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Oxorhenium(V) Complexes with Pyrazole Based Aryloxide Ligands and Application in Olefin Epoxidation

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We synthesized and characterized a set of new oxorhenium(V) complexes coordinated by various pyrazole containing phenol (**L1**−**L3**) and naphthol ligands (**L4**−**L7**). Depending on the starting material, we were able to selectively synthesize monosubstituded or disubstituted complexes of the type $[ReOBr_2L(PPh_3)]$ (**1**−**7**; L = **L1**−**L7**) and $[ReOCl_2L_2]$ (L = L1 **8**; L2 **9**; L4 **10**; L6 **11**), respectively. All complexes are stable to air and moisture, both in solid state as well as in solution. Furthermore, the cationic oxorhenium(V) complex $[ReO(L1)_2(NCMe)](OTf)$ (**8a**) was obtained upon chloride abstraction with silver triflate from **8**. All new complexes were able to catalyze the epoxidation of *cis*-cyclooctene in yields up to 64%. The ease of preparation and their tolerance to air and moisture, as well as the simple ligand modifications, make them an interesting class of novel catalysts. An attempted reduction of perchlorate ClO_4^- with complex **8** was unsuccessful. Molecular structures of complexes **1**, **4**, **6**, **7**, **8**, **8a**, **10**, and **11** were determined by single crystal X-ray diffraction analyses.

Introduction

High-valent oxorhenium complexes are of great importance as oxidation catalysts and because of their capability to transfer an oxygen atom (OAT) to suitable organic substrates. Especially the epoxidation of olefins catalyzed by oxorhenium(VII) compounds has been thoroughly investigated in the past decade, the most prominent example being methyltrioxorhenium (MTO).[1−5] The latter is a highly efficient catalyst; however, its pronounced sensitivity toward water or alcohols sometimes hampered high turnover numbers.[6] Rhenium(V) complexes are usually less prone toward hydrolysis. For this reason, several were tested as catalysts in epoxidation reactions, albeit with limited success.[7−13] Previously investigated Re(V) catalyzed olefin epoxidations with *tert*-butylhydroperoxide (TBHP) exhibit an induction period of 50 to 120 min and reaction times of up to 10 h with cyclooctene conversions ranging between 30 and 66%.[7,9] In contrast, our group investigated β-ketiminate containing Re(V) complexes that could epoxidize 50% of cyclooctene in 60 min with no induction period.[11,12] However, all these systems suffer from concomitant catalyst oxidation, giving unproductive perrhenate salts.[9] Re(V) complexes on the other hand are highly successful in OAT reactions. Espenson and co-workers found OAT reactivity from pyridine-*N*-oxide to phosphines.[14] Abu-Omar and coworkers described rhenium(V) compounds employing oxazoline or thiazoline phenol ligands (2-(2′-hydroxyphenyl)-2-oxazoline = Hhoz and 2-(2′-hydroxyphenyl)-2-thiazoline = Hthoz, respectively) capable of the kinetically unfavored, and thus rare, perchlorate reduction to chloride by OAT at reasonable rates.[15] The oxazoline complex $[ReOCl(hoz)_2]$

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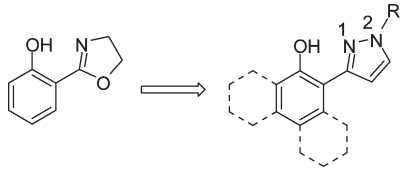


Figure 1. Structural comparison of oxazoline-phenol ligand (Hhoz) and here described pyrazol-phenol (solid line) and -naphthol ligands (dashed line).

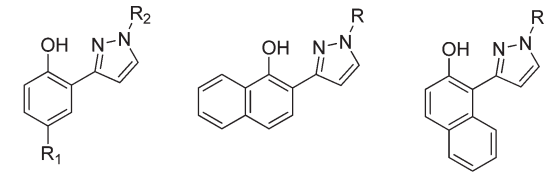


Figure 2. Ligands **L1**−**L7** employed in this study.

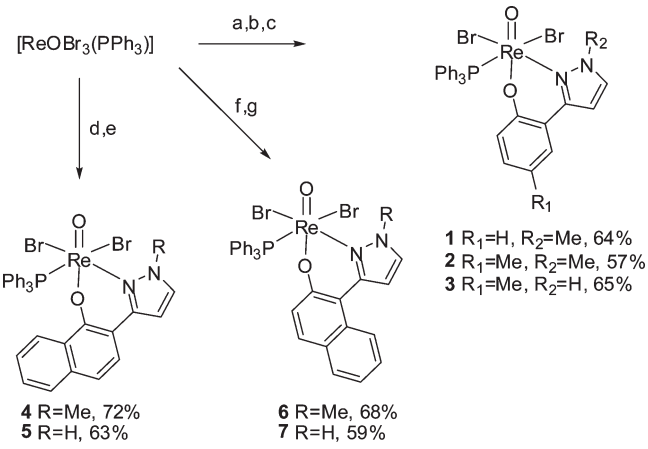
features high stability toward hydrolysis which enabled detailed elucidation of mechanistic aspects. It was found that a stepwise oxygen atom transfer occurs with the first reduction from perchlorate to chlorate being the rate determining step. Interestingly, reversible ring-opening of the oxazoline moiety was observed during the OAT reaction.[16]

The overall high stability of the Re(V) oxazoline complexes toward hydrolysis throughout the catalytic cycle led us to consider the investigation of structurally related types of Re(V) compounds. Herein, we describe the preparation of a series of oxorhenium(V) complexes with phenol and naphthol based ligands connected to a pyrazole ring and their catalytic behavior toward olefin epoxidation. By substitution of the oxazoline ring with a pyrazole ring unfavorable ring-opening should be avoided (Figure 1).

Results and Discussion

Synthesis of Pyrazole Ligands. The phenol and naphthol based pyrazole ligands **L1**−**L7** were prepared according to published literature with slight modifications.[17−21] The synthesis involves a two step procedure by treating the respective methyl aryl ketone with ethyl formate followed by ring closure with methylhydrazine or hydrazine, respectively. We could optimize the reaction of methyl aryl ketone with excess ethyl formate by using NaH (60% in mineral oil) under neat conditions instead of powdered sodium to obtain good yields consistently. The subsequent ring closure procedure of the aldehyde intermediates in acetonitrile (ACN) yielded the desired ligands **L1**−**L7** (Figure 2).

Scheme 1. Monosubstituted Rhenium Complexes **1**−**7**[a]



[a] (a) **L1**, ACN, reflux, 6h. (b) **L2**, ACN/acetone 1 + 1 v/v, reflux, 6h. (c) **L3**, ACN, reflux, 6h. (d) **L4**, THF, reflux, 6h. (e) **L5**, THF, reflux, 6h. (f) **L6**, acetone, reflux, 6h. (g) **L7**, acetone, reflux, 6h.

The monosubstituted rhenium complexes $[ReOBr_2L(PPh_3)]$ (**1**−**7**) (L = **L1**−**L7**) were obtained by reaction of the metal precursor $[ReOBr_3(PPh_3)_2]$[22] with an equimolar amount of the corresponding ligand (**L1**−**L7**) in the solvent indicated in Scheme 1 under refluxing condition. The initial suspension, because of the low solubility of the metal precursor, turned into a dark colored solution on prolonged heating. TLC analyses (silica, cyclohexane/EtOAc) indicated the formation of the expected complex. Removal of solvent resulted in precipitation of the corresponding rhenium complexes **1**−**7** in 57 to 72% yield. They show high stability to air and moisture, both in the solid state and in solution, for several months at ambient temperature. Complexes **1**−**7** exhibit limited solubility in most common solvents which prevented the recording of meaningful ^{13}C NMR spectra. However, ^{1}H and ^{31}P NMR spectroscopy confirm the identity of the complexes as found in the solid state by X-ray crystallography (vide infra). The ^{1}H NMR spectra of all complexes display one set of resonances for a coordinated ligand L as well as one coordinated triphenylphosphine molecule consistent with monosubstitution. Furthermore, ^{31}P NMR spectroscopy confirms the coordination of a phosphine. This type of compound with a very similar phenol based ligand L = 2-(1-*H*-pyrazol-3-yl)-phenolate ($[ReOX_2(EPh_3)L]$; E = P, As; X = Cl, Br) have recently been described in the literature.[23]

Interestingly, when 2 equiv of ligand were reacted with $[ReOBr_3(PPh_3)_2]$, the main products obtained were monosubstituted complexes **1**−**7**, and only minor amounts (∼5−10%) of disubstituted complexes of the type $[ReOBrL_2]$. Also the addition of base (such as Et_3N or lutidine) or using the sodium or potassium salts of the ligands did not increase the yield of disubstituted complexes.

Treatment of the alternative metal precursor $[NBu_4][ReOCl_4]$[24] with 2 equiv of the sodium salt of the

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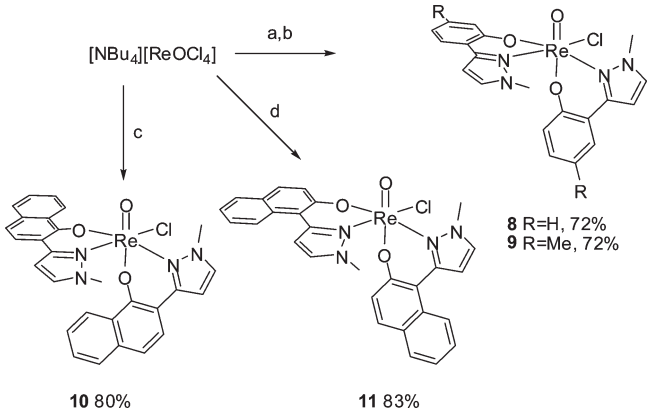
Scheme 2. Disubstituted Rhenium Complexes **8**−**11**[a]



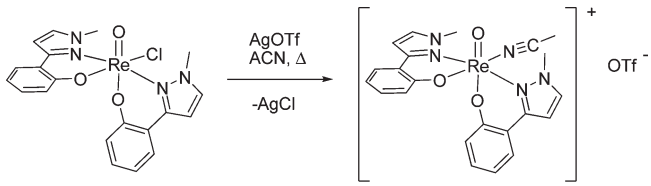
[a] (a) sodium salt of **L1**, MeOH, reflux, 2h. (b) sodium salt of **L2**, MeOH, reflux, 2h. (c) sodium salt of **L4**, MeOH, reflux, 2h. (d) sodium salt of **L6**, MeOH, reflux, 2h.

corresponding pyrazole ligand in refluxing MeOH led to the desired disubstituted complexes [ReOClL$_2$] (**8**−**11**) (L = **L4**−**L7**) in high yields (Scheme 2). Complexes **8**−**11** nicely precipitated directly from the green reaction mixture on prolonged refluxing and were easily isolated by simple filtration. Subsequent washing with MeOH to remove residual free ligand and unreacted metal precursor yielded the complexes in 72−83% yield. The use of the metal precursor [ReOCl$_3$(OPPh$_3$)(SMe$_2$)],[24] a suitable starting material in the synthesis of disubstituted rhenium complexes, also resulted in the formation of the complexes **8**−**11**. However, yields obtained were significantly lower (appr. 35−45%) compared to [NBu$_4$][ReOCl$_4$].

Complexes **8**−**11** also show high stability toward air and moisture both in the solid state and in solution for several months at ambient temperature, similar to their monosubstituted analogues **1**−**7**. The disubstituted compounds are significantly better soluble in polar solvents like CHCl$_3$, ACN, DMSO, and so forth. NMR spectroscopy displayed two sets of signals for the attached ligands, in accordance with their inequivalent coordination geometry. For example in the ^{1}H NMR spectra, the protons of the methyl group at nitrogen gave inequivalent chemical shifts (5.88 and 4.42 ppm for **8**; 4.41 and 3.26 ppm for **9**; 4.52 and 3.31 ppm for **10**; 4.51 and 3.55 ppm for **11**). Single crystal structure analyses of complexes **8**, **10**, and **11** supported the structural assignment (vide infra) where the aryloxide oxygen is in trans position to the oxo group.[25] Attempts to synthesize disubstituted rhenium complexes under various conditions by employing ligands **L3**, **L5**, and **L7** failed. Presumably, the required basic condition during the synthetic procedure resulted in deprotonation of the NH group leading to unidentified polymeric materials.

A previously reported cationic rhenium(V) complex with the related oxazoline ligand showed to be more active in catalytic OAT reactions in comparison to its corresponding neutral complex.[26] For this reason, the conversion of **8** into a cationic compound by abstraction

Scheme 3. Synthesis of Cationic Complex [ReOCl(L1)$_2$(NCMe)](OTf) (**8a**)



of the residual chlorine atom was investigated. Thus, analogous to the published procedure for the oxazoline derivative, [ReOCl(L1)$_2$] (**8**) was treated with silver triflate (AgOTf) in refluxing ACN (Scheme 3) resulting in the cationic rhenium complex [ReOCl(L1)$_2$(NCMe)](OTf) (**8a**).[8,26] The initially green solution became dark red, and after cooling to room temperature the reaction mixture was layered with diethylether from which **8a** crystallized as a dark green solid in almost quantitative yield. NMR spectroscopy and mass spectrometry, as well as a single crystal X-ray analysis, support the formation of the cationic species.

The ^{1}H NMR spectrum of **8a** revealed only one set of ligand resonances indicating a higher symmetric species in contrast to complexes **8**−**11**. However, a single crystal X-ray diffraction analysis of **8a** revealed the molecule to contain two non-equivalent ligands as shown in Figure 5. Therefore, we expected to find a fast dynamic equilibrium for **8a** in solution, rendering the two pyrazole ligands equivalent by symmetry. A variable temperature ^{1}H NMR experiment (VT NMR) between −35 and 30 °C confirmed a dynamic equilibrium in solution (Figure 3). The coalescence of the signal for the methyl group at N2 of the pyrazole moiety is displayed in Figure 3. At 30 °C a singlet is observed for both methyl groups that broadens upon cooling and disappears between 5 and 0 °C. Upon further cooling below 0 °C, two broad singlets start to emerge, finally giving two sharp singlets at −35 °C. It is feasible that above 5 °C the semilabile ligands in **8a** exchange positions via a Berry pseudorotation faster than the NMR time scale, thereby rendering both ligands symmetry equivalent.

The coalescence temperature for **8a** in dimethylformamide (DMF) is 278.15 K, with a peak separation of 97.9 Hz at −35 °C. According to the Eyring theory the rate constant can be estimated with k = 217.5 Hz and with a free activation of energy of ΔG^* = 44.8 kJ/mol at the coalescence temperature.[27]

Crystallographic Structure Determination. The molecular structures of compounds **1**, **4**, **6**, **7**, **8**, **8a**, **10**, and **11** were determined by single crystal X-ray diffraction analysis. Molecular views of all complexes are shown in Figure 4 and Figure 5, selected bond lengths and angles are given in the Supporting Information. Full structural analysis and experimental details of data collection of the compounds can also be found in the Supporting Information.

All complexes show a six coordinate rhenium atom with distorted octahedral geometries and trans O−Re═O and cis halide−Re═O bonds (except cationic compound

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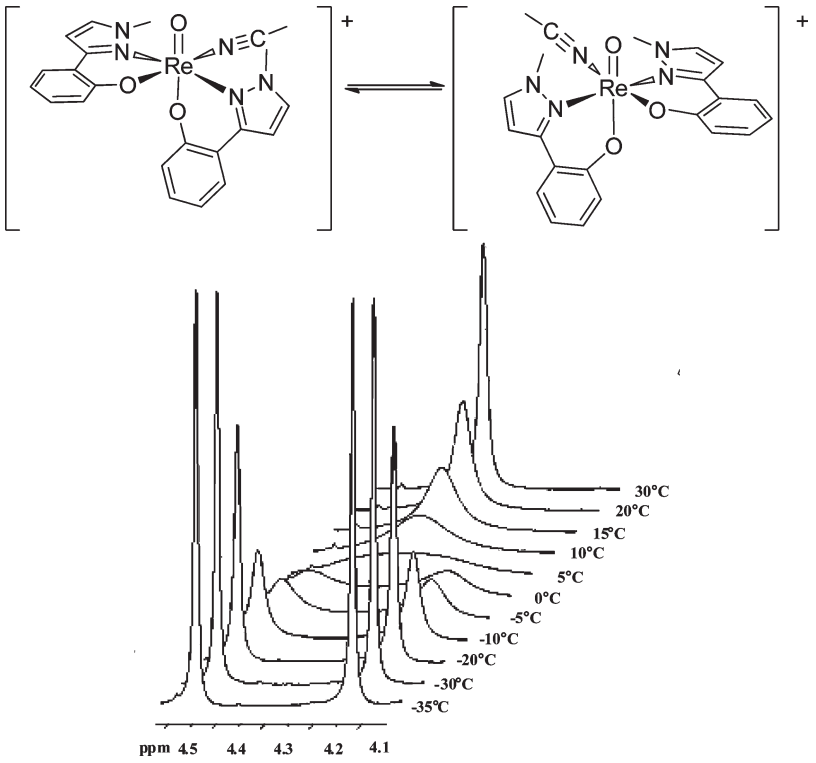

Figure 3. Variable temperature ^{1}H NMR spectra (in d_6-DMF) of resonances for the methyl groups at N2 of complex **8a** between 30 °C (back) and −35 °C (front).

8a). The trans coordination of the ligand oxygen toward the oxo ligand is well documented in the literature.[8,28,29] All complexes gave comparable bond lengths and angles within the expected range for previously published [$ReOX_2L(PPh_3)$] or [$ReOXL_2$] (X = Cl or Br) structures.[11,12,23,30−32]

Since the structures of monosubstituted complexes **1**, **4**, **6**, and **7** and of disubstituted complexes **8**, **8a**, **10**, and **11** are quite similar, only one complex from each class is discussed (**4** and **8**) as a representative example. Furthermore, the cationic complex **8a** is discussed in comparison to its neutral precursor **8**. In complex **4**, bromine atoms Br(1) and Br(2) are coordinated in cis position to each other with bond lengths of Re(1)−Br(1) 2.5668(3) and Re(1)−Br(2) 2.5246(3) Å including an angle Br(1)−Re(1)−Br(2) of 89.265(8)°. The nitrogen atom N(1) is in trans position to the bromine atom Br(2) with an angle of N(1)−Re(1)−Br(2) 162.94(6)°, and the phosphorus atom P(1) is in trans position to the bromine atom Br(1) with an angle of P(1)−Re(1)−Br(1) 174.313(16)°. The naphthol oxygen O(2) shows a trans coordination toward the Re═O unit with an angle of O(1)−Re(1)−O(2) of 173.06(8)°. The pyrazol ring and the naphtholate ring of the attached ligand include a dihedral angle of 9.91°.

In complex **8**, nitrogen atoms N(1) and N(3) of the ligands are coordinated in cis position to each other with bond lengths of Re(1)−N(1) 2.146(2) and Re(1)−N(3) 2.128(3) Å including an angle N(1)−Re(1)−N(3) of 95.82(9)°. The nitrogen atom N(1) of one ligand is in trans position to the oxygen atom O(3) of the second ligand with an angle of N(1)−Re(1)−O(3) 164.95(9)°, the nitrogen atom N(3) of one ligand is in trans position to the chlorine atom Cl(1) with an angle of N(3)−Re(1)−Cl(1) 172.62(7)°. The phenol oxygen O(2) shows a trans coordination toward the Re═O unit with an angle of O(1)−Re(1)−O(2) of 166.69(10)°. The nitrogen atoms and the oxygen atom of the ligands attached to the metal center include angles of N(1)−Re(1)−O(2) 81.13(9)° and N(3)−Re(1)−O(3) 88.40(9)°. The pyrazole and phenol ring of the attached ligands include dihedral angles of 24.81° and 13.75°. In contrast, in cationic complex **8a**, nitrogen atoms N(1) and N(3) of the ligands are coordinated in trans position to each other with lengths of Re(1)−N(1) 2.073(3) and Re(1)−N(3) 2.125(3) Å including an angle N(1)−Re(1)−N(3) of 168.42(10)°. The nitrogen N(1S) from the coordinated solvent Acetonitril has a comparable bond length of Re(1)−N(1S) 2.149(3) Å and is in trans position to the oxygen atom O(2) of the pyrazole ligand with an angle of N(1S)−Re(1)−O(2) 171.87(10)°. The phenol oxygen O(3) shows a trans coordination toward the Re═O unit with an angle of O(1)−Re(1)−O(3) of 162.75(10)°, which is slightly smaller than in **8**. The nitrogen atoms and the oxygen atom of the ligands attached to the metal center include angles of N(1)−Re(1)−O(2) 86.51(10)° and N(3)−Re(1)−O(3) 81.36(10)°. The pyrazole ring and the phenol ring of the attached ligands include dihedral angles of 20.17° and 20.00°.

Catalytic Epoxidations. Complexes **1**−**11** showed catalytic activity in the epoxidation of cyclooctene. This model reaction (Scheme 4) allowed us to study the

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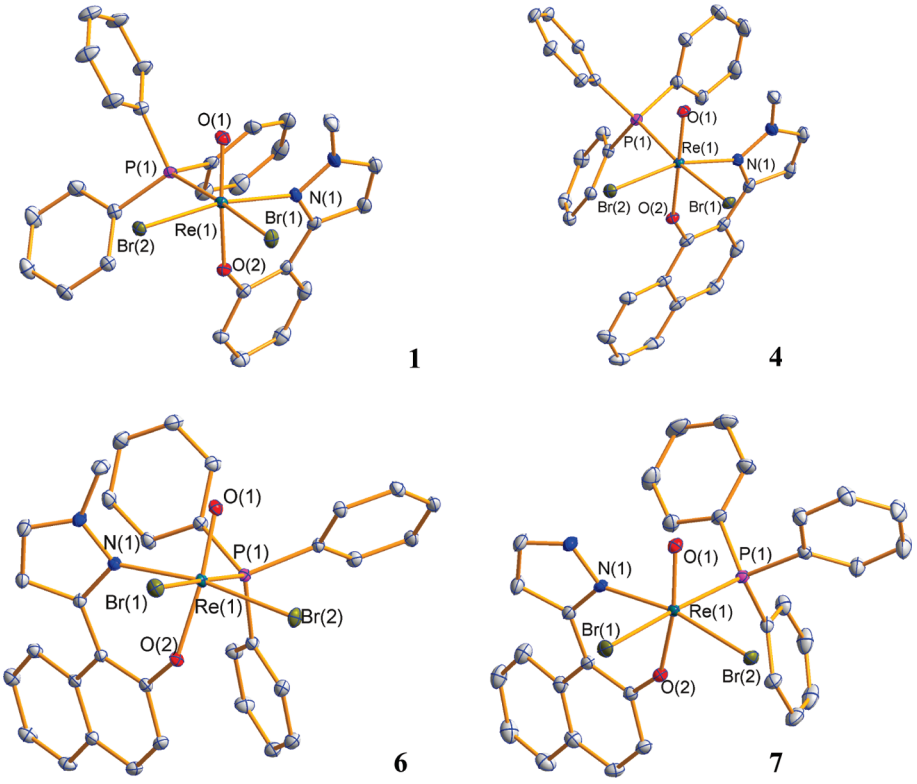


Figure 4. Molecular views of monosubstituted compounds **1**, **4**, **6**, and **7** with selected atom numbering. Hydrogen atoms are omitted for clarity.

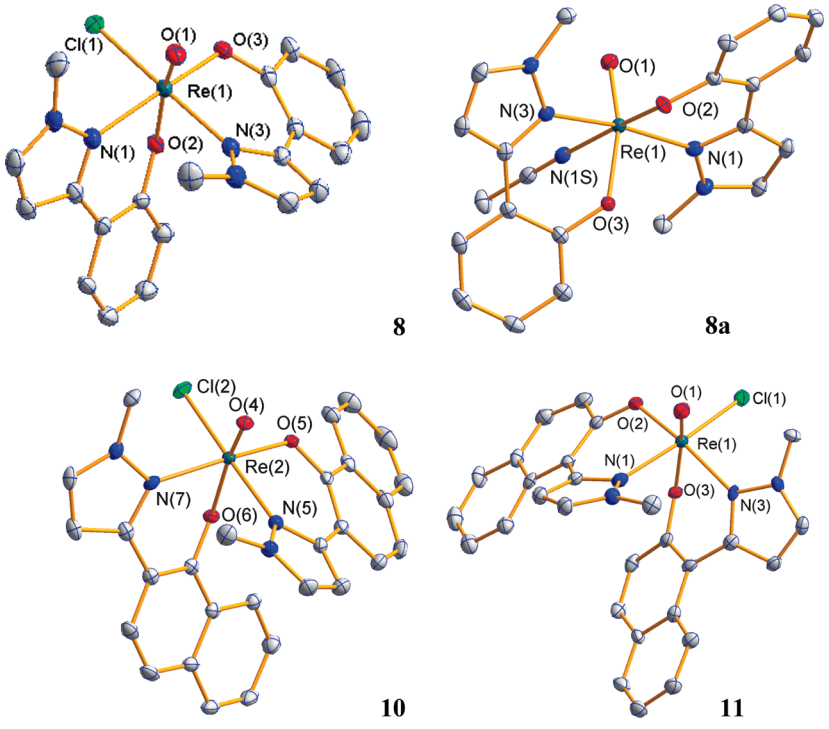
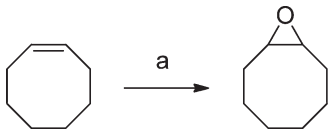


Figure 5. Molecular views of disubstituted compounds **8**, $[\mathbf{8a}]^+$, **10**, and **11** with selected atom numbering. Hydrogen atoms and the anion ($CF_3SO_3^-$) are omitted for clarity.

influence of the different ligands attached to the rhenium center. Few oxorhenium(V) complexes are known to show catalytic activity in epoxidation reactions using *tert*-butylhydrogenperoxide (TBHP) as the oxygen source.[7−11]

To evaluate the best conditions for the epoxidation reaction various solvents including acetonitrile, dichloromethane, chloroform, toluene, xylene, benzene, ethylenechloride, and tetrahydrofuran at several temperatures (25 or 50 °C, 80 °C and reflux for the higher boiling solvents) were investigated. The best results were obtained in $CHCl_3$ at 50 °C as complexes **1**−**11** show a good solubility in this solvent. In general, the low solubility in aromatic solvents probably prevented

Scheme 4[a]



[a] (a) 3 equiv of TBHP, 1−11 (2 mol %), $CHCl_3$, 50°C.

Table 1. Yields of Cyclooctane Epoxide[a]

Cat.	1	2	3	4	5	6	7	8	8a	9	10	11
yield	64	58	62	51	60	57	44	47	57	59	61	49

[a] Determ. by GC-MS. Conditions: 2 mol % catalyst, 3 equiv TBHP, $CHCl_3$, 50 °C, 120 min.

higher catalytic activities. Thus, in a typical experiment, 2 mol % of the corresponding catalyst and a 3-fold excess of the peroxide together with the olefin were heated to 50 °C in chloroform (Scheme 4). The conversion to the epoxide was monitored by GC-MS. Yields of epoxides ranged from 44 to 64% (Table 1). Similar activities were also reported by our group in previous systems tested in the epoxidation of cyclooctene.[11,12] In addition, no other side products, for example, epoxide ring opened 1,2-diols, were observed.

The reaction profile looked quite similar for all complexes. All catalytic reactions proceeded fast within the first 120 min after which no further product formation occurred (Figure 6). Upon addition of fresh TBHP to the reaction mixtures employing **1**−**11** after 420 min, the rate of formation of the epoxide was negligible accompanied by a color change of the initial solution pointing to catalyst decomposition. Attempts to isolate or characterize the decomposed rhenium species were inconclusive.

The catalytic performances of our pyrazole containing catalysts **1**−**11** were found to be only little influenced by the ligand backbone (phenol vs naphthol or NMe vs NH). From an electronic point of view, the properties of phenol and naphthol are possibly too similar which is reflected in the Re−O bond lengths in, for example, **1** and **2** (1.6912(19) Å and 1.6900(18) Å) as well as in **8** and **10** (1.687(2) Å and 1.6994(19) Å). The increased steric bulk of naphthol versus phenol ligands apparently does not influence the approach of the substrate, which occurs on the opposite side. Furthermore, comparison of catalysts **8** and **8a** shows the cationic compound to be slightly superior (57% for **8a** vs 47% for its neutral counterpart **8**) compatible with an expected faster approach of the substrate or the oxidant to the cationic compound.

The catalytically active species of the here described system is as yet unknown; however, in rhenium catalyzed reactions it has been suggested to be a peroxorhenium(VII) species.[7,8] This was elegantly shown in epoxidation using MTO where the 7-coordinate bisperoxo rhenium(VII) complex $[ReO_2(O_2)_2(H_2O)]$[3] is involved.

The high catalytic activity of the pyrazole containing systems prompted us to investigate the challenging catalytic reduction of perchlorate ClO_4^- to Cl^-.[15,16] Thus, similar to the procedure described by Abu-Omar et al., complex **8**, $LiClO_4$, and diphenyl sulfide as oxygen acceptor were dissolved in CD_3CN/D_2O (95/5 vol%) where the formation of diphenyl sulfoxide indicates oxygen atom transfer. However, only traces of diphenyl sulfoxide could be detected by ^1H NMR spectroscopy when using **8**.

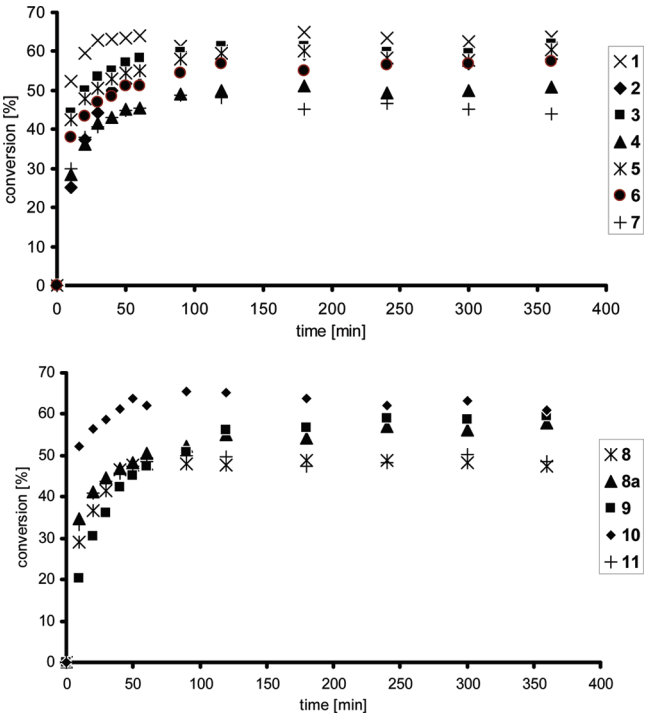


Figure 6. Reaction profile of the catalyzed cyclooctene epoxidation using catalysts **1**−**11**.

The reaction is accompanied by a complete decoloration of the typical green oxorhenium(V) solution indicating the formation of the colorless perrhenate ion.[9]

Conclusion

Within this report 11 new oxorhenium(V) complexes coordinated by pyrazole containing phenol and naphthol ligands are reported. Upon abstraction of a chlorine atom, a cationic complex could be isolated that showed a dynamic behavior in solution. The ligand synthesis was improved which makes them attractive because of their ease of preparation and modularity. All complexes have been fully characterized, 8 of them additionally by X-ray crystallography. The complexes are easy to handle because of their inertness to air and moisture. Consequently, syntheses as well as all further manipulations were performed in air using reagent grade solvents. Complexes **1**−**11** show good catalytic activity and selectivity in the epoxidation of cyclooctene with *tert*-butylhydrogenperoxide. The yield of cyclooctane epoxide varies between 44 and 64%, which is comparable to previously reported oxorhenium(V) systems. The maximum conversion is reached after only 120 min with no observable induction period. A significant difference in the catalytic activity of phenol- versus naphthol-based ligands could not be observed, most likely because of the similar electronic properties. Their ease of handling makes them attractive for further exploration as catalyst in other reactions which we are currently investigating.

Experimental Section

General Procedures. The metal precursors $[NBu_4][ReOCl_4]$[24] and $[ReOBr_3(PPh_3)_2]$[22] were prepared according to known procedures. The ligands **L1**−**L7**[17−20] were prepared with some modifications. Chemicals were purchased from commercial sources and were used without further purification. Solvents

were purified via a Pure Solv Solvent Purification System. NMR spectra were recorded with a Bruker (300 MHz) instrument. Chemical shifts are given in parts per million (ppm) and are referenced to residual protons in the solvent. Signals are described as s (singlet), d (doublet), dd (double doublet), t (triplet), m (multiplet) and coupling constants (*J*) are given in hertz (Hz). Elemental analyses were carried out using a Heraeus Vario Elementar automatic analyzer. Mass spectra were recorded with an Agilent 5973 MSD−Direct Probe using the EI ionization technique. Samples for infrared spectroscopy were directly measured on a Bruker Optics ALPHA FT-IR Spectrometer. GC-MS measurements were performed on an Agilent 7890 A with an Agilent 19091J−433 column coupled to a mass spectrometer type Agilent 5975 C.

Catalytic Epoxidation Reaction. Cyclooctene (0.30 g, 2.72 mmol) and the respective rhenium(V) catalyst (2 mol %) were dissolved in chloroform (20 mL). The reaction mixture was heated to 50 °C followed by addition of TBHP (1.5 mL, 5.5 M solution in decane, 8.2 mmol). Prior to GC-MS analyses aliquot samples were quenched with MnO_2 with subsequent dilution.

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed at low temperature using graphite−monochromated Mo Kα radiation (0.71073 Å) with a BRUKER−AXS SMART APEX CCD diffractometer. The data were reduced to F_o^2 and corrected for absorption effects with SAINT[33] and SADABS,[34] or an empirical absorption correction[35] was applied. The structures were solved by direct methods or by Patterson superposition procedures where direct methods failed, and refined by full−matrix least−squares method (SHELXL97).[36,37] All non−hydrogen atoms were refined with anisotropic displacement parameters without any constraints. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Common isotropic displacement parameters were refined for the H atoms bonded to the same C atom or to the same phenyl ring. All diagrams were drawn with 50% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds **1**, **4**, **6**, **7**, **8**, **8a**, **10**, and **11** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC−800294 (**1**), CCDC−800292 (**4**), CCDC−800293 (**6**), CCDC−800297 (**7**), CCDC−801192 (**8**), CCDC−800295 (**8a**), CCDC−800298 (**10**), and CCDC−800296 (11). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44−1223/336−033; E−mail: deposit@ccdc.cam.ac.uk]. A summary of the crystallographic data can be found in the Supporting Information which is available online free of charge.

General Procedure 1 for Monosubstituted Rhenium Complexes 1−7. To a suspension of the precursor $[ReOBr_3(PPh_3)_2]$ in the indicated solvent was added the respective ligand (**L1**−**L7**). The suspension was heated to reflux whereupon a clear solution was formed. After stirring for 6 h under refluxing conditions, the solution was reduced to a small volume and the compounds were allowed to precipitate to give the desired complexes **1**−**7** in 57 to 72% yields. Recrystallization was performed from a mixture of CH_2Cl_2 and diethylether.

General Procedure 2 for Disubstituted Rhenium Complexes 8−11. The respective ligand was dissolved in diethylether or tetrahydrofuran (THF), and NaH (60% in mineral oil) was added. The mixture was allowed to stir at room temperature for 1 h, after which the solvent was removed. The obtained residue was added in small portion to a solution of $[NBu_4][ReOCl_4]$ in MeOH, and the mixture was refluxed for 2 h. The precipitate formed was filtered, washed with MeOH and diethylether to give complexes **8**−**11** in 72 to 83% yields. Recrystallization was performed from a mixture of CH_2Cl_2 and diethylether.

Synthesis of $[ReOBr_2(L1)(PPh_3)]$ (1). The compound was prepared following the general procedure 1 by the use of $[ReOBr_3(PPh_3)_2]$ (200 mg, 0.20 mmol) and **L1** (35 mg, 0.20 mmol) in ACN (50 mL). The green solution was concentrated in vacuo whereupon green crystals precipitated to give **1** (102 mg, 64%) . ^{1}H NMR (d_6-DMF, 300 MHz) δ: 8.14 (d, *J* 2.9 Hz, 1H, CH), 7.55−7.40 (m, 16H, CH), 7.05 (d, *J* 2.9 Hz, 1H, CH), 7.00 (m, 1H, CH), 6.92 (dt, *J* 7.6, 1.0 Hz, 1H, CH), 6.75 (dd, *J* 8.1, 1.0 Hz, 1H, CH), 4.09 (s, 3H, CH_3) ppm. ^{31}P NMR (DMF, 121 MHz) δ: −22.2 ppm. IR: 3122, 3065, 2955, 1433, 1249, 1090, 691, 868, 743, 690, 497 cm^{-1}. EI-MS: *m*/*z* 536 [M^+ − PPh_3, Re^{187}]. Anal. Calcd. for $C_{28}H_{24}Br_2N_2O_2PRe$ (797.49): C 42.17, H 3.03, N 3.51; found: C 42.38, H 3.02, N 3.50.

Synthesis of $[ReOBr_2(L2)(PPh_3)]$ (2). The compound was prepared following the general procedure 1 by the use of $[ReOCl_3(PPh_3)_2]$ (500 mg, 0.60 mmol) and **L2** (105 mg, 0.56 mmol) in ACN/acetone 1 + 1 v/v (100 mL). The green solution was concentrated in vacuo whereupon green crystals precipitated to give **2** (230 mg, 57%). ^{1}H NMR (d_8-THF, 300 MHz) δ: 7.36 (d, *J* 2.8 Hz, 1H, CH), 7.46 (m, 6H, CH), 7.35 (m, 3H, CH), 7.23 (m, 6H, CH), 6.88 (d, *J* 1.5 Hz, 1H, CH), 6.64 (dd, *J* 8.4, 1.7 Hz, 1H, CH), 6.64 (d, *J* 2.8 Hz, 1H, CH), 6.48 (d, *J* 8.4 Hz, 1H, CH), 4.14 (s, 3H, CH_3), 2.10 (s, 3H, CH_3) ppm. ^{31}P NMR (d_8-THF, 121 MHz) δ: −25.7 ppm. IR: 3123, 3051, 2994, 1434, 1259, 1092, 957, 882, 818, 779, 743, 525, 501 cm^{-1}. EI-MS: *m*/*z* 460 [M^+-PPh_3, Re^{187}]. Anal. Calcd. for $C_{29}H_{26}Br_2N_2O_2PRe$ (811.52): C 42.92, H 3.23, N 3.45; found: C 42.48, H 3.04, N 3.49.

Synthesis of $[ReOBr_2(L3)(PPh_3)]$ (3). The compound was prepared following the general procedure 1 by the use of $[ReOBr_3(PPh_3)_2]$ (500 mg, 0.52 mmol) and **L3** (104 mg, 0.60 mmol) in ACN (100 mL). The green solution was concentrated in vacuo whereupon green crystals precipitated to give **3** (274 mg, 65%). ^{1}H NMR (d_6-DMF, 300 MHz) δ: 13.57 (s, 1H, NH), 7.82 (dd, *J* 2.6, 1.9 Hz, 1H, CH), 7.58−7.40 (m, 16H, CH), 7.08 (m, 1H, CH), 6.88 (dd, *J* 8.3, 1.9 Hz, 1H, CH), 6.64 (d, *J* 8.3 Hz, 1H, CH), 2.18 (s, 3H, CH_3) ppm. ^{31}P NMR (d_6-DMF, 121 MHz) δ: −17.0 ppm. IR: 3211, 3050, 2970, 2862, 2862, 1453, 1247, 1185, 1091, 956, 879, 819, 691, 524 cm^{-1}. EI-MS: *m*/*z* 536 [M^+-PPh_3, Re^{187}]. Anal. Calcd. for $C_{28}H_{24}Br_2N_2O_2PRe$ (797.49): C 42.17, H 3.03, N 3.51; found: C 43.15, H 3.27, N 3.42.

Synthesis of $[ReOBr_2(L4)(PPh_3)]$ (4). The compound was prepared following the general procedure 1 by employing $[ReOBr_3(PPh_3)_2]$ (300 mg, 0.31 mmol) and **L4** (70 mg, 0.31 mmol) in THF (50 mL). The red solution was concentrated in vacuo whereupon dark green crystals precipitated to give **4** (190 mg, 72%). ^{1}H NMR (d_6-DMSO, 300 MHz) δ: 8.05 (m, 1H, CH), 7.97 (m, 1H, CH), 7.84 (m, 3H, CH), 7.63−7.50 (m, 16H, CH), 7.38 (s, 1H, CH), 7.00 (d, *J* 2.3 Hz, 1H, CH), 3.92 (s, 3H, CH_3) ppm. ^{31}P NMR (d_6-DMSO, 121 MHz) δ: −22.4 ppm. IR: 3050, 1432, 1380, 1094, 954, 738, 688, 522, 498 cm^{-1}. EI-MS: *m*/*z* 586 [M^+ − PPh_3, Re^{187}]. Anal. Calcd. for $C_{32}H_{26}Br_2N_2O_2PRe$ (847.55): C 45.35, H 3.09, N 3.31; found: C 45.58, H 3.18, N 3.24.

Synthesis of $[ReOBr_2(L5)(PPh_3)]$ (5). The compound was prepared following the general procedure 1 by employing $[ReOBr_3(PPh_3)_2]$ (250 mg, 0.26 mmol) and **L5** (70 mg, 0.31 mmol) in THF (50 mL). The red solution was concentrated in vacuo whereupon a dark solid precipitated to give **5** (136 mg, 63%). ^{1}H NMR (d_6-DMF, 300 MHz) δ: 8.33 (m, 1H, CH), 8.24 (m, 1H, CH), 8.04 (m, 1H, CH), 8.02 (d, *J* 2.5 Hz, 1H, CH), 7.65−7.51

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(m, 18H, CH), 7.11 (d, *J* 2.5 Hz, 1H, CH) ppm. ^{31}P NMR (d_6-DMF, 121 MHz) δ: −18.0 ppm. IR: 3199, 3050, 1480, 1089, 950, 893, 755, 686, 651, 509, 493 cm^{-1}. EI-MS: *m*/*z* 572 [M$^+$ − PPh_3, Re^{187}]. Anal. Calcd. for $C_{31}H_{24}Br_2N_2O_2PRe$ (833.52): C 44.67, H 2.90, N 3.36; found: C 43.84, H 2.79, N 3.33.

Synthesis of [ReOBr$_2$(L6)(PPh$_3$)] (6). The compound was prepared following the general procedure 1 by employing [$ReOBr_3(PPh_3)_2$] (500 mg, 0.52 mmol) and **L6** (117 mg, 0.52 mmol) in acetone (50 mL). The red solution was concentrated in vacuo whereupon green crystals of **6** precipitated (300 mg, 68%). ^{1}H NMR (d_6-DMF, 300 MHz) δ: 8.42 (d, *J* 2.8 Hz, 1H, CH), 8.02 (m, 2H, CH), 7.78 (dd, *J* 8.1, 1 Hz, 1H, CH), 7.67 (m. 2H, CH), 7.45 (m, 8H, CH), 7.34 (m, 7H, CH), 7.05 (d, *J* 2.8 Hz, 1H, CH), 6.82 (d, *J* 8.9 Hz, 1H, CH), 4.34 (s, 3H, CH_3) ppm. ^{31}P NMR (d_6-DMF, 121 MHz) δ: −22.4 ppm. IR: 3098, 3059, 1520, 1433, 1247, 952, 756, 689, 529, 503 cm^{-1}. EI-MS: *m*/*z* 586 [M$^+$-PPh_3, Re^{187}]. Anal. Calcd. for $C_{32}H_{26}Br_2N_2O_2PRe$ (847.55): C 45.35, H 3.09, N 3.31; found: C 45.08, H 3.06, N 3.19

Synthesis of [ReOBr$_2$(L7)(PPh$_3$)] (7). The compound was prepared following the general procedure 1 by employing [$ReOBr_3(PPh_3)_2$] (500 mg, 0.52 mmol) and **L7** (110 mg, 0.52 mmol) in acetone (50 mL). The red solution was concentrated in vacuum whereupon green crystals precipitated to give **7** (256 mg, 59%). ^{1}H NMR (d_6-DMSO, 300 MHz) δ 7.85 (m, 3H, CH), 7.62−7.48 (m, 16H, CH), 7.26 (m, 3H, CH), 7.17 (d, *J* 8.3 Hz, 1H, CH) ppm. ^{31}P NMR (d_6-DMSO, 121 MHz) δ: −20.0 ppm. IR: 3198, 3053, 1519, 1431, 1237, 1187, 949, 739, 688, 505, 492 cm^{-1}. EI-MS: *m*/*z* 572 [M$^+$-PPh_3, Re^{187}]. Anal. Calcd. for $C_{31}H_{24}Br_2N_2O_2PRe$ (833.52): C 44.67, H 2.90, N 3.36; found: C 44.68, H 2.88, N 3.42.

Synthesis of [ReOCl(L1)$_2$] (8). The compound was prepared following the general procedure 2 by employing [NBu_4]-[$ReOCl_4$] (500 mg, 0.85 mmol) and **L1** (300 mg, 1.72 mmol) in MeOH (50 mL) to give **8** (357 mg, 72%) as a green solid. Recrystallization was performed from CH_2Cl_2/diethylether. ^{1}H NMR (d_6-DMSO, 300 MHz) δ: 8.32 (d, *J* 2.7 Hz, 1H, CH), 7.80 (m, 2H, CH), 7.63 (d, *J* 7.8 Hz, 1H, CH), 7.39 (dt, *J* 8.5, 7.2, 1.6 Hz, 1H, CH), 7.14, 7.12 (2 m, 2H, CH), 6.94, 6.89 (2 m, 3H, CH), 6.79, 6.78 (2t, *J* 6.5 Hz, 1H, CH), 5.88 (d, *J* 8.1 Hz, 1H, CH_3), 4.42 (s, 3H, CH_3), 3.27 (s, 3H, CH_3) ppm. ^{13}C NMR (d_6-DMSO, 75 MHz): δ 165.1, 158.6, 151.4, 148.9, 140.7, 138.4, 131.5, 130.8, 128.6, 128.0, 122.2, 120.8, 120.1, 118.1, 117.5, 103.9, 103.8, 100.0, 40.6, 37.8 ppm. IR: 3135, 2993, 1600, 1517, 1444, 1295, 1227, 1131, 1085, 951, 852, 757 cm^{-1}. EI-MS: *m*/*z* 584 [M$^+$], 549 [M$^+$ − Cl, Re^{187}]. Anal. Calcd. for $C_{20}H_{18}ClN_4O_3Re$ (584.04): C 41.12, H 3.11, N 9.59; found: C 40.18, H 3.32, N 8.63.

Synthesis of [ReO(L1)$_2$](CF$_3$SO$_3$) (8a). A mixture of **8** (200 mg, 0.34 mmol) and silver triflate (88 mg, 0.34 mmol) in ACN (5 mL) was refluxed for 20 min. The initially dark green solution turned dark red and was allowed to cool to room temperature. The mixture was layered with diethylether whereupon dark green crystals precipitated to give **8a** (215 mg, 86%). ^{1}H NMR (d_6-DMF, 300 MHz, 30 °C) δ 8.67 (s, 2H, CH), 8.10 (d, *J* 7.4 Hz, 2H, CH), 7.54 (s, 2H, CH), 7.45 (ddd, *J* 8.6, 7.4, 1.6 Hz, 2H, CH), 7.18 (d, *J* 8.2 Hz, 2H, CH), 7.10 (t, *J* 7.5 Hz, 2H, CH), 4.35 (s, 6H, CH_3), 2.15 (s, 3H, CH_3 of ACN) ppm. ^{1}H NMR (d_6-DMF, 300 MHz, −35 °C) δ 8.90 (d, *J* 2.3 Hz, 1H, CH), 8.58 (d, *J* 2.2 Hz, 1H, CH), 8.24 (d, *J* 7.7 Hz, 1H, CH), 7.98 (d, overlapped by DMF, 1H, CH), 7.80 (d, *J* 2.4 Hz, 1H, CH), 7.43 (m, 3H, CH), 7.17 (m, 3H, CH), 7.03 (t, *J* 7.5 Hz, 1H, CH), 4.46 (s, 3H, CH_3), 4.13 (s, 3H, CH_3), 2.17 (s, 3H, CH_3) ppm. ^{13}C NMR (d_6-DMF, 75 MHz, 30 °C) δ 162.0, 150.2, 141.6, 131.9, 128.9, 123.9, 121.7, 119.1, 104.5, 39.8, 0.6 ppm, triflate carbon not detected. IR: 3112, 2975, 2915, 2283, 1518, 1462, 1262, 1150, 1027, 958, 852, 757, 630 cm^{-1}. EI-MS: *m*/*z* 698 [M$^+$ − ACN], 549 [M$^+$ − CF_3SO_3 − ACN, Re^{187}].

Synthesis of [ReOCl(L2)$_2$] (9). The compound was prepared following the general procedure 2 by employing [NBu_4]-[$ReOCl_4$] (500 mg, 0.85 mmol) and **L2** (320 mg, 1.70 mmol) in MeOH (50 mL) to give **9** (374 mg, 72%) as a green solid. Recrystallization was performed from CH_2Cl_2/diethylether. ^{1}H NMR (d_6-DMSO, 300 MHz) δ: 8.29 (d, *J* 2.7 Hz, 1H, CH), 7.80 (d, *J* 2.7 Hz, 1H, CH), 7.61 (d, *J* 1.6 Hz, 1H, CH), 7.45 (d, *J* 1.6 Hz, 1H, CH), 7.18 (dd, *J* 8.3, 1.9 Hz, 1H, CH), 7.13 (d, *J* 2.7 Hz, 1H, CH), 7.03 (d, *J* 8.3 Hz, 1H, CH), 6.94 (d, *J* 2.8 Hz, 1H, CH), 6.78 (m, 1H, CH), 5.82 (d, *J* 8.2 Hz, 1H, CH), 4.41 (s, 3H, CH_3), 3.26 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.14 (s, 3H, CH_3) ppm. ^{13}C NMR (d_6-DMSO, 75 MHz) δ: 163.4, 156.4, 151.4, 148.9, 140.5, 138.1, 132.2, 131.6, 129.3, 131.6, 128.3, 128.0, 122.0, 118.0, 117.6, 117.0, 103.7, 39.9 (signal overlapped by DMSO) 37.8, 20.8, 20.6 ppm. IR: 3120, 3018, 2918, 1520, 1269, 953, 809, 553 cm^{-1}. EI-MS: *m*/*z* 612 [M$^+$], 577 [M$^+$ − Cl, Re^{187}]. Anal. Calcd. for $C_{22}H_{22}ClN_4O_3Re$ (612.10): C 43.17, H 3.62, N 9.15; found: C 42.90, H 3.65, N 8.96

Synthesis of [ReOCl(L4)$_2$] (10). The compound was prepared following the general procedure 2 by employing [NBu_4]-[$ReOCl_4$] (500 mg, 0.85 mmol) and **L4** (380 mg, 1.70 mmol) in MeOH (50 mL) to give **10** (465 mg, 80%) as a greenish solid. Recrystallization was performed from CH_2Cl_2/diethylether. ^{1}H NMR (d_6-DMSO, 300 MHz) δ 8.95 (m, 1H, CH), 8.34 (d, *J* 2.7 Hz, 1H, CH), 7.96 (m, 1H, CH), 7.80 (d, *J* 2.7 Hz, 1H, CH), 7.77 (d, *J* 8.7 Hz, 1H, CH), 7.67−7.60 (m, 3H, CH), 7.53 (d, *J* 8.7 Hz, 1H, CH), 7.41 (d, *J* 8.7 Hz, 1H, CH), 7.32 (d, *J* 8.7 Hz, 1H, CH), 7.28 (d, *J* 2.6 Hz, 1H, CH), 7.23 (m, 1H, CH), 6.83 (d, *J* 2.7 Hz, 1H, CH), 6.65 (t, *J* 7.6 Hz, 1H, CH), 6.50 (d, *J* 8.3 Hz, 1H, CH), 4.52 (s, 3H, CH_3), 3.31 (s, 3H, CH_3) ppm. ^{13}C NMR (d_6-DMSO, 75 MHz) δ: 161.5, 155.4, 151.9, 149.4, 141.1, 138.5, 135.1, 135.0, 127.9, 127.8, 127.7, 127.5, 127.0, 126.7, 126.0, 125.5, 125.1, 125.0, 124.9, 123.8, 120.4, 119.7, 111.7, 111.6, 104.2, 104.0, 39.9 (signal overlapped by DMSO), 38.1 ppm. IR: 3120, 3050, 2945, 1522, 1357, 1231, 1085, 942, 889, 762, 576 cm^{-1}. EI-MS: *m*/*z* 684 [M$^+$], 649 [M$^+$ − Cl, Re^{187}]. Anal. Calcd. for $C_{28}H_{22}ClN_4O_3Re$ (684.16): C 49.16, H 3.24, N 8.19; found: C 47.80, H 3.27, N 7.93.

Synthesis of [ReOCl(L6)$_2$] (11). The compound was prepared following the general procedure 2 by employing [NBu_4]-[$ReOCl_4$] (500 mg, 0.85 mmol) and **L6** (380 mg, 1.70 mmol) in MeOH (50 mL) to give **11** (480 mg, 83%) as a greenish solid. Recrystallization was performed from CH_2Cl_2/diethylether. ^{1}H NMR (d_6-DMSO, 300 MHz) δ: 8.45 (d, *J* 2.7 Hz, 1H, CH), 8.32 (d, *J* 8.5 Hz, 1H, CH), 7.95 (m, 2H, CH), 7.83−7.34 (m, 3H, CH), 7.52 (t, *J* 7.2 Hz, 2H, CH), 7.46 (d, *J* 8.9 Hz, 1H, CH), 7.36 (m, 3H, CH), 7.14 (d, *J* 2.7 Hz, 1H, CH), 6.77 (d, *J* 2.7 Hz, 1H, CH), 5.68 (d, *J* 8.8 Hz, 1H, CH), 4.51 (s, 3H, CH_3), 3.55 (s, 3H, CH_3) ppm. ^{13}C NMR (d_6-DMSO, 75 MHz) δ: 162.9, 159.7, 148.6, 147.3, 140.8, 138.1, 132.3, 131.5, 130.9, 129.8, 129.4, 128.6, 128.1, 127.0, 124.9, 124.2, 123.9, 123.8, 123.0, 119.9, 111.8, 111.4, 107.6, 107.4, 39.9 (signal overlapped by DMSO) 38.5 ppm. IR: 3118, 3049, 2924, 1589, 1517, 1328, 1235, 977, 821, 791, 743, 555 cm^{-1}. EI-MS: *m*/*z* 684 [M$^+$], 649 [M$^+$ − Cl, Re^{187}]. Anal. Calcd. for $C_{28}H_{22}ClN_4O_3Re$ (684.16): C 49.16, H 3.24, N 8.19; found: C 49.09, H 3.25, N 8.18.

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Supporting Information Available: Full crystallographic details on complexes **1**, **4**, **6**, **7**, **8**, **8a**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.