# Ligand Design for Isomer-Selective Oxorhenium(V) Complex Synthesis

Jinyong Liu,<sup>\*,†,‡</sup> Xiaoge Su,<sup>§</sup> Mengwei Han,<sup> $\parallel$ </sup> Dimao Wu,<sup>#</sup> Danielle L. Gray,<sup> $\perp$ </sup> John R. Shapley,<sup> $\perp$ </sup> Charles J. Werth,<sup> $\Delta$ </sup> and Timothy J. Strathmann<sup>\*,‡</sup>

<sup>†</sup>Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521, United States <sup>‡</sup>Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, Colorado 80401, United States

<sup>§</sup>Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230000, China

<sup>∥</sup>Department of Civil and Environmental Engineering and <sup>⊥</sup>Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States

<sup>#</sup>Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States <sup>Δ</sup>Department of Civil, Architectural, and Environmental Engineering, University of Texas at Austin, Austin, Texas 78712, United States

# **Supporting Information**

**ABSTRACT:** Recently, *N*,*N*-*trans* Re(O)( $L_{N-O}$ )<sub>2</sub>X ( $L_{N-O}$  = monoanionic N–O chelates; X = Cl or Br prior to being replaced by solvents or alkoxides) complexes have been found to be superior to the corresponding *N*,*N*-*cis* isomers in the catalytic reduction of perchlorate via oxygen atom transfer. However, reported methods for Re(O)( $L_{N-O}$ )<sub>2</sub>X synthesis often yield only the *N*,*N*-*cis* complex or a mixture of *trans* and *cis* isomers. This study reports a geometry-inspired ligand design rationale that selectively yields *N*,*N*-*trans* Re(O)-( $L_{N-O}$ )<sub>2</sub>Cl complexes. Analysis of the crystal structures



revealed that the dihedral angles (DAs) between the two  $L_{N-O}$  ligands of  $N_iN$ -cis  $Re(O)(L_{N-O})_2Cl$  complexes are less than 90°, whereas the DAs in most  $N_iN$ -trans complexes are greater than 90°. Variably sized alkyl groups (-Me, -CH<sub>2</sub>Ph, and -CH<sub>2</sub>Cy) were then introduced to the 2-(2'-hydroxyphenyl)-2-oxazoline (Hhoz) ligand to increase steric hindrance in the  $N_iN$ -cis structure, and it was found that substituents as small as -Me completely eliminate the formation of  $N_iN$ -cis isomers. The generality of the relationship between  $N_iN$ -trans/cis isomerism and DAs is further established from a literature survey of 56 crystal structures of  $Re(O)(L_{N-O})_2X$ ,  $Re(O)(L_{O-N-N-O})X$ , and  $Tc(O)(L_{N-O})_2X$  congeners. Density functional theory calculations support the general strategy of introducing ligand steric hindrance to favor synthesis of  $N_iN$ -trans  $Re(O)(L_{N-O})_2X$  and  $Tc(O)(L_{N-O})_2X$  complexes. This study demonstrates the promise of applying rational ligand design for isomeric control of metal complex structures, providing a path forward for innovations in a number of catalytic, environmental, and biomedical applications.

# ■ INTRODUCTION

Oxorhenium complexes have been developed for a broad range of catalytic applications in synthetic chemistry,  $^{1-10}$  biomass conversion,  $^{11-17}$  and environmental remediation.  $^{18-24}$  Nonradioactive  $^{185}\text{Re}/^{187}\text{Re}$  complexes have also been extensively studied as  $^{186}\text{Re}$ ,  $^{188}\text{Re}$ , and  $^{99m}\text{Tc}$  surrogates for radio-pharmaceutical development.  $^{25-29}$  Since 1996,  $^{30}$  a number of Re $^{V}(O)(L_{N-O})_{2}X$  complexes  $(L_{N-O}$  = monoanionic N–O chelates; X = Cl or Br prior to being replaced by solvents or alkoxides) have been synthesized.  $^{31}$  Specific  $L_{N-O}$  ligands enable the Re center to exhibit novel catalytic activities, including hydrosilylation,  $^{32,33}_{2,33}$  H<sub>2</sub> generation from silanes,  $^{34}$  C–H activation,  $^{35}_{3}$  aldol condensation,  $^{36}_{3}$  Of particular note, oxazolinylphenolato (hoz) and thiazolinylphenolato (htz) ligands yield Re(O)(hoz)\_2Cl, Re(O)(htz)\_2Cl, and Re(O)-

(hoz)(htz)Cl (*N,N-trans* **1a**, **2a**, and **3a** in Scheme 1) complexes with high activity for oxygen atom transfer (OAT) reactions<sup>39</sup> with perchlorate ( $\text{ClO}_4^{-}$ ).<sup>20</sup> This unique reactivity inspired our research team to develop a biomimetic catalyst system that integrates these Re complexes and hydrogenation nanoparticles (e.g., Pd and Rh) on carbon support materials. Under 1 atm of H<sub>2</sub> and ambient temperature, these catalysts rapidly and completely reduce the endocrine-disrupting ClO<sub>4</sub><sup>-</sup> in drinking water<sup>40,41</sup> into innocuous Cl<sup>-.21-24</sup>

One of the major challenges of developing functional  $Re(O)(L_{N-O})_2 X$  complexes is isomer selectivity. Upon the reaction of  $Re(O)(OPPh_3)(SMe_2) X_3$  or  $[NBu_4][Re(O) X_4]$  precursor with 2 equiv of  $HL_{N-O}$  ligands, most Re(O)-

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Scheme 1. Previously Developed Isomer Control Strategies (a-c) and the Aim of This Study (d)

 $(L_{N-\Omega})_2X$  products are either N,N-trans or N,N-cis with the ligand O atom coordinating trans to the oxo group. Comparison on both isomers of  $Re(O)(hoz)_2Cl$  and Re(O)-(htz)<sub>2</sub>Cl indicates that the N,N-trans configuration provides significantly higher rates of ancillary ligand dissociation, intramolecular exchange of the two L<sub>N-O</sub>, and catalytic activity in OAT reactions.<sup>20</sup> Despite these advantageous properties, the number of reported N,N-trans Re complexes is much smaller than that of N.N-cis complexes, and knowledge on controlling N,N-trans versus N,N-cis structures has been very limited in the past two decades. In many reports, synthesis yields a mixture of the two isomers,<sup>20,42-44</sup> which are generally difficult to isolate. As pointed out in our previous report,<sup>20</sup> the nonselective synthesis of  $Re(O)(L_{N-O})_2X$  isomers of widely varying reactivity not only results in a waste of the Re element during catalyst preparation but also introduces potential artifacts that can lead to misinterpretation of structure-activity relationships.

We recently introduced two strategies for selective synthesis of *N*,*N*-trans  $Re(O)(L_{N-O})_2X$ <sup>20</sup> First, pyridines with proper steric hindrance (in excess to the amount for scavenging HX byproduct) could promote thermodynamically favored isomer interconversion from the initial mixture of N,N-trans and N,Ncis isomers (Scheme 1a,b). Second, the direction of isomer interconversion could be controlled by hybridization of different  $L_{N-O}$  with the opposite isomer preference, such as incorporating a trans-favoring hoz ligand and a cis-favoring htz ligand in the complex (Scheme 1c). Despite being effective, the first strategy requires heating for a prolonged period of time and using excess base to allow a complete isomer interconversion, and the direction of interconversion is controlled by the  $L_{N-O}$  ligand structure. The second strategy also requires stepwise reactions to ensure a high yield of heteroleptic  $\operatorname{Re}(O)(L^{A}_{N-O})(L^{B}_{N-O})X$  product by minimizing the formation of homoleptic  $Re(O)(L^A_{N-O})_2X$  or Re(O)- $(L^{B}_{N-O})_{2}X$ . A key question is thus raised on how to design new  $L_{N-O}$  structures to efficiently yield only N,N-trans products by minimizing or even eliminating the initial formation of N,N-cis isomers (Scheme 1d).

Comparing crystal structures of our previously synthesized N,N-trans and N,N-cis isomers of both  $\text{Re}(O)(\text{hoz})_2\text{Cl}$  and  $\text{Re}(O)(\text{htz})_2\text{Cl}$  revealed an interesting trend wherein the dihedral angles (DAs) between the two  $L_{N-O}$  ligands in N,N-trans complexes are apparently larger than 90°, whereas the

DAs in *N*,*N*-cis complexes are significantly smaller than  $90^{\circ}$  (Figure 1). Intrigued by this observation, we further



**Figure 1.** Side views of the crystal structures of previously reported  $\text{Re}(O)(\text{hoz})_2\text{Cl}$  (**1a** and **1b**) and  $\text{Re}(O)(\text{htz})_2\text{Cl}$  (**2a** and **2b**) isomers. The narrow spacing in *N*,*N*-*cis* structures are highlighted with a purple sphere.

investigated crystal structures of all previously reported  $\text{Re}(O)(L_{N-O})_2X$  complexes and confirmed that this general trend holds, with a very small number of exceptions (details presented in Discussion Section). The small DA in *N,N-cis* structures indicates a narrow spacing between the two Recomplexed  $L_{N-O}$  ligands. It then follows that introduction of bulky substituents into the  $L_{N-O}$  ligand structure should favor formation of the *N,N-trans* isomer by interfering with *N,N-cis* arrangement of the two  $L_{N-O}$  ligands.

In this contribution, we report on the selective synthesis of several new *N*,*N*-trans  $\text{Re}(O)(L_{N-O})_2\text{Cl}$  complexes. First, we verified the ligand design rationale by attaching alkyl groups of varying size to provide steric hindrance on the oxazoline moiety of hoz and effectively avoid the initial formation of *N*,*N*-cis isomers. The investigation was further generalized by examining all previously reported  $\text{Re}(O)(L_{N-O})_2X$  complexes and Tc- $(O)(L_{N-O})_2X$  congeners. DA measurements were provided, and supporting density functional theory (DFT) calculations

were conducted to extend findings to provide a path forward for selective synthesis of *N*,*N*-*trans* structures of functional Re and Tc complexes for catalytic, environmental, and biomedical applications.

# RESULTS

Synthesis of Alkyl-Substituted hoz Ligands and N,Ntrans Re Complexes. Five  $HL_{N-O}$  ligands were synthesized in one step by reacting 2-hydroxybenzonitrile and corresponding amino alcohols in refluxed toluene, with 2 mol % ZnCl<sub>2</sub> as the catalyst (Scheme 2).<sup>45,46</sup> Hhoz derivatives with a small –Me





(L1),<sup>47</sup> a large  $-CH_2Ph$  (L2),<sup>48</sup> and a geminal dimethyl (L4)<sup>49</sup> substitution at the 4-position of oxazoline moiety and the Hhox ligand with a six-member ring dihydrooxazine moiety (L5, a nonflat ring structure isomer of L1)<sup>50</sup> have been reported in

literature. The ligand with  $-CH_2Cy$  (L3, an L2 analogue with phenyl ring saturated) is first reported in this study.

The corresponding  $Re(O)(L_{N-O})_2Cl$  complexes were synthesized from Re(O)(OPPh3)(SMe2)Cl3 and 2 equiv of the  $HL_{N-\Omega}$  ligands (L1 to L5) in refluxed ethanol. A stoichiometric amount of 2,6-di-tert-butylpyridine (tBu<sub>2</sub>Py) or 2,6-dimethylpyridine (Me<sub>2</sub>Py) was added to scavenge HCl byproduct; thus, no excess base was available to promote the isomer interconversion (Scheme 1).<sup>20</sup> During complex synthesis with L1, the reaction mixture quickly turned from a pale green suspension to a forest green solution within 6 min, and some green solids precipitated by 15 min. <sup>1</sup>H NMR characterization of the precipitates after 4 h of reaction indicated a pure species containing 14 individual proton (i.e., 1H by integration) multiplets and two -CH<sub>3</sub> singlets. Singlecrystal analysis identified the N,N-trans Re(O)(Mehoz)<sub>2</sub>Cl structure 4a (Figure 2a). Crystallography data are provided in Table 1 and Table 2.

In comparison, the previous synthesis of  $Re(O)(hoz)_2Cl$ under the same conditions for 4 h yielded a 60:40 mixture of *N,N-trans* and *N,N-cis* isomers. Thus, we attempted to monitor the much faster interconversion of *N,N-cis*  $Re(O)(Mehoz)_2Cl$ , if any, to the *N,N-trans* isomer at the beginning of synthesis. While the partially precipitated solids at 15 min exclusively contained *N,N-trans* complex **4a** (Figure 3a), <sup>1</sup>H NMR characterization of the reaction mixture (i.e., liquid and solid) indicated that the liquid phase contained two minor impurities, which disappeared at different rates (Figure 3b–d) and are probably  $Re(O)(Mehoz)_2Cl$  isomers (vide infra). More solids precipitated with prolonged heating. After 4 h of reaction, the solid product **4a** was in both high isolated yield (92%) and high purity (like shown in Figure 3a).

As shown in Figure 4, the fixed chirality of the Mehoz ligand and the enantiomeric Re coordination sphere could generate two diastereomers of N,N-trans (Type A and Type B; 4a and 4a') and N,N-cis (Type C and Type D; 4b and 4b') isomers,



Figure 2. Plain view and side view of (a, b) N,N-trans Re(O)(Mehoz)<sub>2</sub>Cl 4a, (c, d) N,N-trans Re(O)(PhCH<sub>2</sub>hoz)<sub>2</sub>Cl 5a, and (e, f) N,N-cis Re(O)(hox)<sub>2</sub>Cl 8b (35% probability displacement ellipsoids displayed with H atoms removed for clarity).

# Table 1. Crystal Data and Refinement Details

	N,N-trans Re(O)(Mehoz) <sub>2</sub> Cl (4a)	<i>N,N-trans</i> Re(O)(PhCH <sub>2</sub> hoz) <sub>2</sub> Cl (5a)	N,N-cis $Re(O)(hox)_2Cl$ (8b)
formula	C <sub>20</sub> H <sub>20</sub> ClN <sub>2</sub> O <sub>5</sub> Re	C <sub>32</sub> H <sub>28</sub> ClN <sub>2</sub> O <sub>5</sub> Re	C <sub>20</sub> H <sub>20</sub> ClN <sub>2</sub> O <sub>5</sub> Re
formula weight	590.03	742.21	590.03
temperature (K)	100(2)	100(2)	193(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	hexagonal	monoclinic	orthorhombic
space group	P6 <sub>1</sub>	$P2_1$	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	11.2324(4)	13.9014(7)	7.9530(6)
b (Å)	11.2324(4)	6.8299(3)	15.1091(12)
c (Å)	27.4564(12)	15.2612(8)	16.3803(12)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	90	91.4735(18)	90
γ (deg)	120	90	90
V (Å <sup>3</sup> )	3000.0(3)	1448.50(12)	1968.3(3)
Ζ	6	2	4
$\rho_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$	1.960	1.702	1.991
absorption coefficient (mm <sup>-1</sup> )	6.244	4.331	6.345
F(000)	1716	732	1144
crystal size (mm <sup>3</sup> )	$0.176 \times 0.115 \times 0.05$	$0.35 \times 0.109 \times 0.089$	$0.226 \times 0.214 \times 0.136$
$\theta$ range (deg)	2.221-29.573	1.957-28.334	1.83-27.29
index ranges	$-15 \le h \le 15$	$-18 \le h \le 18$	$-10 \le h \le 10$
	$-14 \le k \le 15$	$-9 \le k \le 9$	$-19 \le k \le 19$
	$-38 \le l \le 38$	$-20 \le l \le 20$	$-21 \le l \le 20$
No. of reflections collected	107 510	38 153	24 754
No. of independent rflns, R <sub>int</sub>	5600, 0.0658	7190, 0.0280	4412, 0.0571
completeness to $\theta = 25.69^{\circ}$	99.9%	99.9%	99.6%
absorption correction	integration	integration	integration
max. and min transmission	0.78222 and 0.55895	0.7697 and 0.2964	0.5401 and 0.3485
refinement method	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$
data/restraints/parameters	5600/15/283	7190/15/389	4412/0/262
goodness-of-fit on $F^2$	1.209	1.212	1.033
R1/wR2 $(I > 2\sigma(I))$	0.0214/0.0470	0.0232/0.0546	0.0258/0.0574
R1/wR2 (all data)	0.0236/0.0476	0.0250/0.0557	0.0289/0.0588
absolute structure parameter	-0.012(2)	-0.016(4)	0.007(9)
largest diff. peak/hole (e $Å^{-3}$ )	1.627 and -2.163	3.006 and -2.197	0.810 and -0.675
instrument	$A^a$	Α	$B^b$

<sup>a</sup>Burker D8 Venture equipped with a Photon 100 detector using multilayer optics to monochromatize Mo K $\alpha$  radiation. <sup>b</sup>Siemens Platform diffractometer equipped with an Apex II CCD detector using graphite-monochromatized Mo K $\alpha$  radiation.

# Table 2. Selected Bond Distances (Å) for Five $Re(O)(L_{O-N})_2Cl$ Complexes

<sup>8</sup> 01 N1Re <sup>-</sup> , Ch R -02 - N2 04 - 05	$\begin{array}{c} \begin{array}{c} O1\\ O2, \\ H\\ O2, \\ H\\ O4\\ O4\\ O5\\ O5\\ O5\\ O5\\ O5\\ O5\\ O5\\ O5\\ O5\\ O5$
1a (R = H) 4a (R = Me) 5a (R = CH₂Ph)	1b (n = 1) 8b (n = 2)

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	1a <sup><i>a</i></sup>	4a	5a	$1b^a$	8b
Re(1) - O(1)	1.671(4)	1.725(5)/1.727(9)	1.724(12)/1.736(6)	1.6902(18)	1.695(3)
Re(1) - O(4)	1.977(4)	2.006(4)	1.986(4)	1.9863(17)	1.981(3)
Re(1) - O(2)	1.990(4)	1.998(4)	2.001(4)	2.0006(16)	1.978(3)
Re(1) - N(1)	2.038(4)	2.098(4)	2.081(4)	2.099(2)	2.124(3)
Re(1) - N(2)	2.090(4)	2.069(4)	2.103(4)	2.113(2)	2.142(3)
$\operatorname{Re}(1) - \operatorname{Cl}(1)$	2.3824(14)	2.3853(15)/2.376(7)	2.331(6)/2.398(2)	2.3700(6)	2.3728(11)
<sup>a</sup> Data from ref 20 for	comparison.				

respectively. DFT calculations suggest that 4a is the most thermodynamically favored structure among the four isomers. The high-purity <sup>1</sup>H NMR spectrum and the  $P6_1$  crystal space

group of the  $Re(O)(Mehoz)_2Cl$  product suggest a stereoselective formation of the Re coordination sphere. In comparison, the space groups of the previously reported



**Figure 3.** Synthesis of  $Re(O)(Mehoz)_2Cl$  and partial <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ) spectra of products. Symbols \*, +, and (a), respectively, indicate protonated  $tBu_2Py$ , OPPh<sub>3</sub>, and excess HMehoz ligand in the reaction mixture. Symbols & and # indicate two probable isomers gradually disappearing in the reaction mixture at different rates.



Figure 4. Calculated structure and relative Gibbs free energy of the four Re(O)(Mehoz)<sub>2</sub>Cl isomers.

crystals of Re(O)(OPPh<sub>3</sub>)(SMe<sub>2</sub>)Cl<sub>3</sub> precursor (Pcmn)<sup>51</sup> and  $Re(O)(L_{N-O})_2Cl$  complexes with achiral hoz and htz ligands  $(P2_1/c \text{ or } P2_1/n)^{20}$  indicate a racemic mixture of Re coordination enantiomers. Since the  $Re(O)(OPPh_3)(SMe_2)Cl_3$ precursor is racemic, the selective formation of 4a suggests that a chiral  $L_{N-\Omega}$  ligand could induce the interconversion between  $Re(O)(Mehoz)_2Cl$  diastereomers 4a and 4a'. On the basis of the calculated Gibbs energy, one of the two impurities observed during the Re(O)(Mehoz)<sub>2</sub>Cl synthesis (resonances labeled with # symbols in Figure 3b) might be 4a'. The other impurity (labeled with & symbols) that appeared to have symmetry is probably a  $\mu$ -oxo dimer.<sup>52</sup> Enantioselective synthesis of oxorhenium complexes with other types of multidentate ligands have been reported, but the mechanism remains unclear.<sup>53,54</sup> Further investigation is needed to elucidate the interconversion mechanism that alters the chirality of the Re coordination sphere. Nevertheless, results demonstrate that N,N-trans structured complex can be selectively synthesized by introduc-

ing a small methyl group to oxazoline moiety of the original hoz ligand.

The isomer control strategy was further examined with the large benzyl-substituted L2. Similar to the synthesis of  $Re(O)(Mehoz)_2Cl$ , solid products complexing with L2 quickly precipitated. While the product during the first 2 h contained some impurities, heating the mixture for more than 8 h yielded a high-purity product, and its crystal structure was also type A  $N_{,N}$ -trans Re(O)(PhCH<sub>2</sub>hoz)<sub>2</sub>Cl (5a, Figure 2c). The space group P21 also indicates the absence of mirror planes in the crystal unit cell. The <sup>1</sup>H NMR spectrum of 5a showed significant differences with other N,N-trans Re(O)(R-hoz)<sub>2</sub>Cl complexes such as 1a and 4a (e.g.,  $\delta$  3.8,  $\delta$  5.6, and  $\delta$  6.7–7.0; Figure 5c vs 5a,b). For comparison, Re(O)(CyCH<sub>2</sub>hoz)<sub>2</sub>Cl with the even bulkier L3 was synthesized following the same procedure for 5a; the product has a very similar <sup>1</sup>H NMR spectrum to that of 4a (Figure 5d vs 5b), suggesting that the product (6a) is also N,N-trans. Thus, the unique <sup>1</sup>H NMR spectrum of 5a might be attributed to the influence of the ring

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			CH	CI <sub>3</sub>							
(a)			M	M_M	8H	R = H (1a)		M	L	81	ł
	8.0	7.	5	7.0	6.5	6.0	5.5	5.0	4.5	4.0	
(b)	M	M	M	h MIM	8H	R = (S)-Me (4a)			the mille	61	1
	8.0	7.	5	7.0	6.5	6.0	5.5	5.0	4.5	4.0	-
(c)	M		MW	m MM	18H	R = (S)-CH <sub>2</sub> Ph (5a	)	m	~m	6F	•
	8.0	7.	5	7.0	6.5	6.0	5.5	5.0	4.5	4.0	
(d)	M		m_h		8H	R = (S)-CH <sub>2</sub> Cy (6a	)	nM	MMm	61	1
	8.0	7.	5	7.0	6.5	6.0	5.5	5.0	4.5	4.0	
(e)	M		_m_l	MM	8H	R = Me <sub>2</sub> (7a)			M_M	4	4
	8.0	7.	5	7.0	6.5	6.0 (mqq) δ	5.5	5.0	4.5	4.0	

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**Figure 5.** Partial <sup>1</sup>H NMR spectra of five Re(O)(R-hoz)<sub>2</sub>Cl complexes.



Figure 6. Illustration of the DA measurement. Atoms involved in the plane of coordination "arch" are highlighted.

current of benzyl Ph onto the hoz backbone protons. The verification of  $N_{,}N$ -trans configuration for **5a** and **6a** further demonstrates that the ligand design strategy could be applied to alkyl groups of a variety of sizes.

The achiral HMe<sub>2</sub>hoz (L4) led to the exclusive formation of one species 7a, which was characterized as *N*,*N*-trans by <sup>1</sup>H NMR spectra comparison (Figure 5) and crystallography (refined structure unavailable due to high-level disorders).<sup>44</sup> Compared with 4a, the increased number of methyl groups in 7a enhanced its dissolution in the OPPh<sub>3</sub>-containing ethanol, such that no solids precipitated even after 24 h of heating. Nevertheless, the recovered solid after only 15 min of reaction was high-purity 7a, further demonstrating that the alkyl substitution as small as methyl groups could be introduced to eliminate the formation of the *N*,*N*-cis isomer. In contrast to the alkyl-substituted R-hoz ligands, the expansion of the ring size from five-member to six-member in Hhox (L5) yielded a 60:40 mixture of *N,N-trans* and *N,N-cis* Re(O)(hox)<sub>2</sub>Cl isomers (8a and 8b, respectively) within 10 min of synthesis (Figure S1 of the Supporting Information), and prolonged heating led to the undesired interconversion of 8a to 8b (like that shown in Scheme 1b). Both isomers of Re(O)(hox)<sub>2</sub>Cl exhibited low solubility in commonly used solvents (e.g., CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>), such that isolation of 8a from the mixture was challenging. 8b was purified by silica chromatography,<sup>20</sup> and its structure was confirmed by crystallography (Figure 2e). Thus, unlike the side-protruding methyl group in Mehoz, the slight bulkiness of the chair-shaped dihydrooxazine moiety in hox does not favor the formation of *N,N-trans* structure. The new crystal structures of 4a, 5a, and

**8b** follow the DA trend of greater than  $90^{\circ}$  for *N*,*N*-trans (Figure 2b,d) and less than  $90^{\circ}$  for *N*,*N*-cis (Figure 2f).

# DISCUSSION

Characteristic Dihedral Angles in *N*,*N*-trans and *N*,*N*cis  $Re(O)(L_{N-O})_2X$ . To generalize the DA trend initially observed from complexes prepared in our lab, we extended the comparison to other  $Re(O)(L_{N-O})_2Cl$  complexes reported in literature. Because some ligands are not planar, the DAs were measured based on the approximated planes of O-C-C-C-N coordination "arch" (Figure 6). As summarized in Table 3,

Table 3. Summary of Dihedral Angles of  $Re(O)(L_{N-O})_2X$ and  $Tc(O)(L_{N-O})_2X$  Crystal Structures

entry	atom number of the chelation ring (including Re)	number of total examples/ DA trend exception	DA range (excluding exception)	DA average (excluding exception)	detailed information collection
		N,N-trans	$Re(O)(L_{N-O})_2$	Cl	
1	six	13/1	92.5°- 134.4°	105.9°	Table S1
2	five	1/ <i>a</i>	85.6°	85.6°	Table S1
		N,N-cis R	$e(O)(L_{N-O})_2O$	21	
3	six	18/0	32.5°- 81.0°	47.5°	Table S2
4	five	9/0	62.3°- 89.9°	78.6°	Table S3
		N,N-cis T	$c(O)(L_{N-O})_2 O$	21	
5	six	3/0	38.7°- 59.7°	47.3°	Table S5
6	five	4/1	55.6°- 72.1°	61.2°	Table S5

<sup>*a*</sup>With only one example, the general DA trend for five-member chelated  $N_rN$ -trans Re(O)(L<sub>N-O</sub>)<sub>2</sub>X remains uncertain.

there have been 14 examples of *N,N-trans* Re(O)( $L_{N-O}$ )<sub>2</sub>X crystal structures reported to date <sup>20,30,35,42–44,55–57</sup> (X = Cl, Br, or CH<sub>3</sub>CN for cationic form, including the new complexes reported in this work; see Table S1 for details). With only one exception (74.7°), the DAs of all other 12 *N,N-trans* Re(O)( $L_{N-O}$ )<sub>2</sub>X with a variety of six-member ring chelating ligands range from 92.5° to 134.4°. There has been only one example of *N,N-trans* Re(O)( $L_{N-O}$ )<sub>2</sub>X with a five-member ring chelating chelate ligand <sup>57</sup> showing a DA of 85.6°. Thus, DA trend for this specific category is still uncertain; more crystal structure examples are needed.

The previously reported *N*,*N*-*cis* Re(O)( $L_{N-O}$ )<sub>2</sub>X crystal structures are more abundant than *N*,*N*-*trans*. There are 17 structures with six-member ring chelation<sup>19,42–44,56,58,59</sup> (including a dioxo Re<sup>VII</sup>(O)<sub>2</sub>(hoz)<sub>2</sub> complex, Table S2) and 9 structures with five-member ring chelation<sup>58,60–62</sup> (Table S3), all of which show less than 90° DAs. The DAs for six-member ring chelation structures are generally smaller than that for five-member ring counterparts (Table 3, entry 3 vs 4), suggesting the influence of different ring strains by six- and five-member ring chelations.

Although the DA values appear to be also influenced by other factors such as cocrystallized solvent molecules (e.g., Table S2, entry 1 vs 2), crystal system (e.g., Table S2, entry 15 vs 16) and ligand X (e.g., Table S1, entry 1 vs 2), the lack of exception going across the 90° DA dividing line implies that the characteristic DA trend in *N,N-trans* and *N,N-cis* crystal structures might also apply to structures in solution. Indeed,

results of DFT calculations conducted with solvent effects (in ethanol) support this speculation. The calculated structures are reported in a separate .xyz file in the Supporting Information. Although DAs of the calculated structures do not closely match the DAs in crystal structures, there are only two exceptions to the greater than  $90^{\circ}$  or less than  $90^{\circ}$  trend (vide infra). Because Re generally does not locate on the plane of the coordination "arch", the DAs are actually determined by the spatial orientation of the Re-O-C and Re-N-C linkages. Interestingly, an extended survey on all reported non- $C_{c}$ -symmetric, *N,N-cis* and *O,O-cis*  $Re(O)(L_{O-N-N-O})_2X$  crystal structures  $^{63-66}$  (i.e., the same Re coordination sphere as in N,Ncis  $\text{Re}(O)(L_{N-O})_2X$  , but the two  $L_{N-O}$  ligands are linked by two to four carbons) found that all DAs are greater than  $90^{\circ}$  (Table S4). Therefore, it appears that the spatial orientation of the Re-O-C and Re-N-C linkages are influenced by both the *N,N-trans/cis* coordination pattern and the presence/absence of the linker between the two  $L_{N-O}$  ligands. The spatial orientations then determine the relative position of the two  $L_{N-O}$  ligands.

Implications for N,N-trans/cis Configuration Control for  $Re(O)(L_{N-O})_2Cl$  Complexes. Results suggest that the less than 90° DA trend is an intrinsic property of N,N-cis  $Re(O)(L_{N-O})_2X$  complexes. Hence, bulky substitutions such as on the 4-position of hoz oxazoline moiety will significantly increase the energy of N,N-cis isomer. Thus, its formation can be suppressed, or its interconversion to the less strained N.Ntrans can be promoted. We further examined the effect of Me substitution on htz, which has been found to favor the N,N-cis isomer (Table 4, entry 3). DFT calculation suggests that, like Mehoz, Mehtz also favors type A N,N-trans isomer (Table 4, entry 4). In the calculated structure of the two N,N-cis  $Re(O)(Mehtz)_2Cl$  isomers (Figure 7), the small DA between the two Mehtz ligands results in close vicinity of Me with the other Me (Type C) or with the other thiazoline ring (Type D), corresponding to the enhanced Gibbs energy elevation (e.g., 6.48 kcal mol<sup>-1</sup>) in comparison to  $Re(O)(htz)_2Cl$  isomers  $(0.53 \text{ kcal mol}^{-1})$ . Specifically in the type D structure, bonding orientation around the Me-substituted carbon atom of the equatorial thiazoline moiety has distorted, such that the methyl group can avoid pointing into the narrow spacing (Figure 7, also see the .xyz file in Supporting Information). We note that the relatively low Gibbs energy for type D N,N-cis Re(O)- $(Mehoz)_2Cl$  (Table 4, entry 2) is due to a > 90° DA in the calculated structure. This is one of the two DA trend exceptions obtained in our calculated structures. The other one is the Tc congener of the same structure (vide infra).

Literature reviews also suggest that reported  $\text{Re}(O)(L_{N-O})_2X$ complexes with plane-extended  $L_{N-O}$  ligands (e.g., containing benzo-fused heterocycles or naphthanolate) are mostly *N,N-cis* (Table S2, entries 5–8 and 12–13). DFT calculations show that *N,N-cis* isomers are strongly favored by the benzo analogs of hoz and htz (Table 4, entries 5 and 6). Replacing the hoz phenolate with naphthalate could also invert the *trans/cis* preference (Table 4, entries 7–8 versus 1). However, as supported by both the actual crystal structures<sup>55</sup> and calculated energies (Table 4, entries 9 and 10), methyl substitutions strongly favor *N,N-trans*. Therefore, we propose that introducing steric effects into the  $L_{N-O}$  structure could be an effective strategy to selectively prepare a variety of *N,N-trans*  $\text{Re}(O)(L_{N-O})_2X$  complexes.

Implications for  $Tc(O)(L_{N-O})_2CI$  complexes. The results for Re complexes motivated us to further examine, with a

Table 4. DFT-calculated relative Gibbs free energy (in kcal mol^-1) for Re(O)( $L_{N-O}$ )<sub>2</sub>Cl isomers (in EtOH at 78 °C)

entry	HL <sub>N-O</sub>	N,N–trans	N,N–cis
$1^a$		0	+0.59
2		$0 (A)^b$ +0.56 (B)	+2.86 (C) +1.53 (D)
3 <sup><i>a</i></sup>	⟨S OH	+0.53	0
4	OH S	$0 (A)^b$ +0.99 (B)	+1.17 (C) +6.48 (D)
5		+1.46	0
6		+2.58	0
7		+0.208	0
8		+0.036	0
9		0	+4.74
10		0	+4.53

<sup>*a*</sup>Data from ref.<sup>20</sup> <sup>*b*</sup>A to D refer to diastereoisomers as shown in Figure 4.



Figure 7. Calculated structure of the two  $N_iN$ -cis  $Re(O)(Mehtz)_2Cl$  isomers (hydrogens shown).

calculation approach, whether or not the DA trend and isomer control strategy could be applied to radioactive Tc(O)- $(L_{N-O})_2X$  congeners. To the best of our knowledge, there have been 7 crystal structures reported to date,  ${}^{30,67-70}$  all of which are *N,N-cis* with only a single exception to the <90° DA trend (Table 3 and Table S5). DFT calculations suggest that *N,N-trans* is the favored configuration for both Tc(O)(hoz)<sub>2</sub>Cl and Tc(O)(htz)<sub>2</sub>Cl (Table 5, entries 1 and 3). However, the reported crystal structure of Tc(O)(htz)<sub>2</sub>Cl was *N,N-cis*.<sup>30</sup> The <sup>1</sup>H NMR spectra for these complexes were reported to be of poor quality, and we propose that the most probable reason is the formation of a *trans/cis* mixture, from which a *N,N-cis* single crystal was picked for X-ray diffraction analysis. We speculate

Table 5. DFT-calculated relative Gibbs free energy	(in kcal
$mol^{-1}$ ) for Tc(O)(L <sub>N-O</sub> ) <sub>2</sub> Cl isomers (in EtOH at 78	3 °C)

entry	HL <sub>N-O</sub>	N,N–trans	N,N–cis
1		0	+1.48
2		0 (A) +1.07 (B)	+2.83 (C) +2.08 (D)
3	⟨ <mark>→</mark> S N OH	0	+0.61
4	OH S	0 (A) -0.01 (B)	+1.00 (C) +5.57 (D)

that excess lutidine and prolonged heating might be helpful in promoting Tc complex isomer interconversion. Calculation results for Tc(O) (Mehoz)<sub>2</sub>Cl and Tc(O) (Mehtz)<sub>2</sub>Cl (Table 5, entries 2 and 4) are similar to those of Re congeners (Table 4, entries 2 and 4), suggesting that the alkyl substitution strategy might also be effective for selective synthesis of *N*,*Ntrans* Tc(O)(L<sub>N-O</sub>)<sub>2</sub>X complexes, which have not been characterized to date. Since coordination sphere (e.g., *trans/ cis*) as well as ligand structure (e.g., hoz and htz) control ligand exchange dynamics and catalytic activity for Re complexes,<sup>20</sup> systematic investigation of Tc congeners is anticipated to promote innovation in both Tc coordination chemistry and radiopharmaceutical development.

# CONCLUSIONS

Inspired from the characteristic DAs between the two  $L_{N-O}$  ligands in *N,N-trans* and *N,N-cis* Re(O)( $L_{N-O}$ )<sub>2</sub>X complexes, we successfully synthesized four *N,N-trans* Re(O)( $L_{N-O}$ )<sub>2</sub>Cl complexes ( $L_{N-O}$  = Mehoz, PhCH<sub>2</sub>hoz, CyCH<sub>2</sub>hoz, and Me<sub>2</sub>hoz) without observing the formation of *N,N-cis* isomers. Literature review, experimental results, and DFT calculations collectively demonstrate that introducing steric hindrance to  $L_{N-O}$  destabilizes *N,N-cis* isomers. DFT calculations also suggest that Tc complex congeners follow the similar trend of Re complexes. Hence, results from this study provide guidance for preparation of a wide range of *N,N-trans* Re(O)( $L_{N-O}$ <sub>2</sub>X and new *N,N-trans* Tc(O)( $L_{N-O}$ <sub>2</sub>X complexes for catalytic and biomedical innovations.

# EXPERIMENTAL SECTION

**General Information.** All chemicals and solvents were purchased from Alfa-Aesar, Sigma-Aldrich, and Cambridge Isotope Laboratories and were used as received. NMR, X-ray structure determination, elemental analysis and electrospray ionization high-resolution mass spectrometry (ESI–HRMS) were conducted in the NMR Lab, George L. Clark X-ray Facility & 3M Materials Lab, Microanalysis Lab, and Mass Spectrometry Lab in the School of Chemical Sciences, University of Illinois. NMR spectra for all ligands and complexes are provided in Supporting Information. Unless specified, all procedures were conducted under air. DA measurement was conducted with Mercury (v3.5.1, The Cambridge Crystallographic Data Centre) on CIF files.

**General Procedures of Ligand Preparation.** In a 15 mL flask, the mixture of 2-hydroxybenzonitrile (358 mg, 3 mmol), substituted ethanolamine (3.3 mmol), ZnCl<sub>2</sub> (8 mg, 0.06 mmol), and toluene (5 mL) was refluxed for 24 h. The solvent was removed in vacuo, and the residue was extracted with Et<sub>2</sub>O (3 mL × 5). The combined organic phase was dried, and the residue was redissolved in minimal amount of EtOAc or CH<sub>2</sub>Cl<sub>2</sub> and purified by silica gel flash chromatography (hexanes/EtOAc = 4/1). All products after solvent removal appeared

as an oil, but some solidified after being placed at -20 °C overnight and remained solid at room temperature.

**HMehoz (L1).** The starting ethanolamine is (*S*)-(+)-2-amino-1propanol (L-alaninol, 248 mg). The final product is a slightly orangepink solid. Yield: 423 mg (80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  12.23 (br, 1H), 7.64 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.36 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.01 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.86 (ddd, *J* = 7.7, 7.4, 1.0 Hz, 1H), 4.51 (dd, *J* = 9.2, 7.8 Hz, 1H), 4.48–4.41 (m, 1H), 3.95 (t, *J* = 7.6 Hz, 1H), 1.37 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 165.1, 160.1, 133.5, 128.2, 118.8, 116.9, 111.0, 73.5, 61.1, 21.7.

**HPh(CH<sub>2</sub>)hoz (L2).** The starting ethanolamine is (*S*)-(-)-2-amino-3-phenyl-1-propanol (ι-phenylalaninol, 499 mg). The final product is a red oil. Yield: 478 mg (62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.05 (br, 1H), 7.63 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.38 (ddd, *J* = 8.4, 7.2, 1.7 Hz, 1H), 7.35–7.31 (m, 2H), 7.27–7.24 (m, 3H), 7.02 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.87 (ddd, *J* = 7.9, 7.2, 1.1 Hz, 1H), 4.67–4.59 (m, 1H), 4.40 (dd, *J* = 9.4, 8.5 Hz, 1H), 4.14 (dd, *J* = 8.5, 7.3 Hz, 1H), 3.12 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.82 (dd, *J* = 13.7, 7.6 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.7, 160.1, 137.8, 133.6, 129.5 (C × 2), 128.9 (C × 2), 128.2, 126.9, 118.9, 117.0, 110.8, 71.4, 67.0, 42.1.

HCy(CH<sub>2</sub>)hoz (L3). The starting ethanolamine, (S)-(+)-2-amino-3cyclohexyl-1-propanol (3-cyclohexyl-L-alaninol), was prepared from its hydrochloride salt. The salt (1.07 g, 5.5 mmol) was dissolved in water (5 mL), and the solution was added dropwise with another water solution (3 mL) containing NaOH (232 mg, 5.8 mmol). A brown oil gradually formed over the water layer. After NaOH addition, the mixture was extracted with EtOAc (5 mL  $\times$  3). The combined organic phase was dried with Na2SO4, and the solvent was removed in vacuo to afford a slightly orange oil. A portion of the oil (519 mg) was used to synthesize the  $HCy(CH_2)$  hoz ligand. The final product is an orange oil. Yield: 649 mg (83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.30 (br, 1H), 7.63 (dd, J = 7.8, 1.8 Hz, 1H), 7.36 (ddd, J = 8.4, 7.2, 1.8 Hz, 1H), 7.00 (dd, I = 8.3, 1.1 Hz, 1H), 6.86 (ddd, I = 8.0, 7.3, 1.1 Hz, 1H), 4.49 (dd, J = 9.4, 7.7 Hz, 1H), 4.41 (dtd, J = 9.4, 7.5, 6.2 Hz, 1H), 3.96 (t, J = 7.6 Hz, 1H), 1.85-1.60 (m, 6H), 1.57-1.47 (m, 1H), 1.45-1.38 (m, 1H), 1.33-1.11 (m, 3H), 1.03-0.91 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.1, 160.0, 133.4, 128.1, 118.8, 116.9, 111.0, 72.7, 63.5, 44.4, 35.3, 33.8, 33.4, 26.7, 26.5 (C × 2).

**HMe**<sub>2</sub>**hoz** (L4). The starting ethanolamine is 2-amino-2-methyl-1propanol (294 mg). The final product is a slightly yellow-green solid. Yield: 360 mg (63%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 12.21 (br, 1H), 7.63 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.36 (ddd, *J* = 8.6, 7.4, 1.6 Hz, 1H), 7.01 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.86 (ddd, *J* = 7.7, 7.4, 0.9 Hz, 1H), 4.10 (s, 2H), 1.40 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 163.7, 160.1, 133.4, 128.1, 118.8, 116.9, 111.1, 78.6, 67.3, 28.7 (C × 2).

**Hhox (L5).** The starting ethanolamine is 3-amino-1-propanol (248 mg). The final product is a slightly yellow-green solid. Yield: 497 mg (94%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 14.20 (s, 1H), 7.66 (dd, J = 7.9, 1.7 Hz, 1H), 7.29 (ddd, J = 8.2, 7.3, 1.7 Hz, 1H), 6.92 (dd, J = 8.3, 1.2 Hz, 1H), 6.79 (ddd, J = 7.7, 7.5, 1.1 Hz, 1H), 4.40 (t, J = 5.8 Hz, 2H), 3.61 (t, J = 5.9 Hz, 2H), 2.04 (p, J = 5.9 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.2, 159.6, 132.6, 126.9, 117.9, 117.4, 114.8, 65.6, 41.1, 21.9.

Preparation of N,N-trans Re(O)(Mehoz)<sub>2</sub>Cl (4a). A mixture of Re(O)(OPPh<sub>3</sub>)(SMe<sub>2</sub>)Cl<sub>3</sub> (100 mg, 0.154 mmol), HMehoz (57 mg, 0.324 mmol), 2,6-lutidine (38 µL, 35 mg, 0.324 mmol), and EtOH (6 mL) was refluxed in a 15 mL flask. Green solid gradually precipitated from the solution. After it was heated for 15 min in total, the suspension was cooled, and the liquid phase was filtered through a glass frit. The solid phase was sequentially washed with EtOH (1 mL  $\times$ 3) and Et<sub>2</sub>O (1 mL  $\times$  3) to afford a green powder. Yield: 84 mg (92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.70 (dd, J = 8.0, 1.6 Hz, 1H), 7.45 (ddd, J = 8.6, 7.1, 1.8 Hz, 1H), 7.24 (ddd, J = 8.2, 7.4, 1.7 Hz, 1H, partially overlaps with the CHCl<sub>3</sub> peak),6.95 (ddd, J = 8.0, 7.0, 0.9 Hz, 1H), 6.89 (dd, J = 8.5, 0.8 Hz, 1H), 6.78 (ddd, J = 8.0, 7.0, 0.9 Hz, 1H), 6.76 (dd, J = 8.4, 0.7 Hz, 1H), 5.39-5.31 (m, 1H), 5.03 (t, J = 8.6 Hz, 1H), 4.78 (t, J = 8.6 Hz, 1H), 4.72 (dd, J = 8.6, 3.8 Hz, 1H), 4.60–4.51 (m, 1H), 4.48 (dd, J = 8.1, 6.0 Hz, 1H), 1.75 (d, J = 6.5 Hz, 3H), 1.72 (d, J = 6.6 Hz, 3H). Single crystals suitable for X-ray diffraction were grown by diffusion of pentane into

the  $CH_2Cl_2$  solution of the product. Elemental analysis  $(C_{20}H_{20}ClN_2O_5Re)$  calculated: C, 40.71%; H, 3.42%; N, 4.75%; Cl, 6.01%; Re, 31.56%, found: C, 40.99%; H, 3.23%; N, 4.59%; Cl, 7.01%; Re, 29.37%. ESI–HRMS: m/z calculated for  $C_{20}H_{20}N_2O_5Re$  (the dominant  $[M-Cl]^+$ ): 555.0930, found: 555.0923.

Preparation of N,N-trans Re(O)(Ph(CH<sub>2</sub>)hoz)<sub>2</sub>Cl (5a). A mixture of Re(O)(OPPh<sub>3</sub>)(SMe<sub>2</sub>)Cl<sub>3</sub> (100 mg, 0.154 mmol), HPh(CH<sub>2</sub>)hoz (82 mg, 0.324 mmol), 2,6-lutidine (38 µL, 35 mg, 0.324 mmol) and EtOH (6 mL) was refluxed in a 15 mL flask. Green solid gradually precipitated from the solution. After it was heated for 48 h, the suspension was cooled, and the liquid phase was filtered through a glass frit. The solid phase was sequentially washed with EtOH (1 mL  $\times$ 3) and Et<sub>2</sub>O (1 mL  $\times$  3) to afford a green powder. Yield: 99 mg (87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (dd, J = 8.1, 1.4 Hz, 1H), 7.62 (dd, J = 8.0, 1.1 Hz, 1H), 7.45-7.15 (m, 12H), 6.93-6.88 (m, 2H), 6.76-6.73 (m, 2H), 5.58-5.52 (m, 1H), 4.88 (dd, J = 9.1, 3.0 Hz, 1H), 4.83-4.74 (m, 2H), 4.65-4.62 (m, 1H), 4.53 (t, J = 8.9 Hz, 1H), 3.86–3.77 (m, 2H), 3.27 (dd, J = 14.1, 8.9 Hz, 1H), 3.02 (dd, J = 13.5, 9.5 Hz, 1H). Single crystals suitable for X-ray diffraction were grown by diffusion of pentane into the CH2Cl2 solution of the product. Elemental analysis (C32H28ClN2O5Re) calculated: C, 51.78%; H, 3.80%; N, 3.77%; Cl, 4.78%; Re, 25.09%, found: C, 51.54%; H, 3.48%; N, 3.73%; Cl, 5.13%; Re, 23.44%. ESI-HRMS: *m/z* calculated for  $C_{32}H_{28}N_2O_5Re$  (the dominant  $[M-Cl]^+$ ): 707.1556, found: 707.1550.

Preparation of N,N-trans Re(O)(Cy(CH<sub>2</sub>)hoz)<sub>2</sub>Cl (6a). A mixture of Re(O)(OPPh<sub>3</sub>)(SMe<sub>2</sub>)Cl<sub>3</sub> (100 mg, 0.154 mmol), HCy(CH<sub>2</sub>)hoz (84 mg, 0.324 mmol), 2,6-lutidine (38 µL, 35 mg, 0.324 mmol), and EtOH (6 mL) was refluxed in a 15 mL flask. Green solid gradually precipitated from the solution. After it was heated for 48 h, the suspension was cooled, and the liquid phase was filtered through a glass frit. The solid phase was sequentially washed with EtOH (1 mL  $\times$ 2) and Et<sub>2</sub>O (1 mL  $\times$  3) to afford a green powder. Yield: 72 mg (62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (dd, J = 8.2, 1.7 Hz, 1H), 7.68 (dd, J = 7.9, 1.7 Hz, 1H), 7.45 (ddd, J = 8.7, 7.1, 1.8 Hz, 1H), 7.25 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H, partially overlaps with the CHCl<sub>3</sub>residue peak), 6.94 (ddd, J = 8.0, 7.2, 0.9 Hz, 1H), 6.87 (dd, J = 8.5, 0.8 Hz, 1H), 6.77 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H), 6.75 (dd, J = 8.2, 0.8 Hz, 1H), 5.31–5.24 (m, 1H), 4.99 (t, J = 8.7 Hz, 1H), 4.86 (dd, J = 8.7, 3.5 Hz, 1H), 4.67 (t, J = 8.7 Hz, 1H), 4.57 (dd, J = 8.3, 6.1 Hz, 1H), 4.53-4.45 (m, 1H), 2.64-2.55 (m, 2H), 1.83-0.88 (m, 24H). Elemental analysis (C32H40ClN2O5Re) calculated: C, 50.95%; H, 5.35%; N, 3.71%; Cl, 4.70%; Re, 24.68%, found: C, 50.63%; H, 4.97%; N, 3.73%; Cl, 4.83%; Re, 24.60%. ESI-HRMS: m/z calculated for  $C_{32}H_{40}N_2O_5Re$  (the dominant  $[M-Cl]^+$ ): 719.2495, found: 719.2480.

Preparation of N,N-trans Re(O)(Me2hoz)2Cl (7a). A mixture of Re(O)(OPPh<sub>3</sub>)(SMe<sub>2</sub>)Cl<sub>3</sub> (150 mg, 0.231 mmol), H-4,4-Me<sub>2</sub>hoz (93 mg, 0.485 mmol), 2,6-lutidine (59 μL, 55 mg, 0.509 mmol), and EtOH (8 mL) was refluxed in a 15 mL flask. After it was heated for 15 min in total, the green solution was cooled, and the solvent was evaporated in the fume hood overnight. The solid residue was redissolved in  $\sim 0.5$ mL of EtOH, and this liquid was added dropwise in 10 mL of Et<sub>2</sub>O to precipitate both the green product and white OPPh<sub>3</sub>. After the liquid phase was filtered through a glass frit, the solid was quickly washed with EtOH (0.5 mL  $\times$  2) and Et<sub>2</sub>O (0.5 mL  $\times$  3) to afford a green powder. Yield: 87 mg (61%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.94 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.39 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.21 (ddd, J = 8.6, 7.1, 1.4 Hz, 1H), 6.93 (ddd, J = 8.1, 7.1, 0.8 Hz, 1H), 6.83 (dd, J = 8.4, 0.8 Hz, 1H), 6.76 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H), 6.74 (dd, J = 7.1, 0.7 Hz, 1H), 4.66-4.53 (m, 4H), 1.96 (s, 3H), 1.94 (s, 3H), 1.85 (s, 3H), 1.65 (s, 3H). Elemental analysis (C<sub>22</sub>H<sub>24</sub>ClN<sub>2</sub>O<sub>5</sub>Re) calculated: C, 42.75%; H, 3.91%; N, 4.53%; Cl, 5.74%; Re, 30.13%, found: C, 42.14%; H, 3.57%; N, 4.45%; Cl, 6.94%; Re, 29.40%. ESI-HRMS: m/z calculated for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub>Re (the dominant [M-Cl]<sup>+</sup>): 583.1243, found: 583.1243.

Preparation of N,N-cis  $Re(O)(hox)_2Cl$  (8b). A mixture of Re(O)-(OPPh<sub>3</sub>)(SMe<sub>2</sub>)Cl<sub>3</sub> (150 mg, 0.231 mmol), Hhox (86 mg, 0.485 mmol), 2,6-lutidine (59  $\mu$ L, 55 mg, 0.509 mmol), and EtOH (9 mL) was refluxed in a 15 mL flask for 48 h. After it was cooled and filtered, the solid phase was washed with EtOH and then redissolved in

 $CH_2Cl_2$  for silica gel flash chromatography (EtOAc). The product ( $R_f$ 0.55) was isolated from the N.N-trans isomer (tailed in silica) as a green solid after solvent removal in vacuo. Yield: 97 mg (71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (dd, J = 8.3, 1.7 Hz, 1H), 7.63 (dd, J= 8.0, 1.7 Hz, 1H), 7.44 (ddd, J = 8.1, 7.6, 1.7 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.16 (ddd, J = 8.7, 6.8, 1.7 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.75 (t, J = 7.6 Hz, 1H), 6.29 (d, J = 8.3 Hz, 1H), 4.82 (t, J = 5.5 Hz, 2H), 4.54 (dt, J = 15.9, 5.3 Hz, 1H), 4.32 (dt, J = 9.9, 4.7 Hz, 1H), 4.00 (dt, J = 15.0, 4.7 Hz, 1H), 3.67 (ddd, J = 15.8, 8.3, 4.7 Hz, 1H), 3.51 (td, J = 9.7, 3.1 Hz, 1H), 3.21 (ddd, J = 14.9, 9.3, 5.2 Hz, 1H), 2.42 (dp, J = 13.4, 6.0 Hz, 1H), 2.27 (dp, J = 15.3, 5.1 Hz, 1H), 1.93 (dtt, J = 13.9, 9.1, 4.5 Hz, 1H), 1.55-1.52 (m, 1H, partially overlaps with the water peak). Single crystals suitable for X-ray diffraction were grown by diffusion of pentane into the CH2Cl2 solution of the product. Elemental analysis (C20H20ClN2O5Re) calculated: C, 40.71%; H, 3.42%; N, 4.75%; Cl, 6.01%; Re, 31.56%, found: C, 40.70%; H, 3.02%; N, 4.65%; Cl, 6.23%; Re, 30.56%. ESI-HRMS: m/z calculated for  $C_{20}H_{20}N_2O_5Re$  (the dominant  $[M-Cl]^+$ ): 555.0930, found: 555.0938.

**X-ray Crystallography.** Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer equipped with a Photon 100 detector using multilayer optics to monochromatize Mo K $\alpha$  radiation (for 4a and 7a) and a Siemens Platform diffractometer equipped with an Apex II CCD detector using graphite-monochromatized Mo K $\alpha$  radiation (for 8b). Combinations of 0.5°  $\varphi$  and  $\omega$  scans were used to collect the data. The collections, cell refinements, and integrations of intensity data were performed with the APEX2 software package.<sup>71</sup> Face-indexed absorption corrections were performed numerically along with incident beam correction using the program SADABS.<sup>72</sup> The structures were solved with the direct methods program<sup>73</sup> and refined with the full-matrix least-squares SHELXL<sup>74</sup> program. Additional refinement details and metrical parameters are provided in Table 1.

**Computational Details.** DFT<sup>75,76</sup> was applied to all Re complex structures at the B3LYP level.<sup>77–79</sup> The basis set used for rhenium was effective-core-potential (ECP) based LANL2DZ basis,<sup>80</sup> with reoptimized functions of Couty and Hall<sup>81</sup> and a set of polarization f function.<sup>82</sup> The 6-31G (d, p) basis sets<sup>83,84</sup> were used for all H, C, N, O, and Cl atoms. The 6-311G(d) basis sets<sup>85,86</sup> were used for S atoms. For all Re complexes, ethanol was used as solvent, and solvation energies were obtained by applying SMD solvation model<sup>87</sup> with default radii and nonelectrostatic terms. All of the geometry optimization and thermochemistry results were gained using Gaussian09 (Revision D01) package of programs.<sup>88</sup> Calculated energies and optimized structure coordinate files (.xyz format) are provided in Supporting Information.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b03076.

NMR spectra, tabulated dihedral angles, additional references (PDF)

Calculated structure coordinate file (XYZ)

Crystallographic data (CIF)

# AUTHOR INFORMATION

#### **Corresponding Authors**

\*E-mail: jyliu@engr.ucr.edu. (J.L.)

\*E-mail: strthmnn@mines.edu. (T.J.S.)

# ORCID <sup>©</sup>

Jinyong Liu: 0000-0003-1473-5377

Danielle L. Gray: 0000-0003-0059-2096

#### **Present Address**

Xiamen Intellectual Property Office, Room 1301 (West Bldg.), 191 Changqing Rd, Xiamen, Fujian, 361012, P. R. China.

# Notes

The authors declare no competing financial interest.

CCDC 1492182 (structure 4a), 1492183 (5a), and 1492184 (8b) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac. uk/getstructures.

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## REFERENCES

(1) Kühn, F. E.; Scherbaum, A.; Herrmann, W. A. Methyltrioxorhenium and Its Applications in Olefin Oxidation, Metathesis and Aldehyde Olefination. *J. Organomet. Chem.* **2004**, *689*, 4149–4164.

(2) Sousa, S. C.; Cabrita, I.; Fernandes, A. C. High-Valent Oxo-Molybdenum and Oxo-Rhenium Complexes as Efficient Catalysts for X–H (X= Si, B, P and H) Bond Activation and for Organic Reductions. *Chem. Soc. Rev.* **2012**, *41*, 5641–5653.

(3) Owens, G. S.; Arias, J.; Abu-Omar, M. M. Rhenium Oxo Complexes in Catalytic Oxidations. *Catal. Today* 2000, 55, 317–363.
(4) Bernardo, J. R.; Fernandes, A. C. Deoxygenation of Carbonyl Compounds Using an Alcohol as an Efficient Reducing Agent Catalyzed by Oxo-Rhenium Complexes. *Green Chem.* 2016, 18, 2675–2681.

(5) Dinda, S.; Genest, A.; Rösch, N.  $O_2$  Activation and Catalytic Alcohol Oxidation by Re Complexes with Redox-Active Ligands: A DFT Study of Mechanism. *ACS Catal.* **2015**, *5*, 4869–4880.

(6) Das, B. G.; Nallagonda, R.; Dey, D.; Ghorai, P. Synthesis of Airand Moisture-Stable, Storable Chiral Oxorhenium Complexes and Their Application as Catalysts for the Enantioselective Imine Reduction. *Chem. - Eur. J.* **2015**, *21*, 12601–12605.

(7) Martins, L. M.; Alegria, E. C.; Smoleński, P.; Kuznetsov, M. L.; Pombeiro, A. J. Oxorhenium Complexes Bearing the Water-Soluble Tris(pyrazol-1-yl)methanesulfonate, 1,3,5-Triaza-7-phosphaadamantane, or Related Ligands, as Catalysts for Baeyer–Villiger Oxidation of Ketones. *Inorg. Chem.* **2013**, *52*, 4534–4546.

(8) Lilly, C. P.; Boyle, P. D.; Ison, E. A. Synthesis of Oxorhenium Acetyl and Benzoyl Complexes Incorporating Diamidopyridine Ligands: Implications for the Mechanism of CO Insertion. *Organometallics* **2012**, *31*, 4295–4301.

(9) Alegria, E. C.; Kirillova, M. V.; Martins, L. M.; Pombeiro, A. J. Pyrazole and Trispyrazolylmethane Rhenium Complexes as Catalysts for Ethane and Cyclohexane Oxidations. *Appl. Catal., A* **2007**, *317*, 43–52.

(10) Kirillov, A. M.; Haukka, M.; Kirillova, M. V.; Pombeiro, A. J. Single-Pot Ethane Carboxylation Catalyzed by New Oxorhenium(V) Complexes with N,O Ligands. *Adv. Synth. Catal.* **2005**, 347, 1435–1446.

(11) Kasner, G. R.; Boucher-Jacobs, C.; McClain, J. M.; Nicholas, K. M. Oxo-Rhenium Catalyzed Reductive Coupling and Deoxygenation of Alcohols. *Chem. Commun.* **2016**, *52*, 7257–7260.

(12) Boucher-Jacobs, C.; Nicholas, K. M. Oxo-Rhenium-Catalyzed Deoxydehydration of Polyols with Hydroaromatic Reductants. *Organometallics* **2015**, *34*, 1985–1990.

(13) Raju, S.; Moret, M. E.; Klein Gebbink, R. J. Rhenium-Catalyzed Dehydration and Deoxydehydration of Alcohols and Polyols:

Opportunities for the Formation of Olefins from Biomass. *ACS Catal.* **2015**, *5*, 281–300.

(14) Yi, J.; Liu, S.; Abu-Omar, M. M. Rhenium-Catalyzed Transfer Hydrogenation and Deoxygenation of Biomass-Derived Polyols to Small and Useful Organics. *ChemSusChem* **2012**, *5*, 1401–1404.

(15) Shiramizu, M.; Toste, F. D. Expanding the Scope of Biomass-Derived Chemicals through Tandem Reactions Based on Oxorhenium-Catalyzed Deoxydehydration. *Angew. Chem., Int. Ed.* **2013**, *52*, 12905–12909.

(16) Shiramizu, M.; Toste, F. D. Deoxygenation of Biomass-Derived Feedstocks: Oxorhenium-Catalyzed Deoxydehydration of Sugars and Sugar Alcohols. *Angew. Chem., Int. Ed.* **2012**, *51*, 8082–8086.

(17) Ahmad, I.; Chapman, G.; Nicholas, K. M. Sulfite-Driven, Oxorhenium-Catalyzed Deoxydehydration of Glycols. *Organometallics* **2011**, *30*, 2810–2818.

(18) Abu-Omar, M. M.; McPherson, L. D.; Arias, J.; Béreau, V. M. Clean and Efficient Catalytic Reduction of Perchlorate. *Angew. Chem., Int. Ed.* **2000**, *39*, 4310–4313.

(19) McPherson, L. D.; Drees, M.; Khan, S. I.; Strassner, T.; Abu-Omar, M. M. Multielectron Atom Transfer Reactions of Perchlorate and Other Substrates Catalyzed by Rhenium Oxazoline and Thiazoline Complexes: Reaction Kinetics, Mechanisms, and Density Functional Theory Calculations. *Inorg. Chem.* **2004**, *43*, 4036–4050.

(20) Liu, J.; Wu, D.; Su, X.; Han, M.; Kimura, S. S.; Gray, D. L.; Shapley, J. R.; Abu-Omar, M. M.; Werth, C. J.; Strathmann, T. J. Configuration Control in the Synthesis of Homo- and Heteroleptic Bis(oxazolinylphenolato/thiazolinylphenolato) Chelate Ligand Complexes of Oxorhenium(V): Isomer Effect on Ancillary Ligand Exchange Dynamics and Implications for Perchlorate Reduction Catalysis. *Inorg. Chem.* **2016**, *55*, 2597–2611.

(21) Liu, J.; Choe, J. K.; Wang, Y.; Shapley, J. R.; Werth, C. J.; Strathmann, T. J. Bioinspired Complex-Nanoparticle Hybrid Catalyst System for Aqueous Perchlorate Reduction: Rhenium Speciation and Its Influence on Catalyst Activity. *ACS Catal.* **2015**, *5*, 511–522.

(22) Zhang, Y.; Hurley, K. D.; Shapley, J. R. Heterogeneous Catalytic Reduction of Perchlorate in Water with Re–Pd/C Catalysts Derived from an Oxorhenium(V) Molecular Precursor. *Inorg. Chem.* **2011**, *50*, 1534–1543.

(23) Liu, J.; Chen, X.; Wang, Y.; Strathmann, T. J.; Werth, C. J. Mechanism and Mitigation of the Decomposition of an Oxorhenium Complex-Based Heterogeneous Catalyst for Perchlorate Reduction in Water. *Environ. Sci. Technol.* **2015**, *49*, 12932–12940.

(24) Liu, J.; Han, M.; Wu, D.; Chen, X.; Choe, J. K.; Werth, C. J.; Strathmann, T. J. A New Bioinspired Perchlorate Reduction Catalyst with Significantly Enhanced Stability via Rational Tuning of Rhenium Coordination Chemistry and Heterogeneous Reaction Pathway. *Environ. Sci. Technol.* **2016**, *50*, 5874–5881.

(25) Nguyen, H. H.; Pham, C. T.; Abram, U. Rhenium and Technetium Complexes with Pentadentate Thiocarbamoylbenzamidines: Steps toward Bioconjugation. *Inorg. Chem.* **2015**, *54*, 5949–5959.

(26) Jürgens, S.; Herrmann, W. A.; Kühn, F. E. Rhenium and Technetium Based Radiopharmaceuticals: Development and Recent Advances. J. Organomet. Chem. 2014, 751, 83–89.

(27) Le Bideau, F.; Dagorne, S. Synthesis of Transition-Metal Steroid Derivatives. *Chem. Rev.* **2013**, *113*, 7793–7850.

(28) Aufort, M.; Gonera, M.; Le Gal, J.; Czarny, B.; Le Clainche, L.; Thai, R.; Dugave, C. Oxorhenium-Mediated Assembly of Noncyclic Selective Integrin Antagonists: A Combinatorial Approach. *Chem-BioChem* **2011**, *12*, 583–592.

(29) Abram, U.; Alberto, R. Technetium and Rhenium: Coordination Chemistry and Nuclear Medical Applications. J. Braz. Chem. Soc. 2006, 17, 1486–1500.

(30) Shuter, E.; Hoveyda, H.; Karunaratne, V.; Rettig, S. J.; Orvig, C. Bis(ligand) Rhenium(V) and Technetium(V) Complexes of Two Naturally Occurring Binding Moieties (Oxazoline and Thiazoline). *Inorg. Chem.* **1996**, *35*, 368–372.

(31) Machura, B.; Wolff, M.; Gryca, I. Rhenium(V) Oxocomplexes  $[ReOX(N-O)_2]$  and  $[ReOL(N-O)_2]^+$ -Synthesis, Structure, Spec-

troscopy and Catalytic Properties. Coord. Chem. Rev. 2014, 275, 154-164.

(32) Ison, E. A.; Trivedi, E. R.; Corbin, R. A.; Abu-Omar, M. M. Mechanism for Reduction Catalysis by Metal Oxo: Hydrosilation of Organic Carbonyl Groups Catalyzed by a Rhenium(V) Oxo Complex. *J. Am. Chem. Soc.* **2005**, *127*, 15374–15375.

(33) Du, G.; Abu-Omar, M. M. Catalytic Hydrosilylation of Carbonyl Compounds with Cationic Oxorhenium(V) Salen. *Organometallics* **2006**, *25*, 4920–4923.

(34) Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. Hydrogen Production from Hydrolytic Oxidation of Organosilanes Using a Cationic Oxorhenium Catalyst. *J. Am. Chem. Soc.* **2005**, *127*, 11938– 11939.

(35) Lin, A.; Peng, H.; Abdukader, A.; Zhu, C. Rhenium-Catalyzed Oxidative Cyanation of Tertiary Amines with TMSCN. *Eur. J. Org. Chem.* **2013**, *2013*, 7286–7290.

(36) Wegenhart, B. L.; Abu-Omar, M. M. A Solvent-Free Method for Making Dioxolane and Dioxane from the Biorenewables Glycerol and Furfural Catalyzed by Oxorhenium(V) Oxazoline. *Inorg. Chem.* **2010**, *49*, 4741–4743.

(37) Traar, P.; Schachner, J. r. A.; Steiner, L.; Sachse, A.; Volpe, M.; Mösch-Zanetti, N. C. Oxorhenium(V) Complexes with Pyrazole Based Aryloxide Ligands and Application in Olefin Epoxidation. *Inorg. Chem.* **2011**, *50*, 1983–1990.

(38) Wood, C. S.; Browne, C.; Wood, D. M.; Nitschke, J. R. Fuel-Controlled Reassembly of Metal–Organic Architectures. *ACS Cent. Sci.* 2015, *1*, 504–509.

(39) Holm, R. Metal-Centered Oxygen Atom Transfer Reactions. *Chem. Rev.* **1987**, *87*, 1401–1449.

(40) Greer, M. A.; Goodman, G.; Pleus, R. C.; Greer, S. E. Health Effects Assessment for Environmental Perchlorate Contamination: The Dose Response for Inhibition of Thyroidal Radioiodine Uptake in Humans. *Environ. Health Perspect.* **2002**, *110*, 927–937.

(41) USEPA. Drinking Water: Regulatory Determination on Perchlorate. *Fed. Regist.* **2011**, *76*, 7762–7767.

(42) Traar, P.; Schachner, J. A.; Steiner, L.; Sachse, A.; Volpe, M.; Mösch-Zanetti, N. C. Oxorhenium(V) Complexes with Pyrazole Based Aryloxide Ligands and Application in Olefin Epoxidation. *Inorg. Chem.* **2011**, *50*, 1983–1990.

(43) Schröckeneder, A.; Traar, P.; Raber, G.; Baumgartner, J.; Belaj, F.; Mösch-Zanetti, N. C. Oxorhenium(V) Complexes with Ketiminato Ligands: Coordination Chemistry and Epoxidation of Cyclooctene. *Inorg. Chem.* **2009**, *48*, 11608–11614.

(44) Schachner, J. A.; Terfassa, B.; Peschel, L. M.; Zwettler, N.; Belaj, F.; Cias, P.; Gescheidt, G.; Mösch-Zanetti, N. C. Oxorhenium(V) Complexes with Phenolate–Oxazoline Ligands: Influence of the Isomeric Form on the O-Atom-Transfer Reactivity. *Inorg. Chem.* **2014**, 53, 12918–12928.

(45) Bolm, C.; Weickhardt, K.; Zehnder, M.; Ranff, T. Synthesis of Optically Active Bis(2-oxazolines): Crystal Structure of a 1,2-Bis(2-oxazolinyl)benzene ZnCl<sub>2</sub> Complex. *Chem. Ber.* **1991**, *124*, 1173–1180.

(46) Franco, D.; Gómez, M.; Jiménez, F.; Muller, G.; Rocamora, M.; Maestro, M. A.; Mahía, J. Exo- and Endocyclic Oxazolinyl-Phosphane Palladium Complexes: Catalytic Behavior in Allylic Alkylation Processes. *Organometallics* **2004**, *23*, 3197–3209.

(47) Serrano, J. L.; Sierra, T.; Gonzalez, Y.; Bolm, C.; Weickhardt, K.; Magnus, A.; Moll, G. Improving FLC Properties. Simplicity, Planarity, and Rigidity in New Chiral Oxazoline Derivatives. *J. Am. Chem. Soc.* **1995**, *117*, 8312–8321.

(48) Xi, T.; Mei, Y.; Lu, Z. Palladium-Catalyzed C-2 C-H Heteroarylation of Chiral Oxazolines: Diverse Synthesis of Chiral Oxazoline Ligands. *Org. Lett.* **2015**, *17*, 5939–5941.

(49) Cozzi, P. G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Oxazoline Early Transition Metal Complexes: Functionalizable Achiral Titanium-(IV), Titanium(III), Zirconium(IV), Vanadium(III), and Chiral Zirconium(IV) Bis(oxazoline) Complexes. *Inorg. Chem.* **1995**, *34*, 2921–2930. (50) Kandasamy, K.; Singh, H. B.; Butcher, R. J.; Jasinski, J. P. Synthesis, Structure, and Catalytic Properties of  $V^{IV}$ ,  $Mn^{III}$ ,  $Mo^{VI}$ , and  $U^{VI}$  Complexes Containing Bidentate (N, O) Oxazine and Oxazoline Ligands. *Inorg. Chem.* **2004**, *43*, 5704–5713.

(51) Abu-Omar, M. M.; Khan, S. I. Molecular Rhenium(V) Oxotransferases: Oxidation of Thiols to Disulfides with Sulfoxides. The Case of Substrate-Inhibited Catalysis. *Inorg. Chem.* **1998**, *37*, 4979–4985.

(52) Gerber, T. I.; Luzipo, D.; Mayer, P. Different Coordination Modes of Tetradentate Schiff Bases in Monomeric and Dimeric Oxorhenium(V) Complexes. *J. Coord. Chem.* **2005**, *58*, 1505–1512.

(53) Béreau, V. M.; Khan, S. I.; Abu-Omar, M. M. Synthesis of Enantiopure Oxorhenium(V) and Arylimidorhenium(V) "3 + 2" Schiff Base Complexes. X-Ray Diffraction, Cyclic Voltammetry, UV–Vis, and Circular Dichroism Characterizations. *Inorg. Chem.* **2001**, *40*, 6767–6773.

(54) Basak, S.; Rajak, K. K. Synthesis, Structure, and Spectroscopic Properties of Chiral Oxorhenium(V) Complexes Incorporating Polydentate Ligands Derived from L-Amino Acids: A Density Functional Theory/Time-Dependent Density Functional Theory Investigation. *Inorg. Chem.* **2008**, *47*, 8813–8822.

(55) Terfassa, B.; Schachner, J. A.; Traar, P.; Belaj, F.; Mösch-Zanetti, N. C. Oxorhenium(V) Complexes with Naphtholate-Oxazoline Ligands in the Catalytic Epoxidation of Olefins. *Polyhedron* **2014**, *75*, 141–145.

(56) Kühn, F. E.; Rauch, M. U.; Lobmaier, G. M.; Artus, G. R.; Herrmann, W. A. Multiple Bonds between Main-Group Elements and Transition Metals, CLXV. Rhenium(V) Oxo Complexes with Bidentate Schiff Bases: Structures and Catalytic Applications. *Chem. Ber.* **1997**, *130*, 1427–1431.

(57) Machura, B.; Kruszynski, R. New Oxorhenium Complexes with the 8-Quinolinolato Ligand: X-Ray Structure and DFT Calculations for [ReOBr(hqn)<sub>2</sub>]. *Polyhedron* **2007**, *26*, 2957–2963.

(58) Machura, B.; Wolff, M.; Tabak, D.; Schachner, J. A.; Mösch-Zanetti, N. C. Oxidorhenium(V) Complexes with Phenolate- and Carboxylate-Based Ligands: Structure and Catalytic Epoxidation. *Eur. J. Inorg. Chem.* **2012**, 2012, 3764–3773.

(59) Zwettler, N.; Schachner, J. A.; Belaj, F.; Mösch-Zanetti, N. C. Oxorhenium(V) Complexes with Phenolate–Pyrazole Ligands for Olefin Epoxidation Using Hydrogen Peroxide. *Inorg. Chem.* **2014**, *53*, 12832–12840.

(60) Machura, B.; Wolff, M.; Benoist, E.; Schachner, J. A.; Mösch-Zanetti, N. C. Oxorhenium(V) Complexes of Quinoline and Isoquinoline Carboxylic Acids–Synthesis, Structural Characterization and Catalytic Application in Epoxidation Reactions. *Dalton Trans.* **2013**, *42*, 8827–8837.

(61) Machura, B.; Kusz, J. Synthesis, Spectroscopic Characterisation, Crystal and Molecular Structure of  $[ReOBr(quin-2-c)_2]$  and  $[ReOCl-(quin-2-c)_2]$  Complexes: DFT and TD-DFT Calculations for  $[ReOBr(quin-2-c)_2]$ . Polyhedron 2008, 27, 187–195.

(62) Lobmaier, G. M.; Frey, G. D.; Dewhurst, R. D.; Herdtweck, E.; Herrmann, W. A. Rhenium, Palladium, and Copper Pyridylalkoxide Complexes: Synthesis, Structural Characterization, and Catalytic Application in Epoxidation Reactions. *Organometallics* **2007**, *26*, 6290–6299.

(63) Herrmann, W. A.; Rauch, M. U.; Artus, G. R. Multiple Bonds between Main Group Elements and Transition Metals. 153.<sup>1</sup> Rhenium(V) Oxo Complexes with Tetradentate Schiff Bases: Structural Considerations. *Inorg. Chem.* **1996**, *35*, 1988–1991.

(64) Zwettler, N.; Schachner, J. r. A.; Belaj, F.; Mösch-Zanetti, N. C. Oxidorhenium(V) Complexes with Tetradentate Iminophenolate Ligands: Influence of Ligand Flexibility on the Coordination Motif and Oxygen-Atom-Transfer Activity. *Inorg. Chem.* **2016**, *55*, 5973–5982.

(65) Van Bommel, K. J.; Verboom, W.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. Rhenium(V)-Salen Complexes: Configurational Control and Ligand Exchange. *Inorg. Chem.* **1998**, *37*, 4197–4203.

(66) Benny, P. D.; Green, J. L.; Engelbrecht, H. P.; Barnes, C. L.; Jurisson, S. S. Reactivity of Rhenium(V) Oxo Schiff Base Complexes with Phosphine Ligands: Rearrangement and Reduction Reactions. *Inorg. Chem.* 2005, 44, 2381–2390.

(67) Wilcox, B. E.; Cooper, J. N.; Elder, R. C.; Deutsch, E. A Technetium(V) Complex Resulting from Intramolecular Ring Closure of a Tridentate Schiff Base Ligand. X-Ray Crystal Structure of Chlorobis(2-(2-hydroxyphenyl)benzothiazolato)oxotechnetium(V). *Inorg. Chim. Acta* **1988**, *142*, 55–58.

(68) Bandoli, G.; Mazzi, U.; Clemente, D. A.; Roncari, E. Synthesis of Six-Coordinate Technetium(V) Complexes with N-Phenylsalicylideneimine. X-Ray Crystal Structure of Chlorooxobis(Nphenylsalicylideneiminato)technetium(V). J. Chem. Soc., Dalton Trans. 1982, 2455–2459.

(69) Wilcox, B. E.; Heeg, M. J.; Deutsch, E. Synthesis and Characterization of Technetium(V) 8-Quinolinolates. X-Ray Crystal Structure of Cis-Chlorobis(2-methyl-8-quinolinolato)oxotechnetium-(V). *Inorg. Chem.* **1984**, *23*, 2962–2967.

(70) Rochon, F. D.; Melanson, R.; Kong, P. C. Synthesis and Crystal Structures of Oxo Pyridinemethanolate Technetium(V) Complexes. *Inorg. Chim. Acta* **1997**, *254*, 303–307.

(71) APEX2; Bruker AXS, Inc.: Madison, WI, 2004.

(72) SADABS; Bruker AXS, Inc.: Madison, WI, 2007.

(73) Sheldrick, G. M. SHELXS-97, 97–2; University of Göttingen: Germany, 1997.

(74) Sheldrick, G. M. SHELXL-97, 97–2; University of Göttingen: Germany, 1997.

(75) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871.

(76) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.

(77) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. **1993**, 98, 5648–5652.

(78) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

(79) Devlin, F.; Finley, J.; Stephens, P.; Frisch, M. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields: A Comparison of Local, Nonlocal, and Hybrid Density Functionals. *J. Phys. Chem.* **1995**, *99*, 16883–16902.

(80) Wadt, W. R.; Hay, P. J. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for Main Group Elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284–298.

(81) Couty, M.; Hall, M. B. Basis Sets for Transition Metals: Optimized Outer P Functions. J. Comput. Chem. **1996**, 17, 1359–1370.

(82) Ehlers, A.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K.; Stegmann, R.; Veldkamp, A.; Frenking, G. A Set of F-Polarization Functions for Pseudo-Potential Basis Sets of the Transition Metals Sc-Cu, Y-Ag and La-Au. *Chem. Phys. Lett.* **1993**, 208, 111–114.

(83) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

(84) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(85) McLean, A.; Chandler, G. Contracted Gaussian Basis Sets for Molecular Calculations. I. Second Row Atoms, Z= 11–18. *J. Chem. Phys.* **1980**, *72*, 5639–5648.

(86) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72*, 650–654.

(87) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. J. Phys. Chem. B 2009, 113, 6378–6396.

(88) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.