H), 4.83 (d, $J = 8.3$ Hz, 1H), 7.11 (d, $J = 9.0$ Hz, 1H), 7.34 (m, 4H), 7.50 (ddd, $J = 8.1$, 6.8, 1.3 Hz, 1H), 7.62 (m, 1H), 7.69 (m, 1H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.91 (d, $J = 9.0$ Hz, 1H), 7.96 (m, 1H), 8.36 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.55, 27.43, 28.10, 28.46, 72.87, 78.52, 79.37, 81.87, 102.42, 103.31, 117.28, 119.06, 124.52, 124.78, 125.01, 125.14, 125.51, 125.72, 126.65, 126.84, 127.21, 129.46, 129.70, 137.25, 137.80, 164.31, 166.34, 170.71, 177.23, 1C obscured. Selected IR frequencies (cm^{-1}): 1617 $\nu_{(C=N)}$, 956 $\nu_{(Re=O)}$. EI-MS (m/z): 718.1 [M$^+$], 683.1 [M$^+$]–Cl. *Anal.* Calc. for $C_{30}H_{28}ClN_2O_5Re$ (718.21): C, 50.17; H; 3.93; N, 3.90. Found: C, 50.47; H, 4.00; N, 3.83%.

Synthesis of **3c**. To a green solution of $(NBu_4)[ReOCl_4]$ (0.586 g, 1 mmol) in methanol (25 mL), **2c** (0.426 g, 2 mmol) was added with stirring. Triethylamine (0.202 g, 2 mmol) was slowly added to the mixture which resulted in a deep green precipitate. The mixture was refluxed for 3 h, cooled to RT and concentrated to ~5 mL of solvent to enforce precipitation of **3c**. After filtration, washing with small amounts of methanol and drying under vacuo analytically pure **3c** was obtained (0.477 g, 0.73 mmol, 73%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.67 (s, 1H), 8.29 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.90 (m, 2H), 7.63 (m, 3H), 7.36 (m, 3H), 7.01 (s, 1H), 4.96 (m, 4H), 4.15 (m, 4H). Due to the low solubility of **3c** no ^{13}C NMR spectrum could be obtained. Selected ATR IR frequencies (cm^{-1}): 1610 ($\nu_{C=N}$), 966 ($\nu_{Re=O}$). EI-MS (m/z): = 662.3 [M^+], 627.4 [M^+−Cl]. *Anal.* Calc. for $C_{26}H_{20}ClN_2O_5Re$ (662.11): C, 47.16; H, 3.04; N, 4.23. Found: C, 46.77; H, 2.89; N, 4.39%.

Synthesis of **3d**. To a green solution of $(NBu_4)[ReOCl_4]$ (0.586 g, 1 mmol) in methanol (20 mL) **2d** (0.482 g, 2 mmol) was added with stirring. Triethylamine (0.202 g, 2 mmol) was slowly added to the mixture which resulted in a deep green solution. The mixture was refluxed for 3 h, cooled to RT and concentrated to ~2 mL of solvent to enforce precipitation of **3d**. The product obtained was filtered, washed with small amounts of methanol and dried in vacuo to yield 0.256 g of **3d** (0.256 mmol, 25%) as a deep green powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.32 (s, 1H), 7.78 (m, 1H), 7.74 (m, 1H), 7.60 (m, 2H), 7.43 (m, 1H), 7.32 (m, 2H), 7.24 (m, 1H), 7.17 (s, 1H), 7.10 (s, 1H), 4.73 (dd, J = 8.3, 2.6 Hz, 2H), 4.65 (dd, J = 8.3, 5.1 Hz, 2H), 2.08 (s, 3H), 1.98 (s, 6H), 1.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.62, 170.02, 166.50, 159.63, 138.35, 138.26, 133.78, 133.66, 129.79, 129.25, 129.11, 127.57, 126.58, 126.24, 125.97, 124.03, 123.22, 114.61, 113.68, 112.64, 82.27, 79.65, 79.43, 73.44, 27.55, 27.11, 26.98, 26.06, 2C obscured. Selected IR frequencies (cm^{-1}): 1599 $\nu_{(C=N)}$, 952 $\nu_{(Re=O)}$. EI-MS (m/z): 718.4 [M^+], 683.1 [M^+−Cl]. *Anal.* Calc. for $C_{30}H_{28}ClN_2O_5Re$ (718.21): C, 50.17; H, 3.93; N, 3.90. Found: C, 49.97; H, 3.93; N, 4.00%.

4.3. Epoxidation of cyclooctene

In a typical experiment, cyclooctene (100 mg, 0.91 mmol, 1 equiv.) and TBHP, (246.03 mg, 2.73 mmol, 3 equiv.) in chloroform (1.5 mL) were stirred at room temperature, then heated in a pre-heated oil bath at 50 °C and the respective oxorhenium(V) complex was added. Aliquots for GC–MS (10 μL) were withdrawn over 8 h, quenched with MnO_2 and diluted with HPLC grade ethyl acetate. The reaction products were analyzed by GC–MS (Agilent Technologies 7890 GC System), and the epoxide produced from each reaction mixture was quantified vs. *n*-decane as the internal standard.

Appendix A. Supplementary data

CCDC 935186 and 942214 contains the supplementary crystallographic data for **3b** and **3d**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.03.024.

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