Diastereoselective Synthesis and Electronic Asymmetry of Chiral Nonracemic Rhenium(V) Oxo Complexes Containing the Hydrotris(1-pyrazolyl)borate Ligand

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The compounds [TpReO(η^2-N−X)] (X = N, O; Tp = hydrotrispyrazolylborate) were prepared from TpReOCl$_2$ and chiral, bidentate ligands in which η^2-N−X = the alcoholates or amidates derived from (1*S*,2*R*)-ephedrine, (1*S*,2*S*)-diphenylethylenediamine, and L-proline. The three complexes have been fully characterized by ^{1}H NMR, IR, circular-dichroism, elemental analysis, polarimetry, and X-ray crystallography. All have a chiral center at rhenium. The complexes derived from (1*S*,2*R*)-ephedrine and L-proline were formed diastereoselectively as a single diastereomer. All of the complexes exhibited similar Re−O bond distances, ranging from 1.687(7) to 1.707(7) Å, consistent with distances found in other Re(V) oxo complexes. The electronic asymmetry at the metal caused by the different donor properties of the ligands leads to tilting of the Re−oxo bond relative to the plane of the equatorial ligands. The compounds were found to be robust and resisted oxo transfer even when subjected to harsh conditions.

Introduction

The stability of high oxidation state rhenium complexes has been exploited in recent years for use as oxo transfer complexes.[1] In particular, the asymmetric oxidation of prochiral sulfides and olefins, with subsequent reduction of the rhenium center, is a field of continued interest.[2] To date, there have been a number of reports on the catalytic oxidation of sulfides with rhenium complexes. Notably, Espenson et al. have described the oxidation of sulfides with methyltrioxorhenium.[3] Arterburn et al. have investigated the oxidation of sulfides using the catalyst Re(O)Cl$_3$(PPh$_3$)$_2$ and diphenyl sulfoxide as the sacrificial oxidant.[2b] Furthermore, McKervey et al. were able to demonstrate the first example of catalytic enantioselection using a rhenium(V) oxo/(+)-camphor pyrazine carboxylic acid complex to achieve an ee of 15% in the oxidation of methyl phenyl sulfide.[4] The asymmetric oxidation of sulfides via Re(V) oxides has not, to our knowledge, resulted in high ee. It would seem that suitable modification of

ligands would lead to better asymmetric catalysis. With mixed ligand complexes, there are possibilities of multiple isomers with different selectivities. Therefore, as a first step in an effort to develop the chemistry of chiral Re(V) oxides for use in asymmetric oxidations, we report the synthesis and characterization of TpReO[(1*S*,2*S*)-η^2-NHCH(Ph)CH(Ph)NH-*N*,*N*], **1**; (S_{Re},$S_{C−O}$,$R_{C−N}$)-TpReO(η^2-N(CH$_3$)CH(CH$_3$)CH(Ph)O-*N*,*O*)], **2**; and (S_{Re},S_c)-TpReO(η^2-N(CH$_2$)$_3$CHCO$_2$-*N*,*O*), **3**.

Results

Complexes **1**−**3** were readily synthesized by heating TpReOCl$_2$ and the appropriate chiral bidentate ligand in CH$_3$CN under reflux in the presence of NEt$_3$.[5] This protocol results in the loss of two protons from either the diamine or amino alcohol to yield stable neutral Re(V) complexes. Complexes **1**−**3** were soluble in polar solvents, but insoluble in Et$_2$O and hexane.

Complex **1** was isolated as a single isomer by virtue of the C_2 symmetric enantiopure (1*S*,2*S*)-diphenylethylenediamine ligand. The crystal structure of **1** and its numbering scheme are shown in Figure 1. (Note the amide hydrogens were not found in the difference Fourier and were placed assuming the N was sp^2 hybridized.) The coordination environment of the rhenium atom in **1** can be described as a distorted octahedron with an equatorial plane occupied by the Tp nitrogen donors N(5) and N(7) along with the diamido nitrogen atoms N(1) and N(2). As such, the axial positions are occupied by N(3) of the Tp ligand and the terminal oxo ligand O(1). A five-membered metal-containing ring M(HNCH$_2$CH$_2$NH) has the potential of two chiral conformations, which in analogy with ethyl-

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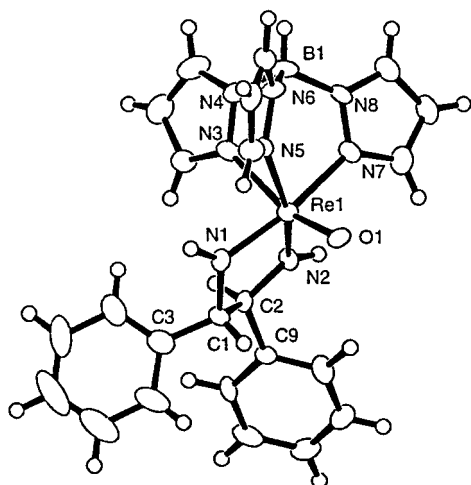(5) Brown, S.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091−4100.

Figure 1. ORTEP representation of [TpReO((1*S*,2*S*)-η²-HNCH(Ph)CH(Ph)NH-*N,N*] (**1**), with 50% probability ellipsoids.
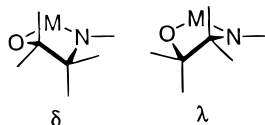

Figure 2. Conformations in a five-membered chelate ring.

enediamine complexes might be called k and k′ or δ and λ,[6] as shown in Figure 2. Conformational effects have been previously noted in other Re complexes with ethanediamido and ethanediolates.[7] However, in the case of the comparable ethanediolate, [B(pz)₃]ReO-(OCH₂CH₂O), an envelope conformation with both carbons on the same side of the O−Re−O plane was found. For diamido complex **1**, stereogenic centers at carbons C(1) and C(2) force a conformation that maintains the phenyl groups in equatorial positions and the H atoms in axial positions. This conformation would be expected to dominate in solution, and this is implied somewhat by $J_{vic} = 8.6$ Hz. This is a moderately large coupling considering the electronegative substituents, but it could accommodate equilibration with other conformers. This conformation also requires one phenyl group below and one above the N(1)−N(2)−N(5)−N(7) equatorial plane. In this manner, the production of complex **1** was biased by the C_2-symmetry of the ligand from which only one isomer was possible.

The synthesis as depicted in Figure 3 with (1*S*,2*R*)-ephedrine as the ligand is representative of that for the three complexes. Characterization of **2** by ¹H NMR and X-ray crystallography revealed that a single diastereomer was produced. An X-ray structure of **2** is depicted in Figure 4.

The coordination of the rhenium atom can be described as distorted octahedral. It is convenient to consider an equatorial plane of the two Tp nitrogen atoms N(4) and N(6), respectively, trans to O(2) and N(1) of the ephedrine ligand. The remaining axial positions
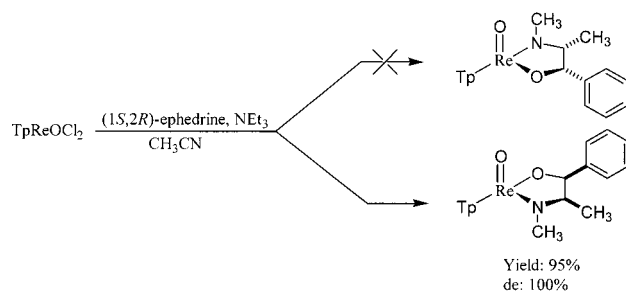
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Figure 3. Preparative strategy for (S_{Re},$S_{O−C}$,$R_{C−N}$)-TpReO-(η²-N(CH₃)CH(CH₃)CH(Ph)O-*N,O*)] (**1**).
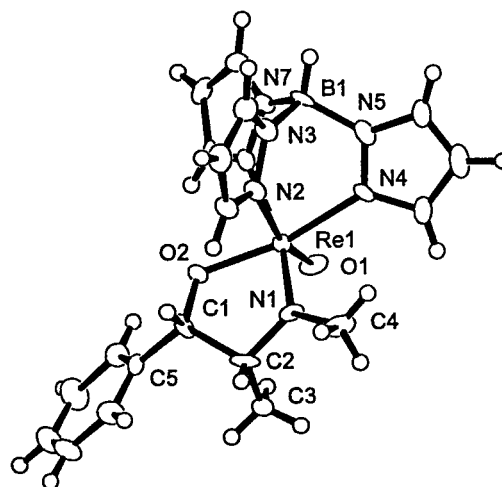
Figure 4. ORTEP representation of (S_{Re},$S_{C−O}$,$R_{C−N}$)-TpReO(η²-N(CH₃)CH(CH₃)CH(Ph)O-*N,O*)] (**2**), with 50% probability ellipsoids.

are occupied by N(2) of the Tp ligand and the terminal oxo ligand O(1).

Complex **2** was formed exclusively as one diastereomer with three chiral centers: one at rhenium and two that are ligand based. The selective formation of a single isomer of **2** can be attributed to steric interactions between the Tp and the ephedrine ligands. As shown in Figure 4, the orientation of the ephedrine ligand directed the methyl C(3) and phenyl substituents away from the Tp ligand. In this manner, steric interactions between the Tp ligand and the bulky substituents on the ephedrine were minimized. The result was the selective formation of **2**, which contained a chiral five-membered ring with a phenyl group equatorial and the adjacent methyl group axial. It is this axial group that would provide the major steric interaction if the ligand were flipped over and the chirality at the metal reversed. An equatorial C-Me in either case would appear to be destabilized by steric interaction with N-Me. Note that the Re−N(C$_{Me}$)(C$_{CHMe}$) fragment is nearly planar, suggesting sp² hybridization at N.

The crystal structure of **3** and its numbering scheme are shown in Figure 5. A single isomer was produced in which the proline ring was situated between two of the Tp-pyrazole rings in order to reduce steric interactions. The environment of the rhenium atom is distorted octahedral with an equatorial plane occupied by N(4) and N(6) of the Tp ligand along with O(2) and N(1) of the proline ligand. The remaining axial positions are occupied by N(2) of the Tp and O(1) of the oxo ligand. As a consequence, the rhenium center was surrounded

Figure 5. ORTEP representation of [(S_{Re},S_c)-TpReO(η^2-N(CH$_2$)$_3$CHCO$_2$-*N*,*O*)] (**3**), with 50% probability ellipsoids.

Figure 6. Side view of [(S_{Re},S_c)-TpReO(η^2-N(CH$_2$)$_3$CHCO$_2$-*N*,*O*)] (**3**) illustrating the tilt of the oxo group toward the equatorial pyrazolyl rings and away from the N and O of the ligand derived from proline.

by four different ligands (counting Tp as one ligand), resulting in an *S* configuration at rhenium. Since the five-membered ring now contains an sp^2 carboxyl carbon, the ring is quite flat; hence, there is no "axial" substituent directed toward significant interactions with the Tp. The interactions that are responsible for the formation of **3** as a single diastereomer are less obvious than in **2**.

Spectroscopic methods have been used to characterize complexes **1**–**3**. The Re−O bond strengths of compounds **1**–**3** appear to be similar, as suggested by infrared spectroscopy. All complexes exhibited characteristically strong ν(Re=O) bands at 980 (**1**), 984 (**2**), and 981 cm^{-1} (**3**). These stretching frequencies are similar to those found in other Re(V) oxo compounds.[8,9] Additionally, CD spectra were recorded for the complexes **1**–**3**. Complex **1** showed a positive band at 345 nm and a negative band at 450 nm, with a shoulder at 501 nm. Complex **2** exhibited positive bands at 306 and 466 nm, with

negative bands at 386 and 561 nm. Complex **3** had a positive band at 307 nm, with negative bands at 579 and 658 nm. A band that appears in the visible at 425 nm has low rotational strength and is not readily observable in the CD.

We have not attempted to assign the electronic spectra, but note that some charge transfer transitions would be expected. The variations in colors and UV/vis spectra show that the transitions are very sensitive to the nature of the ligands. The rotational strengths in the visible are quite high, and we observe that in **3** the Δε for the long-wavelength transitions are the same order of magnitude as those in the UV. Thus the *g*-number (or anisotropy factor = Δε/ε) is ∼0.0008 for the 307 nm transition, whereas it is ∼0.05 for the bands at 579 and 658 nm, indicating that they are magnetically allowed transitions. These *g*-numbers are quite large in comparison with most chiral inorganic complexes and suggest the possibility of asymmetric induction in racemic analogues with circularly polarized light photolysis.[10]

Compounds **1**–**3** were robust and able to withstand harsh conditions without reaction or decomposition. For example, **2** was able to undergo heating in toluene (111 °C) for 2 days, in the presence of PMe$_3$, without oxidation of the phosphine and concomitant reduction of the metal center. Furthermore, **2** did not undergo reduction in the presence of Na/Hg. Similarly, complexes **1** and **3** were heated for 1 day, in CH$_2$Cl$_2$ (82 °C) and PMe$_3$ (5 equiv), without reaction. In all cases, **1**–**3** were recovered without any noticeable signs of decomposition.

Discussion

The stability of compounds **1**–**3** and the inert nature of the oxo ligands can be attributed to the Lewis basic nature of the ligands. Such electron donation occurs from both the Tp ligand[11] and the chelating-amide ligands. Similar examples of limited reactivity of Re−O with the TpReO fragment have previously been reported.[2g] In effect there is sufficient donation that the Re(V) is stabilized and there is little driving force for conversion to Re(III). The reactivity can be presumably increased by adjusting the donation to the metal, and a recent report has suggested that charge effects can cause significant increases in rates for oxygen atom transfer in rhenium−oxo complexes bearing the neutraly charged tris(1-pyrazolyl)methane ligand.[12]

The X-ray data collection parameters are shown in Table 1. The bond distances and angles are given in Table 2. The Re−O bond lengths are as expected for Re(V). The pyrazolyl N that is trans to the oxo shows a trans influence that increases the Re−N length more than 0.1 Å over those in the cis positions. This produces an interesting distortion effect on the bite angles within the Tp: whereas two bite angles are ∼77°, the other is ∼90°. All of the bite angles of the ligands derived from the diamine or amino alcohols are ∼80°.

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Table 1. Crystallographic Data for X-ray Diffraction Study of TpReO(chelates)

	1	2	3
	TpRe(S_C,S_C)-Ph$_2$en	(S_{Re})-TpRe (1S_C,2R_C)ephed	(S_{Re})-TpRe (L)prol
formula	ReON$_8$C$_{23}$BH$_{24}$	ReO$_2$N$_7$C$_{19}$H$_{23}$	ReO$_3$N$_7$C$_{14}$H$_{17}$
cryst syst	tetragonal	monoclinic	monoclinic
space group	$P4_12_12$ (No. 92)	$P2_1$ (No. 4)	$P2_1$ (No. 4)
a, Å	11.1050(3)	7.4989(5)	8.9282(3)
b, Å		13.557(1)	8.8046(2)
c, Å	37.309(1)	11.1230(7)	11.1414(3)
β, deg	90	104.154(4)	95.346(2)
V, Å^3	4601.1(2)	1096.1(1)	872.01(4)
fw	625.51	578.45	528.35
ρ_{calcd}, g/cm^3	1.806 ($Z = 8$)	1.752 ($Z = 2$)	2.012 ($Z = 2$)
abs coeff (cm^{-1})	53.19	55.74	70.01
cryst size, mm	0.12 × 0.15 × 0.15	0.29 × 0.15 × 0.02	0.27 × 0.19 × 0.07
diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
monochromator	graphite	graphite	Nonius KappaCCD
radiatn	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
max 2θ, deg	55.0	55.0	55.0
no. of reflns measd	11 890 (unique: 2774)	3402 (unique: 2570)	11 049 (unique: 2146)
no. of data used, $F^2 > 3\sigma(F^2)$	1945	2239	1986
no. of params refined	307	270	234
p factor	0.02	0.01	0.01
final residuals R, R_w	0.034; 0.031	0.034; 0.037	0.030, 0.031
convergence, largest shift/error	0.0	0.0	0.0
GOF	1.03	1.64	1.27
largest $\Delta(\rho)$, e Å^{-3}	0.82	1.26	2.06

Table 2. Bonds and Angles

	TpReO(chelates)		
	1	**2**	**3**
	TpRe(S_C,S_C)-Ph$_2$en	(S_{Re})-TpRe (1S_C,2R_C)ephed	(S_{Re})-TpRe L-prol
Re(1)−O(1)	1.695(7)	1.687(7)	1.707(7)
Re(1)−O(2)		1.947(7)	2.016(5)
Re(1)−N(1)	1.938(8)	1.929(8)	1.930(5)
Re(1)−N(2)	1.955(8)	2.278(8)	2.246(7)
Re(1)−N(x)pzcis^a	2.175(8)	2.15(1)	2.145(5)
Re(1)−N(y)pzcis^b	2.157(8)	2.156(8)	2.107(6)
Re(1)−N(z)pztrans^c	2.296(9)	2.278(8)	2.246(7)
O(1)−Re(1)−N(z)pztrans^c	162.9(3)	164.1(3)	163.5(3)
O(1)−Re(1)−N(y)pzcis^b	90.2(3)	90.2(4)	91.2(3)
O(1)−Re(1)−N(x)pzcis^a	90.5(3)	92.7(3)	91.9(3)
O(1)−Re(1)−N(1)cis^d	105.7(3)	105.2(3)	105.9(3)
O(1)−Re(1)−N(2)cis^e	108.6(3)		
O(1)−Re(1)−O(2)cis		105.6(4)	104.2(3)
Pyrazolylborate Angles			
N(z)pz−Re(1)−N(y)pz	76.6(3)	76.3(3)	77.6(3)
N(z)pz−Re(1)−N(x)pz	78.3(3)	78.4(3)	76.5(2)
N(x)pz−Re(1)−N(y)pz	88.3(3)	87.2(4)	91.7(2)
Chelate Bite Angles			
N(1)−Re−N(2)	78.5(3)		
N(1)−Re−O(2)		80.9(3)	81.5(2)

^{a} x = 7, 6, 6 for **1**, **2**, and **3**, respectively. ^{b} y = 5, 4, 4 for **1**, **2**, and **3**, respectively. ^{c} z = 3, 2, 2 for **1**, **2**, and **3**, respectively.

All of the O−Re−L angles are greater than 90°, as observed in a large number of compounds.[13] This has generally been attributed to rehybridization at the metal, which increases the Re=O multiple bond overlap.[14,15] An interesting feature here is that the angles to the pyrazole nitrogen atoms are ∼90° [90.2−92.7°], whereas those to the amidate N's or alcoholate O's are in the range 104.2−108.6°. This strongly suggests that the distortion is related to the π donor/acceptor properties of the ligands. Thus, the filled p orbitals on aliphatic O$^-$ and N$^-$ acting as donors lead to a large distortion, whereas the π* acceptor of the pyrazolyl ligand dominates its interaction and there is little distortion from 90°. The electronic asymmetry produced by these different ligand types thus produces what is in effect a tilting of the oxo ligand relative to the plane of the four equatorial ligands. We anticipate that this will have a significant effect on the reactivity and the stereocontrol in oxo transfer reactions.

Conclusion

Compounds **1**−**3** have been isolated as single isomers. Comparisons of the oxo ligands, for complexes **1**−**3**, by infrared spectroscopy and X-ray crystallography have revealed that the Re−O bonds are similar in bond length and bond strength. Owing to the strength of these bonds, oxygen atom transfer has not been ob-

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served. As such, these robust complexes were able to withstand harsh conditions without reaction or noticeable decomposition. Since the complexes are formed with high diastereoselectivity, more reactive analogues may be useful in asymmetric oxygen transfer reactions. The electronic asymmetry that can tilt the oxo relative to the equatorial plane may ultimately play a role in the selectivity of oxygen transfer reactions.

Experimental Section

General Methods. All synthetic manipulations were carried out using standard Schlenk techniques under inert atmosphere. Reagent grade acetonitrile was dried over CaH_2, and absolute methanol was bubble degassed prior to use. Reagent grade ethyl acetate, dichloromethane, chloroform, and Silica-60 (EM Separation Technologies) were used for chromatography without further purification. The ligands $(1S,2R)$-ephedrine, 99% anhydrous (Janssen Chimica), L-proline, (Matheson Coleman and Bell Laboratories), and $(1S,2S)$-diphenylethylenediamine, 97% (99% ee, Aldrich), were used without further purification. TpReOCl$_2$ was prepared according to a published literature procedure.[6] ^{1}H NMR spectra were recorded on a GE Omega 300 MHz or GE 500 MHz spectrometer, and chemical shifts are reported in ppm relative to residual solvent peaks (^{1}H). Proton resonances for protons attached to boron were not observed owing to quadrupolar broadening and relaxation. Circular dichroism spectra were recorded on an AVIV model 202 spectrometer equipped with a 450 W xenon arc lamp. Spectra were recorded from 800 to 230 nm in 1.0 nm intervals with a 0.2 s averaging time. CD spectra for samples **1** and **2** were dissolved in dichloromethane, and **3** was dissolved in chloroform. Complexes **1**–**3** were placed in a 1 mm path length quartz cell and thermostated to 25.0 °C. Optical rotations were measured on a Perkin-Elmer model 341 polarimeter at 589 nm and 25.0 °C, using a 1 dm path length. IR spectra were measured on a Nicolet FT-IR spectrometer. X-ray crystallographic structure determination utilized a Nonius Kappa CCD diffractometer. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

Preparation of TpReO[(1S,2S)-η²-HNCH(Ph)CH(Ph)-NH-N,N] (1). A 20 mL, three-neck flask was equipped with a reflux condenser and was charged with TpRe(O)Cl$_2$ (50 mg, 0.10 mmol), $(1S,2S)$-diphenylethylenediamine (26 mg, 0.12 mmol), and a stir bar. The apparatus was purged with nitrogen, and then CH$_3$CN (10 mL) and NEt$_3$ (57 μL, 0.41 mmol) were added. The solution was heated under reflux (82 °C) for 12 h and gradually became burgundy in color. The solution was cooled in an ice bath, and then solvent and excess NEt$_3$ were removed under reduced pressure. The solid was dissolved in CH$_2$Cl$_2$ (10 mL) and then washed with H$_2$O (2 × 10 mL) in a separatory funnel to remove triethylamine hydrochloride. After removal of solvent, the solid was dried under reduced pressure to yield analytically pure product. Yield: 58 mg, (90%). ^{1}H NMR (CD$_2$Cl$_2$, 298 K, δ): 10.63 (br m, 1H, N**H**), 10.15 (br m, 1H, N**H**), 8.15 (d, 2H, J = 2 Hz, Tp), 7.97 (d, 2H, J = 2 Hz, Tp), 7.76 (d, 1H, J = 2 Hz, Tp), 7.44 (d, 1H, J = 2 Hz, Tp), 7.32 (m, 10H, Ph), 6.46 (t, 2H, J = 2 Hz, Tp), 6.15 (t, 1H, J = 2 Hz, Tp), 5.12 (br d, 1H, J = 7.9 Hz, NC**H**) 4.92 (br d, 1H, J = 7.9 Hz, NC**H**). CD (CH$_2$Cl$_2$, 293 K, $\lambda_{max/min}$ (nm), $\Delta\epsilon$ (M^{-1} cm^{-1}): 593sh (−4.4), 561 (−5.3), 466 (+2.5), 386 (−0.4), 306 (+9.2), 269 (−0.5). UV/vis (CH$_2$Cl$_2$, 293 K, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 556 (160), 309 (6500). IR: (Nujol, cm^{-1}): 981 (s, ν_{ReO}); 2517 (m,ν_{BH}). [α]$^{20}_{D}$ −104.0° (CH$_2$Cl$_2$). Anal. Calcd for C$_{23}$H$_{24}$BN$_8$ORe: C, 44.16; H, 3.87; N, 17.91. Found: C, 43.90; H, 3.94; N, 17.48.

Preparation of (S$_{Re}$,S$_{C-O}$,R$_{C-N}$)-TpReO(η²-N(CH$_3$)CH-(CH$_3$)CH(Ph)O-N,O)] (2). A 50 mL, three-neck flask was equipped with a reflux condenser and was flame dried. The flask was purged with nitrogen and then charged with TpRe-

OCl$_2$ (200 mg, 0.41 mmol), $(1S,2R)$-ephedrine (272 mg, 1.64 mmol), CH$_3$CN (10 mL), NEt$_3$ (460 mL, 3.30 mmol), and a stir bar. The blue solution was heated to reflux (82 °C) for 12 h to yield a purple-brown solution. This solution was cooled to room temperature, and then the solvent was removed under reduced pressure. The resultant brown solid was taken up in CH$_2$Cl$_2$ (2 mL) and was purified via chromatography on silica gel with CH$_2$Cl$_2$ as the eluent. The product was eluted as the first band and was evaporated under reduced pressure. Recrystallization was achieved by slow evaporation from a solution of 1:1 CH$_2$Cl$_2$/Et$_2$O to yield dark red-brown crystals. Yield: 227 mg (95%). ^{1}H NMR (CH$_2$Cl$_2$, 293 K, δ): 8.05 (t, 1 H, J = 2 Hz, Tp), 7.9−7.8 (m, 2 H, J = 2 Hz, Tp), 7.5−7.3 (m, 5 H, Ph), 7.2 (m, 2 H, J = 2 Hz, Tp), 6.45 (t, 2 H, J = 2 Hz, Tp), 6.15 (dd, 1 H, J = 2 Hz, Tp), 6.05 (t, 1 H, J = 2 Hz, Tp), 4.03 (q, 1 H, J = 6 Hz, NC**H**), 3.62 (t, 3 H, J = 1 Hz, NC**H**$_3$), 1.56 (m, 1 H, OC**H**), 0.86 (d, 3 H, J = 6 Hz, CC**H**$_3$). CD (CH$_2$Cl$_2$, 293 K, $\lambda_{max/min}$ (nm), $\Delta\epsilon$ (M^{-1} cm^{-1}): 501 (−4.0), 450 (−5.4), 345 (+5.6), 303 (−6.5), 275 (−3.2), 253 (3.6). UV/vis (CH$_2$Cl$_2$, 293 K, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 493 (240), 447 (260), 329 (6800), 265 (14300). IR (Nujol, cm^{-1}): 980 (s, ν_{ReO}); 2492 (m, ν_{BH}). [α]$^{20}_{D}$ −16.6° (CH$_2$Cl$_2$). Anal. Calcd for C$_{19}$H$_{23}$BN$_7$ORe: C, 39.45; H, 4.01; N, 16.95. Found: C, 39.19; H, 4.02; N, 16.95.

Preparation of [(S$_{Re}$,S$_c$)-TpReO(η²-N(CH$_2$)$_3$CHCO$_2$-N,O)] [3]. A 25 mL, three-neck flask was equipped with a reflux condenser and was flame dried. The flask was charged with TpReOCl$_2$ (50 mg, 0.10 mmol) and L-proline (14 mg, 0.12 mmol). The apparatus was purged with nitrogen, and then CH$_3$CN (3 mL), CH$_3$OH (3 mL), and NEt$_3$ (57 μL, 0.41 mmol) were added. The solution was heated (82 °C) for 21 h to yield a dark green solution, which was then cooled to room temperature. The solvent was removed on a rotary evaporator, and the solid was dissolved in CH$_2$Cl$_2$ (5 mL) and extracted with water (2 × 10 mL). The organic fraction was isolated, and the solvent was removed under reduced pressure. The resultant solid was washed with Et$_2$O (2 × 10 mL) to yield an analytically pure blue-green solid. Recrystallization was achieved via slow evaporation from a solution of 1:1 CH$_2$Cl$_2$/Et$_2$O to yield deep blue-green crystals. Yield: 25.3 mg (47%). ^{1}H NMR (CD$_2$Cl$_2$, 293 K, δ): 7.96 (d, 1 H, J = 2 Hz, Tp), 7.93 (m, 2 H, Tp), 7.85 (d, 1 H, J = 2 Hz, Tp), 7.46 (d, 1 H, J = 2 Hz, Tp), 7.19 (d, 1 H, J = 2 Hz, Tp), 6.49 (t, 1 H, J = 2 Hz, Tp), 6.43 (t, 1 H, J = 2 Hz, Tp), 6.04 (t, 1 H, J = 2 Hz, Tp), 5.43 (t, 1 H, J = 7 Hz, C(2)**H**), 4.23 (m, 1 H, C(5)**H**), 3.59 (m, 1 H, C(5)**H**), 2.65 (m, 1 H, C(3)**H**), 2.25 (m, 1 H, C(3)**H**), 2.02 (m, 2 H, C(4)**H**). CD (CH$_2$Cl$_2$, 293 K, $\lambda_{max/min}$ (nm), $\Delta\epsilon$ (M^{-1} cm^{-1}): 658 (−4.6), 579 (−4.4), 307 (+9.7), 275 (−8.1). UV/vis (CH$_2$Cl$_2$, 293 K, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 636 (84), 425 (340), 307 (7300). IR (KBr, cm^{-1}): 984 (s, $\nu_{Re=O}$), 1702 (s, $\nu_{C=O}$), 2521 (m,ν_{BH}). [α]$^{20}_{D}$ +144° (CHCl$_3$). Anal. Calcd for C$_{14}$H$_{17}$BN$_7$O$_3$Re: C, 31.83; H, 3.24; N, 18.56. Found: C, 31.87; H, 3.28; N, 18.07.

X-ray Crystallography. Single crystals suitable for X-ray analysis were formed by evaporation of methylene chloride for **1** and diethyl ether/methylene chloride solutions for **2** and **3**. Crystallographic data are summarized in Table 1. All structures were determined from data collected with a Nonius KappaCCD at −90 °C. Lorentz and polarization corrections were applied to all data. An empirical absorption correction was applied for **1** and **3** using SORTAV.[11] The data were scaled for **2**, and the inherent correction for absorption from scaling appeared adequate based on R factors compared to SORTAV results. Intensities of equivalent reflections, excluding Friedel pairs, were averaged. The structures were solved by heavy-atom Patterson methods using the teXan crystal structure analysis package, and the function minimized was $\sum w(|F_o| - |F_c|)^2$ in all cases. Hydrogen atoms were placed at calculated positions before each refinement and were included in the refinement, but were not refined. The absolute configuration was determined by reference to the known configurations of the ligands. The configurations were also confirmed by refine-

ment of the inverted structures (**1** in $P4_32_12$), which gave higher R's than the correct structure.

The blue-green color of **3** observed in solution is observed to some extent in the crystals; however the crystals are dichroic, with different faces showing somewhat different shades of color. Under transmitted polarized light the colors of some faces change from blue to yellow depending on the orientation. The Re=O vectors are very approximately oriented parallel to the b axis in the $P2_1$ space group. Thus polarized light parallel and perpendicular to the b axis tends to excite different transitions.

Supporting Information Available: CD and UV/vis spectra for **1**−**3**. Listings of crystal data and collection parameters, atomic positional parameters, anisotropic thermal parameters, and bond lengths and angles for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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