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Oxidorhenium(V) Complexes with Tetradentate Iminophenolate Ligands: Influence of Ligand Flexibility on the Coordination Motif and Oxygen-Atom-Transfer Activity

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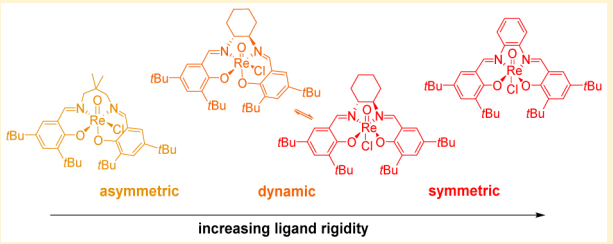
Supporting Information

ABSTRACT: The synthesis of oxidorhenium(V) complexes **1**−**3** coordinated by tetradentate iminophenolate ligands H_2**L1**−H_2**L3** bearing backbones of different rigidity (alkyl, cycloalkyl, and phenyl bridges) allows for the formation of distinct geometric isomers, including a symmetric *trans*-oxidochlorido coordination motif in complex **3**. The complex employing a cycloalkyl-bridged ligand (**2**) of intermediate rigidity exhibits an interesting solvent- and temperature-dependent equilibrium between a symmetric (trans) isomer and an asymmetric (cis) isomer in solution. The occurrence of a symmetric isomer for **2** and **3** is confirmed by single-crystal X-ray diffraction analysis. Chlorido abstraction from **2** with AgOTf yields the corresponding cationic complex **2a**, which does not exhibit an isomeric equilibrium in solution but adopts the isomeric form predominant for **2** in a given solvent. All complexes were, furthermore, employed in three benchmark oxygen-atom-transfer (OAT) reactions, namely, the reduction of perchlorate, the epoxidation of cyclooctene, and OAT from dimethyl sulfoxide (DMSO) to triphenylphosphane (PPh_3), to assess the influence of the isomeric structure on the reactivity in these reactions. In perchlorate reduction, a clear structural influence was observed, where the trans arrangement in **3** led to the complete absence of activity. In the epoxidation reaction, all complexes led to comparable epoxide yields, albeit higher catalytic activity but lower overall stability of the catalysts with a trans arrangement was observed. In OAT from DMSO to PPh_3, also a clear structural dependence was observed, where the trans complex **3** led to full phosphane conversion with an excess of oxidant, while the cis compound **1** was completely inactive.



INTRODUCTION

Over the past decades, rhenium has become a very important element for oxygen-atom-transfer (OAT) reactions, with the major interest focusing on oxidation states V+ and VII+.[1] One of the rhenium compounds most intensely investigated for its application in oxidation reactions is the rhenium(VII) complex methyltrioxidorhenium (MTO).[2] MTO has been successfully employed as a catalyst in a variety of transformations such as aldehyde olefination, olefin metathesis, and epoxidation of olefins by using of hydrogen peroxide as the oxidant.[3] To date, research interest in MTO and its catalysis remains high.[4−8] The benefits of MTO as an epoxidation catalyst are its ease of preparation, broad range of feasible substrates like cycloalkenes, allyl alcohols, and *n*-alkenes, and its broad activity range in both catalyst loading and reaction conditions.[9] Nevertheless, sensitive epoxides are sometimes found to be catalytically hydrolyzed to the respective diols or follow-up reaction products.[9−14] The addition of nitrogen-containing Lewis base ligands often prevents hydrolysis.[4,6,7,10−12,14,15] Also the beneficial use of ionic liquids as well as an ionic rhenium(VII) system has recently been explored.[16] However, there is still interest in robust catalyst alternatives. In this endeavor, the attention turned to rhenium(V) compounds because of their high stability under ambient conditions. They were at first investigated for their catalytic activity in several other OAT reactions.[17,18] Consequently, oxidorhenium(V) complexes with various ligand systems were investigated for their applicability in the epoxidation of olefins, albeit with varying success. Generally, the investigated complexes were coordinated by bi- or tetradentate chelating N,O ligands. With bidentate ligands, monosubstituted complexes of the type $[ReOCl_2L(EPh_3)]$ (E = P, As) and disubstituted complexes of the type $[ReOXL_2]$ (X = monoanionic, monodentate ligand) were investigated.[19−22] A comprehensive survey of previous work was recently published by Machura.[23] In our group, very promising results were obtained by employing bidentate pyrazole phenolate ligands, where full conversion of cyclooctene within 3 h and a noteworthy tolerance toward aqueous H_2O_2 as the oxidant were observed for the first time in oxidorhenium(V)-catalyzed oxidation reactions.[24,25]

An OAT reaction of growing importance is the homogeneous reduction of the persistent perchlorate anion. Because perchlorate has been identified as a dangerous pollutant incorporating severe health risks, the development of robust and stable catalyst systems suitable for the clean reduction of perchlorate to harmless chloride ions is of high importance.[26,27]

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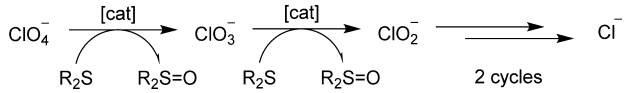
In such a reaction, perchlorate acts as an oxygen donor and is stepwise reduced according to Scheme 1.

Scheme 1. Stepwise Reduction of Perchlorate via Catalytic OAT to an Organic Sulfide as an Oxygen Acceptor



Similar to epoxidation reactions, rhenium(V) systems have also been investigated for perchlorate reduction. Abu-Omar and co-workers showed three oxidorhenium(V) compounds to be active catalysts in perchlorate reduction with organic sulfides as oxygen acceptors.[28] They investigated neutral and cationic oxidorhenium(V) complexes with two bidentate oxazolinephenolato ligands (hoz) (Figure 1) as well as an oxidorhenium(V)

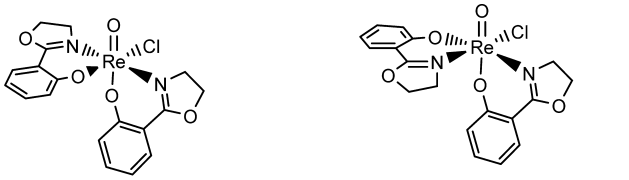


Figure 1. Stereoisomers of the catalyst $[ReOCl(hoz)_2]$ and oxygen-acceptor conversion in a perchlorate reduction according to Scheme 1. Conversions correspond to diphenyl sulfide as the oxygen acceptor (3.2 mol % catalyst at room temperature vide infra).[28,29]

complex employing a tetradentate iminophenolate ligand related to **H_2L1** (Figure 2), first reported by Herrmann and co-workers.[21] The neutral complexes $[ReOCl(hoz)_2]$ and its cationic analogue $[ReO(hoz)_2](OTf)$ were able to reduce perchlorate quantitatively after 4 h with Me_2S and Et_2S as oxygen acceptors. The compound employing the tetradentate ligand, on the other hand, reached 57% and 69% conversion after 48 h, with Ph_2S and Me_2S as substrates, respectively.[28] The catalytic pathway of the reaction employing an oxazoline-based catalyst has been thoroughly investigated by Abu-Omar and co-workers as well as our group.[29−31] Within our investigations, a stereoisomer of the originally reported catalyst could be isolated. We subsequently found that the isomeric form of the employed catalyst is of crucial importance for catalytic activity and is presumably retained during the course of the reaction (Figure 1).[29] Research interest in oxazoline-based systems remains high, as demonstrated by a recent study about the configuration dynamics and catalytic activities of oxazoline- and thiazolinephenolate-based oxidorhenium(V) complexes.[32]

Considering the importance of the coordination motif on the activity and bearing in mind that complexes employing tetradentate iminophenolate ligands exhibit significant catalytic activity in the reduction of perchlorate as well as olefin epoxidation, we decided to continue our investigation of the influence of the coordination motif on these OAT reactions in a systematic fashion. To do so, oxidorhenium(V) complexes with tetradentate iminophenolate ligands incorporating bis(imine) backbones of different rigidity were synthesized, in an attempt to enforce specific coordination motifs, i.e., ligand arrangements at the metal center. Here we present the successful synthesis of a series of monomeric oxidorhenium(V) complexes coordinated by tetradentate ligands with increasing rigidity in the backbone. Furthermore, the cationic analogue of a complex employing a cyclohexyl-bridged ligand was prepared via chlorido abstraction using AgOTf. In that course, we present two new rare examples of oxidorhenium(V) complexes employing a *trans*-O═Re−Cl moiety,[33,34] with one being a chiral oxidorhenium(V) catalyst structurally related to Jacobsen's well-known manganese(III) species.[35] The previously published complex **1** (Scheme 2) is included in the study, for which a more atom-efficient synthesis is reported.[21] Reactivity trends in three benchmark OAT reactions—perchlorate reduction, epoxidation, and OAT from dimethyl sulfoxide (DMSO) to a phosphane—are discussed with respect to the coordination motif.

RESULTS AND DISCUSSION

Ligand Synthesis. Ligands **H_2L1**−**H_2L3** were prepared according to published procedures in high yield.[21,36,37] The ligands differ in their backbone, i.e., the unit bridging the two phenolate moieties. For this study, alkyl, cycloalkyl, and aryl moieties were used as backbones. To increase the solubility of the envisioned oxidorhenium complexes, the phenolate moieties were equipped with *t*Bu substituents. The ligand **H_2L2** was used in both its racemic and enantiopure *R*,*R* forms. The ligands, ordered by increasing rigidity, are depicted in Figure 2.

Complex Synthesis. For the synthesis of oxidorhenium(V) complexes with ligands **H_2L1**−**H_2L3**, the metal precursor $[ReOCl_3(Me_2S)(OPPh_3)]$[38,39] was used and a method according to a published protocol was employed.[21] Heating a solution of 2 equiv of the respective ligand (1 equiv acts as HCl scavenger) and $[ReOCl_3(Me_2S)(OPPh_3)]$ in anhydrous acetonitrile (MeCN) under a N_2 atmosphere resulted in a color change to dark brown (**1** and **2**) or deep red (**3**), respectively, indicating the formation of complexes. Careful workup of the resulting crude products (vide infra) led to the

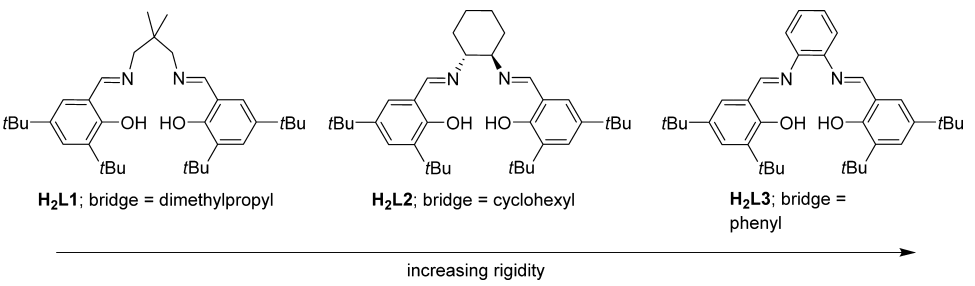


Figure 2. Ligands **H_2L1**−**H_2L3** investigated within this study. The chiral ligand **H_2L2** was used in both its racemic and enantiopure *R*,*R* forms.

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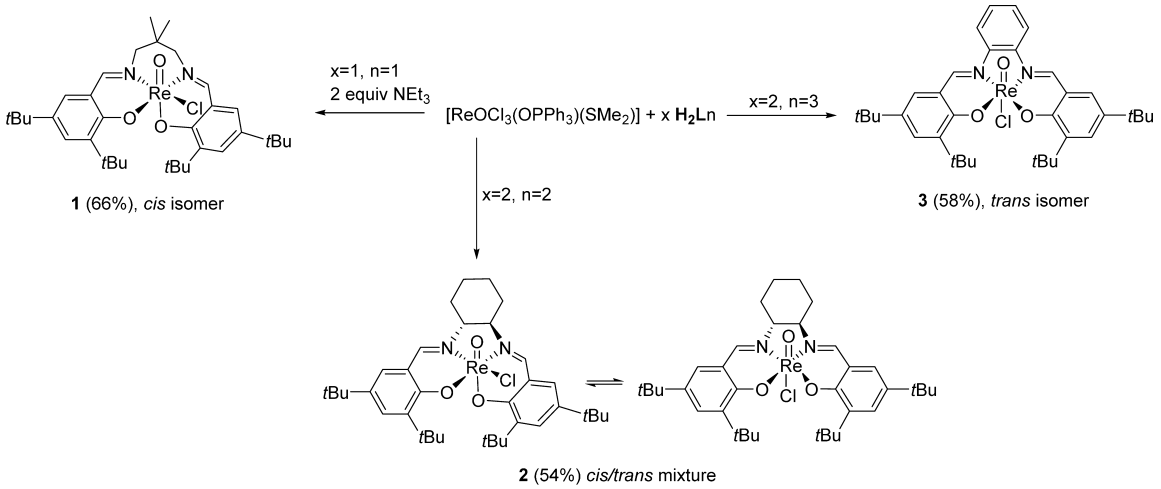
Scheme 2. Synthesis of Complexes 1−3[a]



[a]Complex **2** is isolated as a mixture of two isomers (cis and trans, with respect to the oxido and chlorido ligands) that are in dynamic equilibrium in solution (vide infra).

Table 1. Selected Crystallographic Data and Structure Refinement for Complexes 1−3

	1	*trans*-2	3
empirical formula	$C_{35}H_{52}ClN_2O_3Re$	$C_{36}H_{52}ClN_2O_3Re$	$C_{36}H_{46}ClN_2O_3Re$
fw	770.43	782.45	776.40
cryst description	block, yellow	needle, orange	plate, red
cryst system, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	orthorhombic, *Pbca*
a, Å	16.4474(5)	11.9835(8)	10.8495(8)
b, Å	11.7992(4)	12.9480(9)	20.5248(16)
c, Å	18.4902(5)	13.1585(9)	30.165(3)
α, deg		70.315(2)	
β, deg	101.6019(11)	81.226(2)	
γ, deg		72.538(2)	
volume, Å^3	3515.01(19)	1830.8(2)	6717.3(9)
Z	4	2	8
reflns collected/unique	35370/10249	12947/7159	17726/6588
R(int), *R*(*σ*)	0.0253, 0.0235	0.0292, 0.0695	0.0556, 0.1407
completeness, % (Θ_{max}, deg)	100.0 (30.0)	99.9 (26.0)	99.7 (26.0)
data/param/restraints	10249/412/0	7159/421/19	6588/324/9
signif unique reflns [$I > 2\sigma(I)$]	9300	5748	3731
GOF on F^2	1.048	1.142	1.029
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0168, wR2 = 0.0403	R1 = 0.0450, wR2 = 0.0869	R1 = 0.0661, wR2 = 0.1071
R indices (all data)	R1 = 0.0204, wR2 = 0.0416	R1 = 0.0642, wR2 = 0.0913	R1 = 0.1301, wR2 = 0.1172
largest difference peak and hole, e/Å^3	1.227 and −0.712	0.789 and −1.052	1.425 and −2.776
CCDC no.	1439655	1439656	1439657

mononuclear oxidorhenium(V) complexes **1−3** (Table 1) in moderate-to-good yield as brown-to-red solids. The synthesis gave the same product and similar yields for both racemic and enantiopure H_2**L2**. Substitution of the second equiv of the ligand by 2 equiv of NEt_3 also led to the desired complex **1**; attempts to synthesize **2** or **3** in that manner did not yield the targeted species. However, the readily precipitating H_2**L**·2HCl could easily be recycled via treatment with, e.g., Na_2CO_3. Complexes **1−3** are stable toward air and moderately stable toward moisture. They are well soluble in most polar and apolar organic solvents including benzene and heptane. Direct exposure to hydrous solvents as well as prolonged standing in solution at ambient atmosphere slowly led to decomposition to a free ligand and NMR-inactive rhenium species due to hydrolysis. Scheme 2 depicts the synthesized complexes **1−3** and their structural motifs.

In principle, there are four possible coordination modes of a tetradentate ligand (Figure 3). Structure **A** corresponds to a trans isomer with respect to the O═Re−Cl moiety, whereas in structures **B−D**, the O═Re−Cl moiety is arranged in a cis fashion, differing in the overall ligand orientation. Structures of type **A** are uncommon,[33,34] and the vast majority of oxidorhenium(V) complexes bearing tetradentate ligands

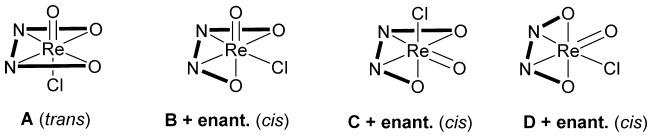


Figure 3. Possible coordination motifs at the oxidorhenium(V) metal center with a tetradentate O,N,N,O ligand.

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employ a *cis*-O═Re−Cl motif and are of the structure type **B**. Structure types **C** and **D** have not been described in the literature. It has also been observed that complexes of the structure type **A** tend to dimerize in the presence of water, yielding μ-oxido-bridged dinuclear complexes of the type $[(ReOL)_2(\mu\text{-}O)]$.[33,34,40−42]

The ^{1}H NMR spectrum of complex **1** is consistent with the literature[21] and shows two distinct sets of aromatic and imine protons, thus pointing toward an asymmetric coordination motif. Subsequent single-crystal X-ray diffraction analysis of **1** confirmed the asymmetric structure type **B** in the solid state (vide infra). In contrast, the rigid ligand $\mathbf{H_2L3}$ enforces the symmetric coordination motif **A**, as demonstrated by the ^{1}H NMR spectrum of **3**, showing only signals for a symmetric ligand. With the cyclohexyl-bridged ligand $\mathbf{H_2L2}$, the resulting complex **2** exists as a mixture of two isomers, supposedly symmetric trans (structure type **A**) and asymmetric cis (structure type **B**) isomers. For **2**, the respective resonances are distinguishable by ^{1}H NMR spectroscopy. Interestingly, the aromatic region shows six resonances for each isomer (two imine and four aromatic protons). Thus, also in the proposed trans isomer, all protons are nonhomotopic because of the asymmetric cyclohexyl bridge. The proposal of such a trans isomer is corroborated by the fact that there are two sets of aromatic signals with only minor differences in chemical shifts (Figure 5) and single-crystal X-ray diffraction analysis, which confirmed the existence of the trans conformation in the solid state (vide infra). The postulation is, furthermore, in compliance with the literature, where van Bommel et al. suggest an equilibrium between the structure types **A** and **B** for related alkoxide complexes.[41]

^{1}H NMR measurements of a sample of **2** at two different temperatures in CD_3CN revealed a temperature dependence of the isomeric ratio. The experiment showed an increase of the trans isomer from approximately 35% at 25 °C to 45% at 60 °C (Figure 4).

To provide the thermodynamic parameters of the isomeric equilibrium in MeCN, we additionally performed a variable-temperature NMR experiment in CD_3CN (−30 to +60 °C in steps of 10 °C) and determined the isomeric ratios via integration of the respective ^{1}H NMR resonances (Figure S9). With the help of a van't Hoff plot (linear fit, $R^2 = 0.996$; Figure S10), the thermodynamic equilibrium parameters ΔH = (8.48 ± 0.18) kJ·mol^{-1} and ΔS = (24.3 ± 0.6) J·mol^{-1}·K^{-1} were calculated. From the data, it is evident that the cis isomer is thermodynamically favored and the conversion of cis isomer to trans isomer is thus endothermic. The increase of the entropy could be the result of easier chloride dissociation in *trans*-**2**.

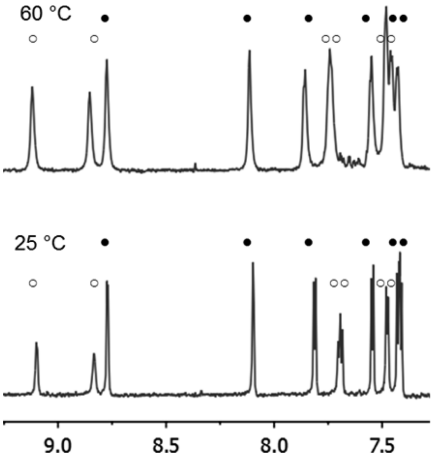

Figure 4. ^{1}H NMR spectra of **2** in CD_3CN at 25 °C (bottom) and 60 °C (top) showing a change in the ratio between isomers *cis*-**2** (●) and *trans*-**2** (○).

Compound **2** also exhibits an interesting solvent-dependent dynamic behavior in solution, which can be nicely studied via ^{1}H NMR spectroscopy in different solvents. Whereas the cis/trans ratio in the apolar solvent C_6D_6 is approximately 1:5, the equilibrium shifts toward the cis isomer with increasing solvent polarity, leading to a ratio of 2:1 in CD_3CN (Figure 5).

The arrangement of the chlorido and oxido ligands leads to a higher overall dipole moment of *cis*-**2** in comparison to the trans isomer. Polar solvents thus possibly stabilize the more polar isomeric form, leading to the observed solvent dependency.

To further our understanding of the isomeric form of **2** during catalytic processes, the cationic complex **2a** of the formula [ReO(**L2**)(MeCN)](OTf) was synthesized. This compound was obtained via the addition of 1 equiv of AgOTf to a solution of **2** in MeCN and subsequent removal of the insoluble AgCl precipitate, according to Scheme 3. The macroscopic behavior of complex **2a** is comparable to that of the related compound **2**, with a noteworthy difference being a generally lower solubility and pronounced sensitivity in solution. This sensitivity is also reflected in the electrospray ionization mass spectriometry (ESI-MS) spectrum of **2a**, where a significant peak for the oxidized rhenium(VII) species $[ReO_2(\mathbf{L2})]^+$ is observed (Figure S9).

For complex **2a**, only signals corresponding to one isomer are observed in ^{1}H NMR spectroscopy, which is in contrast to the dynamic isomerism observed for compound **2**. In $CDCl_3$, the ^{1}H NMR spectrum of cationic species **2a** nicely resembles the signal set for the major symmetric isomer *trans*-**2**, corroborating this arrangement to be sterically favored after chlorido abstraction. Because of the conditions employed in perchlorate reduction (vide infra), ^{1}H NMR data for **2a** have also been collected in CD_3CN. Here a situation different from that in $CDCl_3$ is found: the two imine protons as well as all four aromatic signals are distinct, which hints toward an asymmetric arrangement, suggesting that the cationic species **2a** exclusively adopts the isomeric cis form in CD_3CN, which is also predominant for **2** in the same solvent (Figure 6). These findings are in accordance with an enhanced dynamic behavior in five-coodintate complexes. In the cationic species **2a**, where the solvent molecule is only weakly bound, isomerization occurs readily. Similarly, also in **2**, dissociation of chloride enables isomerization albeit to a weaker extent, giving rise of two isomers.

Additionally, in the ^{1}H NMR spectrum of **2a**, a broad peak denoting the coordinating MeCN solvent was present in the aliphatic region. Whereas the peaks integrated for roughly three protons in $CDCl_3$, in CD_3CN, the integral was lower, likely because of the exchange of coordinating CH_3CN with CD_3CN (Figures S6−S8).

Molecular Structures. Solid-state molecular structures of complexes **1**, **2** (trans isomer; crystals from a batch employing racemic $\mathbf{H_2L2}$), and **3** were obtained by single-crystal X-ray diffraction analysis. Molecular views are given in Figure 7, and selected angles and bond lengths are provided in Table 2. In general, all bond distances are within the expected range of

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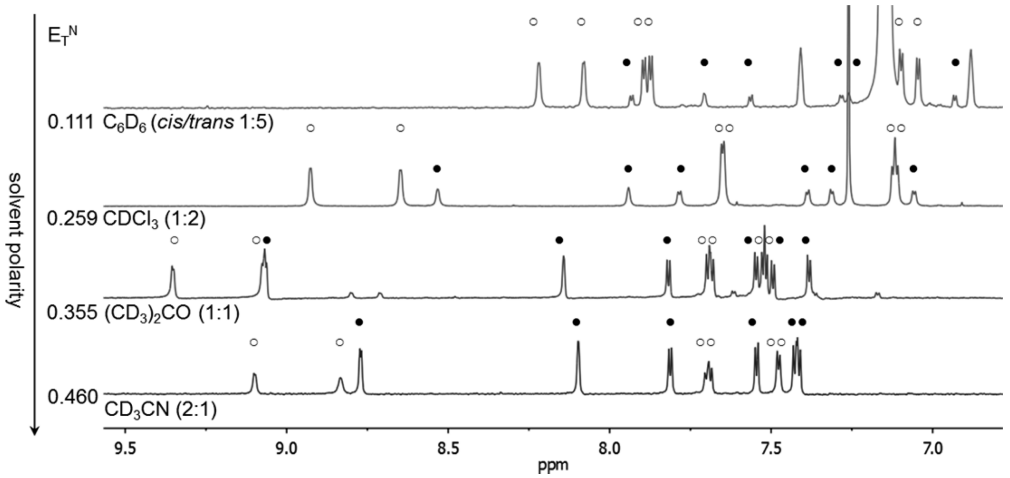
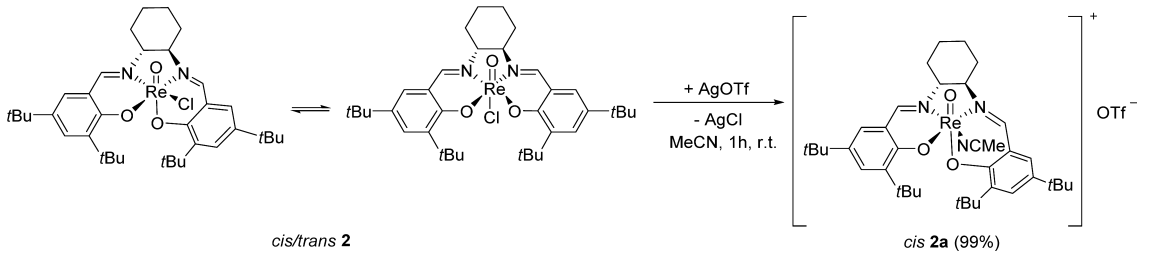


Figure 5. Ratio of the coordination isomers *cis*-**2** (●) and *trans*-**2** (○) depending on the solvent polarity (E_T^N values according to Reichardt).[43] Because of the low solubility in C_6D_6, the ^{13}C satellites of the solvent residual signal are visible as two peaks that are unaccounted for. The additional peaks in the spectrum recorded in $(CD_3)_2CO$ most likely correspond to a μ-oxido-bridged dimer originating from H_2O traces in the solvent.

Scheme 3. Synthesis of the Cationic Complex 2a[a]



[a]The vacant coordination site originating from abstraction of the chlorido ligand is occupied by an MeCN molecule. Whereas compound **2** exists as an isomeric mixture in solution, **2a** shows no such behavior and adopts a single isomer in a given solvent (vide infra).

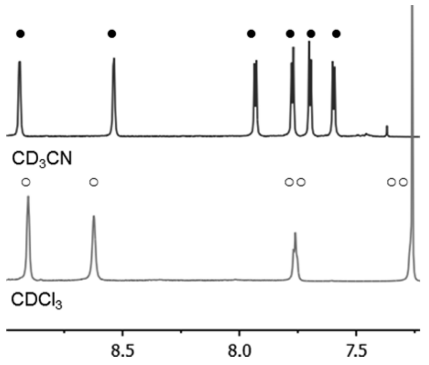


Figure 6. Aromatic region of the ^1H NMR spectra of **2a** in CD_3CN (top) and $CDCl_3$ (bottom), featuring resonances corresponding to asymmetric cis (CD_3CN, ●) or symmetric trans ($CDCl_3$, ○) conformation in solution. One aromatic signal in the bottom spectrum is obscured by the residual solvent peak.

related previously reported oxidorhenium(V) complexes.[21,33,34,42]

In all complexes, the rhenium atoms are coordinated in a distorted octahedral fashion by the dianionic tetradentate Schiff base ligand and by the terminal oxido and chlorido ligands. The alkyl-bridged ligand $L1^{2-}$ is arranged in an asymmetric fashion around the metal center (structure type **B**, Figure 3) in complex **1**, while the ligands in complexes *trans*-**2** and **3** are arranged in a symmetric fashion around the metal center (structure type **A**, Figure 3). Whereas the phenyl-bridged ligand only allows for this arrangement, the cycloalkyl-bridged ligand is more flexible and leads to a partial rearrangement to *cis*-**2** in solution, a putative structural isomer of **1** (vide supra). These coordination modes lead to a *cis*-O═Re−Cl arrangement in **1** (and *cis*-**2**) and to an unusual *trans*-O═Re−Cl arrangement in *trans*-**2** and **3**. This results in an elongated Re−Cl bond in the symmetric complexes *trans*-**2** and **3** in comparison to that of **1**. In **3**, also the Re═O bond length is elongated. Furthermore, the O═Re−Cl bond angles show significant deviations from 180° in the symmetric structures of *trans*-**2** and **3**, which is in agreement with a generally favorable *cis*-O═Re−Cl arrangement (Table 2).

Perchlorate Reduction. OAT from perchlorate ions to organic sulfides R_2S (R = Me, Ph) according to Scheme 4, using oxidorhenium(V) complexes **1**−**3** and **2a** as OAT catalysts, was investigated.

Catalytic data are summarized in Table 3. Yields of sulfoxide were determined via ^1H NMR measurements at given times and integration of the respective sulfide and sulfoxide peak areas with the solvent residual signal as internal standards. Only compound **1** exhibits a significant catalytic reactivity, while compounds **2** and **2a** react very little and compound **3** is inactive. Generally, obtained yields were found to be low at room temperature but increase at 50 °C. Nevertheless, after 24 h of reaction time at 50 °C, a significant discoloration was observable, likely due to catalyst decomposition to perrhenate because of oxidation and hydrolysis. This is also reflected in only a minute increase in the sulfoxide yield from 24 to 60 h. The activity of **1** is significantly lower than that obtained with

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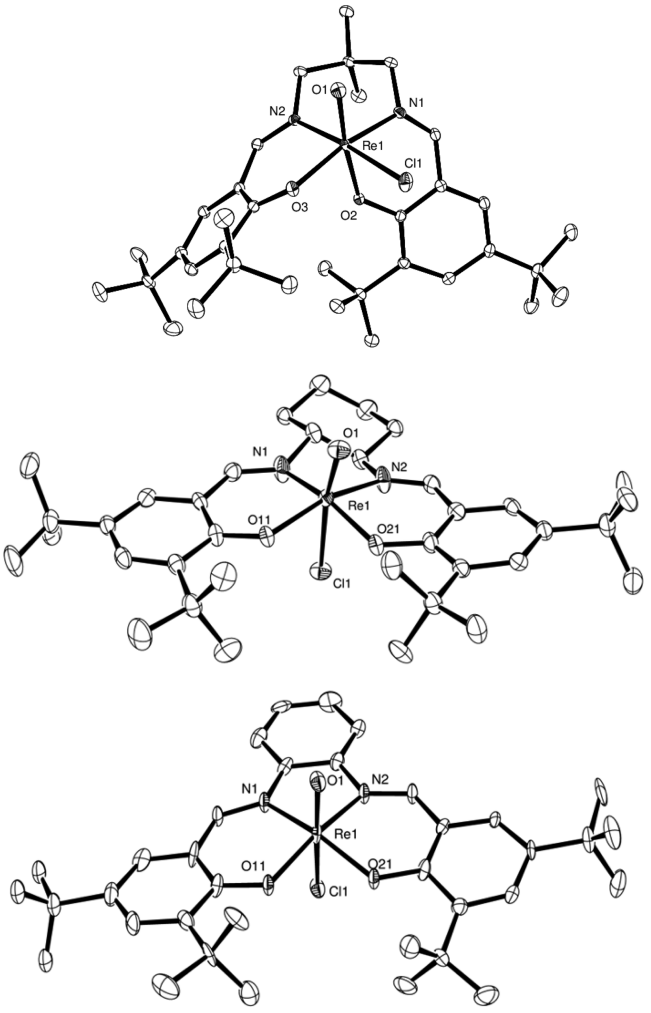
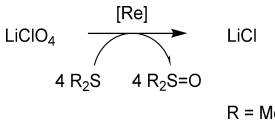


Figure 7. Molecular views (50% probability level) of **1** (top), *trans*-**2** (middle), and **3** (bottom). Hydrogen atoms as well as solvent molecules are omitted for clarity reasons. For disordered fragments, only atoms with a higher site occupation factor are depicted.

Table 2. Selected Bond Lenghts [Å] and Angles [deg] for Complexes 1, *trans*-2, and 3

	1	*trans*-2	3
Re–O1	1.6952(11)	1.664(8)	1.721(9)
Re–O2 (O11)	1.9935(11)	1.983(3)	1.973(5)
Re–O3 (O21)	2.0078(11)	1.993(3)	1.999(5)
Re–Cl1	2.3814(4)	2.518(3)	2.494(3)
Re–N1	2.0773(13)	2.014(4)	2.042(7)
Re–N2	2.0773(13)	2.078(3)	2.059(6)
O1–Re1–Cl1	95.65(4)	171.6(3)	165.3(3)

Scheme 4. Reduction of Lithium Perchlorate to Lithium Chloride via Catalytic OAT Using an Organic Sulfide as the Oxygen Acceptor



complexes coordinated by bidentate oxazoline phenolate ligands in the N,N-trans position (Figure 1), supporting the importance of the N,N-trans position in the catalyst, because in

Table 3. Yields (%) of Sulfoxide after 4/24/60 h[a]

substrate	1 (cis)	2 (cis/trans)	2a (cis)	3 (trans)
Me_2S	2/8/15	1/3/5	1/2/4	0/0/0
Ph_2S	2/7/13	1/3/5	1/3/3	0/0/0
Ph_2S[b]	13/28/31	5/9/9		0/2/2
Me_2S[c]	8/24/48	1/3/4		1/1/1

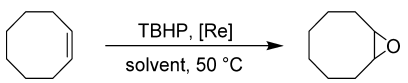
[a]Conditions: 3.2 mol % catalyst, 4 equiv of R_2S, 95:5 (v/v) CD_3CN/D_2O, room temperature. [b]Reaction temperature: 50 °C. [c]$AgClO_4$ as the oxygen source.

all tested complexes the tetradentate ligand framework restricts the arrangement of the two nitrogen donors in the cis position.[28,29] However, the reactivity of **1** is also lower compared to not only the N,N-cis isomer of the oxazoline coordinated catalyst (Figure 1) but also a rhenium(V) catalyst coordinated by a tetradentate iminophenolate ligand, where 69% (Me_2S) and 57% (Ph_2S) conversions were observed after 48 h at room temperature.[28] The only structural differences between **1** and the latter compound are the *tert*-butyl substituents in **1**. The introduction of *tert*-butyl groups has a significant impact on the steric and electronic situations, both presumably reducing the catalytic activity. Whereas steric hindrance obviously hampers substrate coordination, the additional electron density at the metal center possibly stabilizes the rhenium(VII) dioxido intermediate, thus decreasing the catalytic activity.[27−31] The occurrence of a significant peak for $[ReO_2L]^+$ in the ESI-MS spectrum of **2a** substantiates this assumption (Figure S9).

The inactivity of **3**, where the oxido group and the potential active site remain in the trans position to each other, is interesting and delivers ample evidence for the previously reported mechanistic details with the oxazoline system where the active site remains cis to oxido throughout the catalytic cycle, avoiding a highly unfavorable rhenium(VII) *trans*-dioxido intermediate.[27−30,32] However, an explanation of the low reactivity of complexes **2** and **2a** remains elusive. Although found in an isomeric mixture in solution, the predominant isomer of **2** in the reaction solvent exhibits an active site cis to the oxido ligand (vide supra). Furthermore, abstraction of Cl^- leads solely to the cis isomer in the reaction solvent. This would suggest that higher reactivity should be observable. Thus, at the current stage of research, we attribute the very low activity of **2** and **2a** to the pronounced sensitivity of **2a** under reaction conditions.

Catalytic Epoxidation. Complexes **1**−**3** and **2a** were tested in the catalytic epoxidation of cyclooctene according to Scheme 5. Conditions used were 1 mol % of catalyst with 3 equiv of *tert*-

Scheme 5. Rhenium(V)-Catalyzed Oxidation of Cyclooctene



butyl hydroperoxide (TBHP) in three different solvents at 50 °C. The solvents were chosen for their decreasing polarity, namely, chloroform, toluene, and *n*-heptane.

All tested complexes were active in cyclooctene epoxidation, albeit with moderate yields. As summarized in Table 4, the maximum conversion to epoxide was reached within the first 7 h, in essentially all catalytic experiments. Prolonged reaction times did not lead to a significant increase in the epoxide yield. Conversions between 50 and 70%, as reported herein, were

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Table 4. Yields (%) of Epoxide in the Epoxidation of *cis*-Cyclooctene with TBHP after 1/4/7/24 h[a]

solvent	1 (cis)	2 (cis/trans)	2a (trans)	3 (trans)
chloroform	16/52/54/52	50/59/68/62	39/28/24/8	42/48/50/44
toluene	17/35/43/65	31/46/51/52	0/45/47/40	37/49/51/50
n-heptane	7/19/32/43	15/28/32/38	0/51/52/46	18/30/34/37

[a]Conditions: 1 mol % catalyst, 3 equiv of TBHP, 50 °C.

observed for the vast majority of oxidorhenium(V) complexes.[20,22,25,44−46] This limitation in the catalytic activity can be attributed to two main effects: oxidation to unreactive perrhenate(VII) species by the oxidant TBHP as well as inhibition by accumulating *t*BuOH, the follow-up product after TBHP oxidation.[21,22,45,46]

However, by a direct comparison of the performance of complexes **1**−**3** and **2a** in catalysis, interesting trends regarding the influence of the isomeric form could be observed. Compound **1** was previously used in the same epoxidation reaction in chloroform.[21] In our hands, a similar yield was obtained, but we could not detect an induction period of 70 min without catalysis. Nonetheless, conversion is low (16%) within the first hour for **1**, whereas complexes **2** and **3** showed the highest catalytic activity within this period. No significant catalytic activity was observed after 1 h (compounds **2** and **3**) and 4 h (compound **1**). The cationic complex **2a** was practically inactive after 4 h of reaction time in toluene and heptane, whereas in chloroform, the epoxide yield decreased from 39% after 1 h to 8% after 24 h, hinting toward fast decomposition and follow-up reactions in the chlorinated solvent (Table 4). These results clearly indicate a higher activity but lower stability of complexes with a trans arrangement in comparison to the *cis*-O═Re−Cl arrangement in compound **1**. In all reactions, no significant amount of substrate was found after 24 h of reaction time, but several new peaks, corresponding to side and follow-up products, could be observed in the gas chromatography−mass spectrometry (GC−MS) spectra. Similarly, in catalysis experiments run at 80 °C in toluene, heptane, and 1,2-dichloroethane, full substrate conversion but only a minute yield of epoxide were observed with all tested compounds after 7 h. All tested complexes were inactive in the epoxidation of styrene and 1-octene.

To confirm the suggested stability difference of compounds **1**−**3** in epoxidation catalysis, at the end of a catalytic run in toluene (after 24 h), a new aliquot of cyclooctene and TBHP was added to each catalyst solution, respectively, and samples were withdrawn to determine conversion via GC−MS. Interestingly, all three catalysts were still active in the epoxidation of cyclooctene, albeit with lower selectivity than that in the first 24 h. A total of 9 h after the second addition of cyclooctene and TBHP, complexes **1**−**3** reached respective yields of epoxide of 48%, 46%, and 41%. At prolonged reaction time (33 h after the second addition of cyclooctene and TBHP), complexes **2** and **3** showed no more conversion of substrate and complex **1** showed an increase from 48% to 53% epoxide. These results are in agreement with a higher stability of the cis complex **1**.

OAT from DMSO to Triphenylphosphane (PPh_3). Complexes **1**−**3** were tested for their ability to catalyze the OAT reaction from DMSO to PPh_3 according to Scheme 6. The conditions used were 5 mol % catalyst with 1 or 10 equiv of DMSO in deuterated benzene at room temperature.

The activity of complexes **1**−**3** in the investigated OAT reaction is strongly dependent on their structures. Whereas the asymmetric cis complex **1** was completely inactive, as reflected by no observable amount of phosphane oxide after 24 h, the cis/trans dynamic complex **2** showed mediocre conversion and complex **3** fully converted PPh_3 to its oxide within the reaction time if 10 equiv of DMSO was used. After 5 days (120 h) of reaction time, complex **2** reached full conversion under the same conditions. All results are summarized in Table 5.

Scheme 6. Rhenium(V)-Catalyzed OAT from DMSO to PPh_3

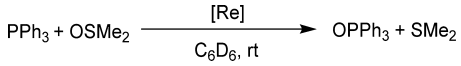

Table 5. Yields (%) of $OPPh_3$ after 24 h of OAT from DMSO[a]

DMSO	1 (cis)	2 (cis/trans)	3 (trans)
10 equiv	0	38 (100[b])	100
1 equiv	0	15	31 (7[c])

[a]Conditions: 5 mol % catalyst, room temperature, C_6D_6. [b]Full conversion after 120 h of reaction time. [c]1 mol % catalyst.

The significant activity difference of **1** and **3** is likely a result of the readily dissociating oxido trans chloride in complex **3**, which provides a vacant coordination site for the DMSO molecule.[18]

CONCLUSION

The synthesis of oxidorhenium(V) complexes with three tetradentate iminophenolate ligands of increasing rigidity is described. While the previously reported compound **1** exhibits a *cis*-O═Re−Cl arrangement, **2** and **3** belong to the group of uncommon rhenium complexes with a *trans*-O═Re−Cl moiety. Furthermore, in solution, **2** has been found to exhibit a solvent- and temperature- dependent equilibrium of symmetric trans and asymmetric cis isomers, likely caused by an interplay of steric strain and the disfavored *trans*-O═Re−Cl arrangement. In contrast, cationic **2a** was found to be isomerically pure in solution, adopting the conformation found to be major for **2** in a given solvent, thus symmetric in $CDCl_3$ and asymmetric in CD_3CN. In perchlorate reduction, an influence of the coordination motif on the reactivity could be observed. Only the asymmetric complex **1** exhibits significant activity, whereas **3** remains completely inactive, substantiating that species with an active site trans to the oxido moiety do not partake in catalytic perchlorate reduction.[28,29] Also, a clear influence of the *tert*-butyl substituents' electronic and steric properties in perchlorate reduction was observed. In the epoxidation of cyclooctene, all complexes were found to be catalytically active but suffer from chemoselectivity problems, especially at high temperatures. Interestingly, higher catalytic activity but lower stability of the symmetric trans conformation over the asymmetric cis conformation could be observed. With the cationic compound **2a**, catalysis experiments in toluene and

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heptane led to epoxide yields comparable to those observed with **2** and **3**, whereas in $CHCl_3$, decomposition was predominant for the cationic compound. The most significant structure-related activity difference was observed in the catalytic OAT reaction from DMSO to PPh_3, where the cis compound **1** was completely inactive, whereas the trans compound **3** led to full phosphane oxidation under the employed reaction conditions with an excess of DMSO.

EXPERIMENTAL SECTION

Caution! *Perchlorate salts of complexes with organic ligands are potentially explosive. Personal safety equipment has to be worn at all times when handling perchlorate salts in OAT reactions.* Unless specified otherwise, experiments were performed under inert conditions using standard Schlenk equipment. Commercially available chemicals were purchased from Sigma-Aldrich and used as received. No further purification or drying operations were performed. The metal precursor $[ReOCl_3(OPPh_3)(SMe_2)]$ was synthesized according to known procedures.[39] Solvents were purified via a Pure Solv MD-4-EN solvent purification system from Innovative Technology, Inc. Methanol was refluxed over activated magnesium for at least 24 h and then distilled prior to use. The ^1H, ^{13}C, and ^{19}F HSQC NMR spectra were recorded on a Bruker Optics instrument at 300, 75, and 282 MHz, respectively. Peaks are denoted as singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), triplet (t), pseudodoublet ("d"), pseudotriplet ("t"), and multiplet (m). Solvents used and the peak assignment are mentioned at the specific data sets. Electron impact mass spectrometry (EI-MS) measurements were performed with an Agilent 5973 MSD mass spectrometer with a push rod. High-resolution mass spectrometry (HR-MS; ESI^+) measurements were performed at the Department of Analytical Chemistry, University of Graz, using a Thermo Scientific Q-Exactive mass spectrometer in positive-ion mode. Peaks are denoted as cationic mass peaks, and the unit is the corresponding mass/charge ion ratio. GC−MS measurements were performed with an Agilent 7890 A gas chromatograph (column type, Agilent 19091J-433), coupled to an Agilent 5975 C mass spectrometer. Samples for IR spectroscopy were measured on a Bruker Optics Alpha FT-IR spectrometer. IR bands are reported with wavenumbers (cm^{-1}) and intensities (s, strong; m, medium; w, weak). UV−vis spectra were recorded with a Varian Cary 50 in absorption scan mode using a Hellma Analytics High Precision Quartz cell with a 2 mm light path. A Heidolph Parallel Synthesizer 1 was used for all epoxidation experiments. Elemental analyses were measured at the Microanalytical Laboratory, University of Vienna.

Single-Crystal X-ray Diffraction Analyses. Single-crystal X-ray diffraction analyses were measured on a Bruker AXS SMART Apex II diffractometer equipped with a CCD detector. All measurements were performed using monochromatized Mo Kα radiation from a fine-focus sealed tube at 100 K (cf. Table 2). Absorption corrections were semiempirically performed from equivalents. Structures were solved by direct methods (*SHELXS-97*)[47] and refined by full-matrix least-squares techniques against F^2 (*SHELXL-2014/6*).[47] CCDC 1439655−1439657 contain the supplementary crystallographic data for this paper. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Full experimental details for single-crystal X-ray diffraction analyses of all compounds are provided in the Supporting Information.

Ligand Synthesis. Ligands H_2L1−H_2L3 were synthesized according to known procedures with slight modifications.[21] The syntheses were performed at ambient atmosphere using standard laboratory glassware. A total of 2 equiv of the respective 2-hydroxybenzaldehyde derivative was dissolved in dry methanol. Subsequently, 1 equiv of the diamine was added and the reaction mixture stirred for several hours [for enantiopure H_2L2, the tartrate salt of (*R*,*R*)-cyclohexyldiamine was used, following Jacobsen's procedure[48]]. After concentration in vacuo, the desired product was obtained in high yield by filtration and subsequent washing with a small amount of cold dry methanol. The ligands match analytical data provided in the literature.[37,48,49]

Complex Synthesis. It is important to note that the metal precursor[39] has to be purified properly; traces of residual HCl or other impurities tend to severely interfere with the complex syntheses disclosed herein.

Synthesis of [ReOCl(L1)] (1).[21] For the synthesis of **1**, 1 equiv of $[ReOCl_3(OPPh_3)(SMe_2)]$ (250 mg, 0.39 mmol) and 1 equiv of H_2L1 (206 mg, 0.39 mmol) were dissolved in 10 mL of dry MeCN under a N_2 atmosphere and refluxed for 1 h. Then 2 equiv of NEt_3 (78 mg, 0.77 mmol) was added, whereupon the greenish suspension immediately turned dark brown. The resulting dark suspension was stirred under reflux for an additional 4 h. After cooling, the reaction mixture was filtered and the filtrate evaporated in vacuo. The crude product was redissolved in a minimal amount of $CHCl_3$ and subsequently stored at 5 °C for several days. The precipitate was filtered and washed thoroughly with dry pentane to obtain **1** as a brownish crystalline solid (195 mg, 66%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via recrystallization from dry MeCN. Analytical data are in compliance with the literature.[21] Mp: 320 °C (dec). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.76 (s, 1H, CH═N), 7.67 (d, 1H, Ar−H), 7.43 (s, 1H, CH═N), 7.22 (d, 1H, Ar−H), 7.14 (d, 1H, Ar−H), 7.00 (d, 1H, Ar−H), 4.38 (q, 2H, CH_2), 3.59 (q, 2H, CH_2), 1.56 (s, 9H, *t*Bu), 1.33 (s, 9H, *t*Bu), 1.29 (s, 9H, *t*Bu), 1.12 (s, 9H, *t*Bu), 1.11 (s, 3H, CH_3), 0.89 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.58, 173.49 (CH═N), 170.31, 161.21, 141.54, 141,51, 140.16, 137.83, 133.11, 129.93, 129.70, 119.02, 117.12 (Ar), 36.04, 35.59, 35.25, 34.63, 34.11 (CH_2, q-C), 31.49, 31.36, 30.43, 29.82 (*t*Bu), 26.23, 26.16, 19.92, 13.85 (CH_3, q-C). IR (ATR, cm^{-1}): $\tilde{\nu}$ 2953 (m), 1605 (m, CH═N), 1248 (s), 944 (s, Re═O), 836 (m), 748 (s), 531(s), 483 (s).

Synthesis of [ReOCl(L2)] (cis/trans-2). For the synthesis of **2**, 1 equiv of $[ReOCl_3(OPPh_3)(SMe_2)]$ (523 mg, 0.85 mmol) and 2 equiv of H_2L2 (930 mg, 1.70 mmol) were dissolved in 20 mL of dry MeCN under a N_2 atmosphere and stirred under reflux for 5 h. The formed precipitate was filtered off and the dark-brown filtrate evaporated in vacuo. After the addition of 5 mL of dry MeCN and sonication, the resulting solid was filtered off and washed twice with a little cold dry pentane to afford **2** as a brick-red powder (366 mg, 54%). Orange crystalline needles of the trans isomer suitable for single-crystal X-ray diffraction analysis were obtained via vapor diffusion of Et_2O into a saturated solution of *rac*-**2** in MeCN. Compound **2** exists in a solvent- and temperature-dependent equilibrium of isomers in solution (vide supra). Mp: 281 °C (dec). ^1H NMR (minor cis isomer, $CDCl_3$, 300 MHz): δ 8.53 (s, 1H, CH═N), 7.94 (s, 1H, CH═N), 7.78 (d, 1H, Ar−H), 7.38 (d, 1H, Ar−H), 7.32 (d, 1H, Ar−H), 7.05 (d, 1H, Ar−H), 4.02 ("t", 1H, CH), 3.06 ("t", 1H, CH), 2.56 (m, 2H, CH_2), 2.08 ("t", 2H, CH_2), 1.85−1.46 (m, 4H, CH_2), 1.63 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.31 (s, 9H, *t*Bu), 1.26 (s, 9H, *t*Bu). ^1H NMR (major trans isomer, $CDCl_3$, 300 MHz): δ 8.93 (s, 1H, CH═N), 8.65 (s, 1H, CH═N), 7.65 (d, 2H, Ar−H), 7.12 ("t", 2H, Ar−H), 4.30 ("t", 1H, CH), 3.67 ("t", 1H, CH), 2.86 ("d", 1H, CH_2), 2.70 ("d", 1H, CH_2), 2.08 ("t", 2H, CH_2), 1.85−1.46 (m, 4H, CH_2), 1.55 ("d", 18H, *t*Bu), 1.31 (s, 18H, *t*Bu). ^{13}C NMR (minor cis isomer, $CDCl_3$, HSQC 300/75 MHz, q-C obscured): δ 173.08, 170.93 (CH═N), 134.92, 132.92, 130.56, 128.51 (Ar), 82.52, 80.64 (CH), 31.21, 31.17, 30.37, 29.83 (*t*Bu), 29.93, 29.70, 25.11, 24.71 (CH_2). ^{13}C NMR (major trans isomer, $CDCl_3$, HSQC 300/75 MHz, q-C obscured): δ 177.33, 176.14 (CH═N), 133.97, 131.72 (Ar), 82.62, 81.61 (CH), 31.21 (2 × *t*Bu), 30.03 (*t*Bu), 30.01 (CH_2), 29.98 (*t*Bu), 28.67, 25.11, 24.71 (CH_2). IR (ATR, cm^{-1}): $\tilde{\nu}$ 2952 (m), 1605 (s, CH═N), 1531 (m), 1242 (s), 1167 (m), 947 (s, Re═O), 833 (m), 570 (s), 547 (s). EI-MS: *m*/*z* 782.6 ([M^+]). Anal. Calcd for $C_{36}H_{32}ClN_2O_3Re$ (782.48): C, 55.26; H, 6.70; N, 3.58. Found: C, 54.99; H, 6.74; N, 3.81.

Synthesis of [ReO(L2)](OTf) (2a). For the synthesis of **2a**, 1 equiv of [ReOCl(**L2**)] (40 mg, 0.05 mmol) and 1 equiv of AgOTf (13 mg, 0.05 mmol) were dissolved in 3 mL of dry MeCN. The resulting orange-brownish solution was stirred for 1 h. After filtration and evaporation of the filtrate in vacuo, **2a** was obtained as a brown powder in quantitative yield (42 mg, 99%). Mp: 155 °C (dec). ^1H NMR ($CDCl_3$,

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300 MHz): δ 8.90 (s, 1H, CH═N), 8.62 (s, 1H, CH═N), 7.76 (m, 2H, Ar−H), 7.27 (m, 2H, Ar−H), 4.19 ("t", 1H, CH), 3.69 ("t", 1H, CH), 3.11 (bs, 3H, CH_3CN), 2.99 (m, 2H, CH_2), 2.17−1.95 (m, 4H, CH_2), 1.75−1.55 (m, 2H, CH_2), 31.54 (s, 9H, *t*Bu), 1.52 (s, 9H, *t*Bu), 1.34 ("d", 18H, *t*Bu). ^{13}C NMR ($CDCl_3$, 300 MHz, OTf^- and MeCN signals obscured): δ 175.57, 174.65 (CH═N), 167.19 (Ar−O), 142.62, 140.66, 135.60, 132.48, 121.56 (Ar), 81.22, 80.15, (CH), 36.22, 34.25 (q, *t*Bu), 31.31 (*t*Bu), 29.94 (*t*Bu), 28.99, 28.09, 24.84, 24.19 (CH_2). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −78.32. IR (ATR, cm^{-1}): $\tilde{\nu}$ 2951 (m), 1599 (s, CH═N), 1536 (s), 1242 (s), 1163 (s), 1026 (s), 987 (m, Re═O), 832 (m), 750 (m), 636 (s), 574 (m), 546 (m), 414 (m). HR-MS (ESI^+). Calcd for $C_{36}H_{52}N_2O_3Re$: *m*/*z* 747.3532 ($[M]^+$). Found: *m*/*z* 747.3572.

Synthesis of [ReOCl(L3)] (3). For the synthesis of **3**, 1 equiv of $[ReOCl_3(OPPh_3)(SMe_2)]$ (266 mg, 0.43 mmol) and 2 equiv of $\mathbf{H_2L3}$ (460 mg, 0.85 mmol) were dissolved in 20 mL of dry MeCN under a N_2 atmosphere and stirred at 60 °C for 4 h. The resulting dark suspension was concentrated in vacuo and stored at −25 °C for 48 h. Subsequently, the precipitate was filtered and washed thoroughly with dry pentane to obtain pure **3** as a dark-red powder (193 mg, 58%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via recrystallization from dry $CHCl_3$. Mp: 292 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.71 (s, 2H, CH═N), 7.92 (m, 2H, Ar−H), 7.78 (d, 2H, Ar−H), 7.48 (m, 2H, Ar−H), 7.30 (d, 2H, Ar−H), 1.59 (s, 18H, *t*Bu), 1.36 (s, 18H, *t*Bu). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.84 (CH═N), 158.70 (Ar−O), 142.88, 140.43, 137.31, 128.30, 127.43, 126.90, 119.93, 118.47 (Ar), 35.25, 34.30 (q-C), 31.60, 29.55 (*t*Bu). IR (ATR, cm^{-1}): $\tilde{\nu}$ 2955 (m), 1602 (m, CH═N), 1578 (m), 1525 (s), 955 (s, Re═O), 830 (m), 751 (s), 543 (s). EI-MS: *m*/*z* 776.5 ($[M^+]$). Anal. Calcd for $C_{36}H_{46}ClN_2O_3Re$ (776.42): C, 55.69; H, 5.97; N, 3.61. Found: C, 55.62; H, 5.61; N, 3.58.

Perchlorate Reduction. In a typical experiment, $LiClO_4$ or $AgClO_4$ (0.1 M) and an organic sulfide (Me_2S or Ph_2S, 0.4 M) were dissolved in 0.4 mL of 95:5 (v/v) CD_3CN/D_2O in a standard NMR tube. After the addition of 3.2 mol % catalyst and the calculated amount of perchlorate from a 0.5 M stock solution in CD_3CN/D_2O, the tubes were sealed, and ^{1}H NMR spectra were recorded after 7/24/60 h. The yield of sulfoxide formed was determined via integration of the respective peak areas. A control experiment without a catalyst was included in the series.

Catalytic Epoxidation. In a typical experiment, 2−3 mg of catalyst (1 mol %) was dissolved in 0.5 mL of the respective solvent and mixed with 1 equiv of substrate. Then 50 μL of mesitylene was added as an internal standard, and the reaction mixtures were heated to the respective temperatures, whereupon the oxidant (3 equiv) was added in one portion. Aliquots for GC−MS (20 μL) were withdrawn with a calibrated Socorex Acura 825 10−100 μL variable-volume pipet at given time intervals, 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 versus mesitylene as the internal standard.

Catalytic OAT. In a typical experiment, ∼4 mg of catalyst (5 mol %) was dissolved in 0.5 mL of C_6D_6 in an oven-dried NMR tube. Subsequently, 1 equiv of a substrate (PPh_3) and 1 or 10 equiv of DMSO were added and the tubes sealed and kept at ambient temperature. After 24 h, ^{1}H NMR spectra were recorded, and the yield of phosphane oxide formed was determined via integration of the respective peak areas. A control experiment without a catalyst was included in the series, showing no conversion.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00466.

Additional data (NMR spectra, van't Hoff plot, and HR-MS data) as well as full crystallographic details (PDF)

X-ray crystallographic data in CIF format (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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