Inorg. Chem. **2001,** *40,* 6767−6773

Synthesis of Enantiopure Oxorhenium(V) and Arylimidorhenium(V) "3 + 2" Schiff Base Complexes. X-ray Diffraction, Cyclic Voltammetry, UV−Vis, and Circular Dichroism Characterizations

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Received July 27, 2001

Two new oxorhenium(V) and two new arylimidorhenium(V) complexes of the Schiff base ligands 2-hydroxybenzaldehyde-((1*R*,2*S*)-1-amino-2-indanol)imine (**1**) (H_2L^1) and 3-(1-adamantyl)-2-hydroxy-5-methylbenzaldehyde-((1*R*,2*S*)-1-amino- 2-indanol)imine (**2**) (H_2L^2) have been prepared from the reaction of the precursor Re(O)($(PPh_3)_2Cl_3$, Re(NC_6H_5)(PPh_3)$_2Cl_3$, or Re($NC_6H_4OCH_3$)(PPh_3)$_2Cl_3$ and the free ligands $H_2L^{1,2}$. The complexes Re(O)(HL^1)(L^1) (**3**), Re(O)(HL^2)(L^2) (**4**), Re(NC_6H_5)(HL^1)(L^1) (**5**), and Re($NC_6H_4OCH_3$)(HL^1)(L^1) (**6**) have been isolated and fully characterized by IR, ^{1}H NMR, circular dichroism, LRMS-FAB, and elemental analysis. All the complexes have a chiral center at rhenium. A single enantiomer is obtained in all cases. Suitable crystals of **3** and **5** were used in X-ray structural determinations. Crystal data: (**3**) $C_{32}H_{27}N_2O_5Re{\cdot}CH_2Cl_2$, orthorhombic, *P*2(1)2(1)2(1), $a = 9.5599(16)$ Å, $b = 9.9579(16)$ Å, $c = 31.712(5)$ Å, $V = 3018.9(9)$ Å^3, $T = 100(2)$ K, $Z = 4$. (**5**) $C_{40}H_{38}N_3O_5Re$, monoclinic, *P*2(1), $a = 9.286(3)$ Å, $b = 18.759(6)$ Å, $c = 9.957(3)$ Å, $\beta = 102.817(6)°$, $V = 1691.3(10)$ Å^3, $T = 100(2)$ K, $Z = 2$. The major characteristic of these complexes is the presence of two coordination modes for the Schiff base ligands on rhenium, a tridentate ligand (noted $L^{1,2}$) and another bidentate ligand (noted $HL^{1,2}$). In the latter, the −OH group of the indanol is free and tilts away from the coordination sphere. X-ray structural analyses in conjunction with circular dichroism were used to assign the absolute configuration at rhenium (*C*). Cyclic voltammetry, UV−vis, and circular dichroism data are presented and discussed. The complexes were found to be highly stable and to resist reduction even when treated with organic phosphanes.

Introduction

The past two decades have seen much effort and interest in developing brain receptor imaging agents based on ^{99m}Tc complexes that are able to cross the blood−brain barrier.[1] The radiophysical properties of the radionucleide ^{99m}Tc (γ-emitter, $E_{max} = 140$ keV, $t_{1/2} = 6$ h) are nearly ideal for diagnosis in nuclear medicine. An added advantage of the radionucleide ^{99m}Tc is its convenient and inexpensive commercial availability from a "technetium generator" containing $[^{99}MoO_4]^{2-}$ in which ^{99}Mo decays by β-emission to give $[^{99m}TcO_4]^-$. The radionuclides of rhenium, the group 7 congener of Tc, are β-emitters and present properties that make them desirable for therapeutic applications (^{186}Re, $E_{max} = 1.07$ MeV, $t_{1/2} = 90$ h; ^{188}Re, $E_{max} = 2.12$ MeV, $t_{1/2} = 17$ h).[2] Re is often studied as a Tc surrogate because of the similarities between these two elements. However, recent investigations on the potential use of ^{186}Re and ^{188}Re radioisotopes in therapeutic nuclear medicine[2−5] have revived the interest in preparing stable rhenium coordination complexes of intermediate oxidation state form ReO_4^- in a reasonable amount of time.[6,7]

Two approaches for the preparation of radiopharmaceuticals having a $\{MO\}^{3+}$ or $\{MN\}^{2+}$ core (M = Re, Tc) have been designed.[1,8] The first one is called the integrated approach and corresponds to the incorporation of the metal into the structure of a bioactive molecule. Most of the time, the physical and chemical properties of the molecules are changed. The second strategy is the conjugate or pendant approach. The biomolecule is tethered to the metal−ligand system. Two classes of complexes prepared by the conjugate approach are known. The "3 + 1" design corresponds to a metal complex exhibiting a square pyramidal geometry with the monodentate ligand bearing the receptor avid moieties.[9,10] The major problem of this class of complexes is their poor stability in vitro and in vivo. To increase stability, the monodentate ligand (usually a thiol) is replaced by a bidentate ligand. Examples of Re "3 + 2" complexes have been reported with the donor atom sets [SNS]/[PO],[11] [ONS]/[OS],[12] and [ONO]/[OP].[13]

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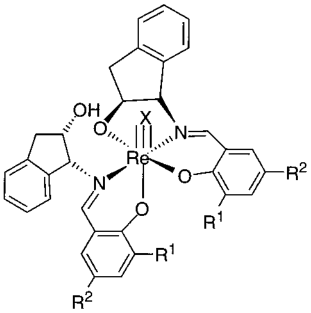
10.1021/ic0108033 CCC: $20.00

Chart 1. Rhenium(V) Oxo and Imido Complexes Featuring "3 + 2" Coordination of the Ligand[a]



[a] X = O, N(C_6H_5), or N(*p*-$C_6H_4OCH_3$). $R^1 = R^2$ = H, or R^1 = adamantyl and $R^2 = CH_3$.

While the coordination chemistries of many Tc^{V} and Re^{V} complexes may be similar, their reaction chemistries are quite different. For example, oxorhenium(V) complexes are easier to oxidize and are more inert toward ligand substitution. A large number of oxorhenium(V) complexes containing nitrogen-,[7,14,15] oxygen-,[16−18] and sulfur-donor[19−21] ligands have been studied extensively. From the wealth of chemical transformations that rhenium compounds undergo,[22] oxygen atom transfer[23−27] and redox[28,29] reactions are most notable in the context of rhenium use in therapeutic nuclear medicine.

In the interest of designing new small, neutral, and lipophilic model complexes for radio imaging and by using the "3 + 2" approach, we have investigated the new system [ONO]/[ON], where [ONO] and [ON] are the same ligands coordinated to the rhenium in two coordination modes. The ligands we have used are the Schiff bases 2-hydroxybenzaldehyde-((1*R*,2*S*)-1-amino-2-indanol)imine (**1**), henceforth referred to as H_2L^1, and 3-(1-adamantyl)-2-hydroxy-5-methylbenzaldehyde-((1*R*,2*S*)-1-amino-2-indanol)imine (**2**), henceforth referred to as H_2L^2. Two new oxorhenium(V) and two new arylimidorhenium(V) complexes have been prepared and fully characterized (Chart 1); their electronic and chiral properties are discussed. The major characteristic of these complexes is the presence of a free hydroxyl group pendant from the indanol of the bidentate ligand. This feature would enable the tethering of a bioactive molecule to the designed Re complexes, a point that will be explored in further studies.

Experimental Section

Materials and Syntheses. Reagents and solvents were obtained commercially and used without further purification. Benzene was distilled over sodium/benzophenone. *mer*,*trans*-Re(O)$Cl_3(PPh_3)_2$ was prepared as previously described.[30] Re(NC_6H_5)$Cl_3(PPh_3)_2$ and Re($NC_6H_4OCH_3$)$Cl_3(PPh_3)_2$ were prepared by slight modification of a literature procedure.[31] Stoichiometric amounts of Re(O)$Cl_3(PPh_3)_2$ and aniline or *p*-anisidine were refluxed for 18 h in dry benzene. The two Schiff base ligands **1** and **2** were obtained by refluxing a stoichiometric amount of the corresponding benzaldehyde and (1*R*,2*S*)-1-amino-2-indanol in ethanol, following literature procedures.[32]

Physical Measurements. NMR spectra were obtained on a Bruker AC200 spectrometer. Infrared spectra were recorded as pressed KBr pellets on a Jasco FT/IR-420 spectrophotometer. UV−vis spectra were recorded on a Shimadzu UV-2501PC spectrophotometer. Circular dichroism (CD) spectra were measured with a Jasco J715 spectropolarimeter. Measurements were made with a ligand or complex concentration of typically 5.0×10^{-4} M in spectroscopic grade methylene chloride employing a 0.2 cm path length cuvette at 293 K. LRFAB mass spectra were recorded on a ZAB-SE by VG Analytical (Manchester, U.K.). Elemental analyses were performed in duplicate by Desert Analytics Laboratory, Tuscon, AZ. Melting point determinations were performed with a Uni-Melt capillary melting point apparatus on samples in glass capillaries. An EG&G Princeton Applied Research potentiostat/galvanostat, model 263A, was used to record the cyclic voltammograms at scan rates of 2.0−0.050 V s^{-1}. Electrochemical studies were performed in methylene chloride solutions (0.10 mol L^{-1} NBu_4BF_4 as electrolyte) by using an electrochemical cell equipped with a graphite working electrode, a platinum counter electrode, and Ag/AgCl (0.10 mol L^{-1} LiCl in acetone) as the reference electrode. The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference.

Synthesis of Re(O)(HL^{1,2})(L^{1,2}). Complexes **3** and **4** were prepared from a mixture of *mer*,*trans*-Re(O)$Cl_3(PPh_3)_2$ and $H_2L^{1,2}$ in a 1:3 molar ratio, in refluxing ethanol and in the presence of 6 equiv of base. A detailed procedure is given for the preparation of Re(O)(HL^1)(L^1).

Re(O)(HL^1)(L^1) (3). *mer*,*trans*-Re(O)$Cl_3(PPh_3)_2$ (200 mg, 0.24 mmol) and **1** (183 mg, 0.72 mmol) were loaded into the same flask. A 20 mL portion of ethanol was added followed by 0.35 mL of 2,6-lutidine (1.44 mmol). The resulting suspension was refluxed for 1 h to give a dark brown colored solution. A light brown solid was precipitated upon cooling the solution to room temperature. After filtration, the solid was washed with ethanol and dried with diethyl ether. Yield: 80%. Mp: 278 °C. Anal. Calcd for $C_{32}H_{27}O_5N_2Re$: C, 54.46; H, 3.86; N, 3.97. Found: C, 54.49; H, 3.79; N, 4.09. ^{1}H NMR (ppm, CD_2Cl_2, 295 K): δ 2.95 (dd, 1H), 3.24 (m, 2H), 3.66 (dd, 1H), 4.73 (dd, 1H), 4.89 (m, 1H), 5.17 (d, 1H), 5.22 (t, 1H), 5.39 (d, 1H), 6.41 (d, 1H), 6.54 (d, 1H), 6.69 (dt, 1H), 6.77 (dt, 1H), 6.92 (dt, 1H), 7.04 (dd, 1H), 7.21−7.38 (m, 8H), 7.44 (dd, 1H), 7.55 (m, 1H), 7.62 (s, 1H), 8.87 (s, 1H). LRMS (FAB, NBA matrix): calcd for $(C_{32}H_{27}O_5N_2Re)^+$ 706.15, found 706.64 with correct rhenium 187/185 isotope ratios. IR (cm^{-1}): 960 (s, $\nu_{Re=O}$), 1293 (s, ν_{C-O}), 1616, 1604 (vs, $\nu_{C=N}$), 3437 (br, ν_{O-H}). UV−vis (CH_2Cl_2, 295 K): λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 788 (95), 462 (3430), 416 (4300), 318 (17500), 254 (28200).

Re(O)(HL^2)(L^2) (4). The same procedure as previously described was used for the preparation of **4**. The complex was isolated as dark red crystals after storage of the reaction solution for several days at −10 °C. Yield: 40%. Mp: 318 °C. Anal. Calcd for $C_{54}H_{59}O_5N_2Re$: C, 64.71; H, 5.93; N, 2.79. Found: C, 64.29; H, 6.06; N, 2.80. ^{1}H NMR (ppm, CD_2Cl_2, 295 K): δ 1.55−1.77 (m, 26H), 1.97 (s, 3H),

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Table 1. Crystal Data and Structure Refinement for **3** and **5**

	3	**5**
empirical formula	$C_{32}H_{27}N_2O_5Re \cdot CH_2Cl_2$	$C_{40}H_{38}N_3O_5Re$
fw	790.68	826.93
temp, K	100(2)	100(2)
λ, Å	0.71073	0.71073
cryst syst	orthorhombic	monoclinic
space group	*P*2(1)2(1)2(1)	*P*2(1)
no. of reflns collected	19818	11169
no. of independent reflns	7155 [*R*(int) = 0.0383]	6275 [*R*(int) = 0.0278]
a, Å	9.5599(16)	9.286(3)
b, Å	9.9579(16)	18.759(6)
c, Å	31.712(5)	9.957(3)
α, deg	90	90
β, deg	90	90
γ, deg	90	102.817(6)
Z	4	2
V, $Å^3$	3018.9(9)	1691.3(10)
ρ(calcd), g cm^{-3}	1.740	1.624
μ, mm^{-1}	4.247	3.643
F(000), e	1560	828
θ range, deg	2.14−28.29	2.10−28.29
cryst size, mm	0.20 × 0.20 × 0.40	0.15 × 0.15 × 0.18
abs correction	empirical	empirical
max and min transm	1.00 and 0.6218	1.00 and 0.866
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	7155/0/389	6725/1/445
GOF on F^2	1.081	0.802
R indices [$I > 2\sigma(I)$]	R1 = 0.0277, wR2 = 0.0618	R1 = 0.0230, wR2 = 0.0362
R indices (all data)	R1 = 0.0292, wR2 = 0.0623	R1 = 0.0322, wR2 = 0.0381

2.16 (s, 3H), 2.92 (dd, 1H), 3.19 (m, 2H), 3.47 (dd, 1H), 4.93 (m, 2H), 5.07 (d, 1H), 5.30 (m, 1H), 5.52 (d, 1H), 6.54 (d, 1H), 6.69 (d, 1H), 6.89 (d, 1H), 7.02 (d, 1H), 7.20−7.28 (m, 9H), 8.68 (s, 1H). LRMS (FAB, NBA matrix): calcd for $(C_{54}H_{59}O_5N_2Re)^+$ 1002.27, found 1002.68 with correct rhenium 187/185 isotope ratios. IR (cm^{-1}): 956 (s, $\nu_{Re=O}$), 1287 (s, ν_{C-O}), 1602 (vs, $\nu_{C=N}$), 3370 (br, ν_{O-H}). UV−vis (CH_2Cl_2, 295 K): λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 815 (105), 500 (2610), 339 (15760), 263 (24290).

Synthesis of Re(NR)($HL^{1,2}$)($L^{1,2}$). Complexes **5** and **6** were prepared using the same procedure detailed below for **5**.

Re(NC_6H_5)(HL^1)(L^1) (5). Re(NC_6H_5)Cl_3(PPh_3)$_2$ (200 mg, 0.220 mmol) and **1** (112 mg, 0.440 mmol) were suspended in 20 mL of ethanol. After addition of 75 μL of NEt_3 (0.880 mmol), the mixture was refluxed for 3 h until complete reaction of the rhenium starting material. After cooling to room temperature and filtration, the dark brown colored solution was stored in the freezer. Brown crystals suitable for X-ray diffraction studies were collected after several days. Yield: 38%. Mp: 288 °C. Anal. Calcd for $C_{38}H_{32}O_4N_3Re$: C, 58.45; H, 4.13; N, 5.38. Found: C, 58.33; H, 4.02; N, 5.38. ^1H NMR (ppm, CD_2Cl_2, 295 K): δ 3.11−3.18 (m, 4H), 4.78 (br, 2H), 5.10 (br, 1H), 5.33−5.44 (m, 2H), 6.54−7.39 (m, 21H), 7.45 (s, 1H), 8.68 (s, 1H). LRMS (FAB, NBA matrix): calcd for $(C_{38}H_{32}O_3N_3Re)^+$ 781.20, found 781.28 with correct rhenium 187/185 isotope ratios. IR (cm^{-1}): 1032 (w), 1290 (s, ν_{C-O}), 1621, 1602 (vs, $\nu_{C=N}$), 3375 (br, ν_{O-H}). UV−vis (CH_2Cl_2, 295 K): λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 786 (106), 440 (8190), 348 (15610), 302 (23730), 269 (29190).

Re($NC_6H_4OCH_3$)(HL^1)(L^1) (6). Brown crystals. Yield: 35%. Mp: 165 °C. Anal. Calcd for $C_{38}H_{32}O_4N_3Re$: C, 57.77; H, 4.23; N, 5.18. Found: C, 56.70; H, 4.44; N, 4.94. ^1H NMR (ppm, CD_2Cl_2, 295 K): δ 3.00 (br d, 4H), 3.24 (br t, 2H), 3.78 (s, 3H), 4.87 (br, 2H), 5.22 (br, 1H), 5.42 (br d, 2H), 5.59 (br d, 2H), 6.61−7.46 (m, 21H), 8.73 (s, 1H). LRMS (FAB, NBA matrix): calcd for $(C_{39}H_{34}O_5N_3Re)^+$ 810.91, found 810.96 with correct rhenium 187/185 isotope ratios. IR (cm^{-1}): 1032 (w), 1288 (s, ν_{C-O}), 1623, 1599 (vs, $\nu_{C=N}$), 3376 (br, ν_{O-H}). UV−vis (CH_2Cl_2, 295 K): λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 795 (100), 427 (11350), 357 (19860), 285 (31020).

X-ray Crystallography. Single crystals of complex **3** that are suitable for X-ray analysis were formed by slow evaporation of a dichloromethane solution at room temperature; suitable crystals of **5** were recovered directly from the reaction solution stored at −10 °C for several days. Crystals of compounds **3** and **5** were mounted onto a glass fiber that was attached to a goniometer head. The X-ray intensity data were measured at 100 K on a Bruker SMART 1000 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at a 2250 W power. The detector was placed at a distance of 4.986 cm from the crystal.

A total of 1321 frames were collected with a scan width of 0.3° in ω, with an exposure time of 30 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm.[33] The final cell constants of the compounds are based upon the refinement of the *XYZ* centroids of 1000 reflections for **3** and 892 for **5** and are listed in Table 1 together with other relevant crystallographic data. Analysis of the data showed negligible decay during data collection.

The structure was refined using the Bruker SHELXTL (version 5.3) software package.[33] The final anisotropic full-matrix least-squares refinement on F^2 converged at R1 = 2.77% for **3** and 2.3% for **5**. Additional crystallographic tables are deposited as Supporting Information.

Results and Discussion

Description of the Molecular Structures. ORTEP views of complexes **3** and **5** are presented in Figures 1 and 2, respectively. Selected bond distances and bond angles are given in Table 2.

For **3**, the asymmetric unit contains one independent Re(O)(HL^1)(L^1) molecule and one methylene chloride solvent molecule. The overall geometry about the central rhenium atom can be best described as a distorted octahedral with the tridentate ONO ligand (L^1) lying in the equatorial plan. The imine nitrogen of the bidentate ligand (HL^1) occupies the remaining fourth equatorial position. The short Re(1)−O(5) bond length of 1.699(3) Å is typical for rhenium(V) monooxo complexes and indicates multiple-bond character (Re≡O).[34,35] The distorted octahedral geometry is characterized by the O(5)−Re(1)−O(3) bond angle of 169.41(14)° deviating from the ideal value of

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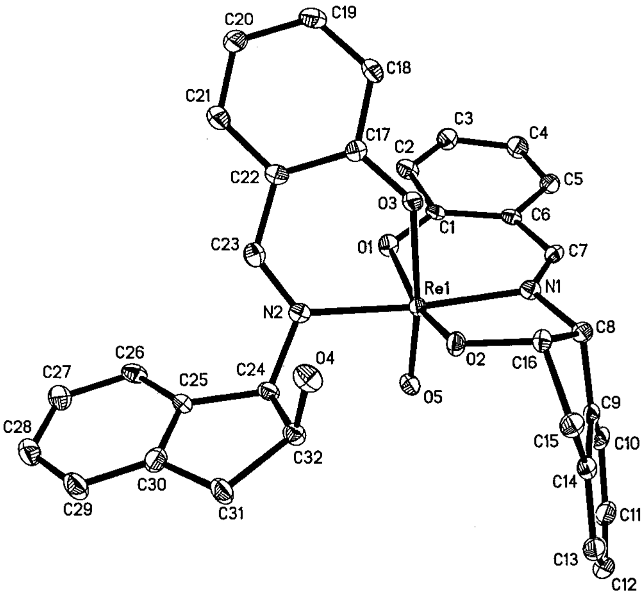


Figure 1. Molecular view and atom labeling scheme of **3** showing thermal ellipsoids at the 50% probability level. H atoms and the methylene chloride solvent molecule have been omitted for clarity.

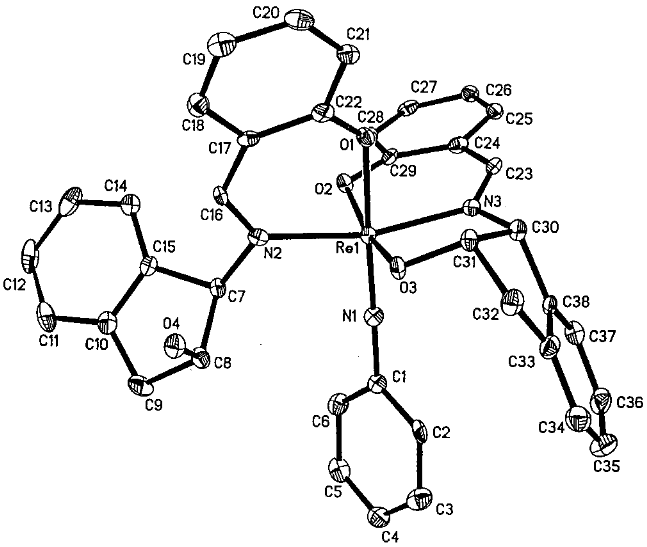


Figure 2. Molecular view and atom labeling scheme of **5** showing thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **3** and **5**

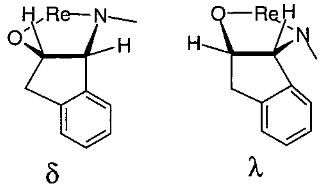
3		5	
Re(1)−O(5)	1.699(3)	Re(1)−N(1)	1.732(3)
Re(1)−O(1)	2.053(3)	Re(1)−O(3)	2.031(3)
Re(1)−O(2)	1.952(3)	Re(1)−O(1)	2.030(3)
Re(1)−N(1)	2.036(4)	Re(1)−N(3)	2.051(3)
Re(1)−O(3)	2.008(3)	Re(1)−O(2)	2.053(3)
Re(1)N(2)	2.119(4)	Re(1)−N(2)	2.098(4)
O(5)−Re(1)−N(2)	90.84(14)	N(1)−Re(1)−O(3)	95.47(12)
O(5)−Re(1)−O(3)	169.41(14)	N(1)−Re(1)−O(1)	176.87(14)
O(5)−Re(1)−O(1)	91.03(14)	N(1)−Re(1)−N(3)	98.7(2)
O(5)−Re(1)−N(1)	97.55(15)	O(3)−Re(1)−N(3)	81.96(15)
O(5)−Re(1)−O(2)	103.88(14)	N(1)−Re(1)−O(2)	97.87(12)
N(2)−Re(1)-O(3)	83.86(13)	N(3)−Re(1)−O(2)	93.21(12)
O(2)−Re(1)−N(1)	81.35(13)	N(1)−Re(1)−N(2)	97.0(2)
N(1)−Re(1)−O(1)	93.79(13)	O(1)−Re(1)−N(2)	84.58(12)
		C(1)−N(1)−Re(1)	169.5(3)

180° and by the rhenium−ligand *cis* donor atom bond distances noted between 1.952(3) Å (for Re(1)−O(2)) and 2.119(4) Å (for Re(1)−N(2)). The Re(1)−O(3) bond distance of 2.008(3) Å is comparable to that of the *cis*-phenoxide.[36] The ligand atoms *cis* to the Re≡O group are bent away from the oxygen atom: the bond angles O(5)−Re(1)−N(2), O(5)−Re(1)−N(1), O(5)−Re(1)−O(1), and O(5)−Re(1)−O(2) are between 90.84(14)° and 103.88(14)°.

Complex **5** exhibits the same distorted octahedral geometry as complex **3** with the same arrangement of tridentate (L^1) and bidentate (HL^1) ligands around the metal center (Figure 2). The phenolate oxygen atom of HL^1 is *trans* to the nitrogen atom of the phenylimido ligand. The Re(1)−N(1) bond length of 1.732(3) Å is nearly equal to that in the starting material $Re(NC_6H_5)Cl_3(PPh_3)_2$ (1.726(6) Å), indicating retention of the multiple bond. Also, the Re(1)−N(1)−C(1) angle is 169.5(3)°. The small deviation from linearity (180°) indicates an sp hybridization on the nitrogen atom and a Re≡NPh triple bond.[37] The angular distortion between the donor atoms *cis* to the Re≡NPh multiple bond is demonstrated in the following bond angles values: N(1)−Re(1)−O(3) = 95.47(2)°, N(1)−Re(1)−N(3) = 98.7(2)°, N(1)−Re(1)−O(2) = 97.87(12)°, N(1)−Re(1)−N(2) = 97.0(2)°. The *trans* Re(1)−O(1) bond distance (2.030(3) Å) is identical to the *cis* Re(1)−O(3) bond distance (2.031(3) Å) and even shorter than the *cis* Re(1)−O(2) bond distance (2.053(3) Å). Similar observations were found in (P,P')-$[Re(NC_6H_5)(PO_2)(PPh_3)Cl]$, where values of Re−O bond distances *cis* and *trans* to the Re≡NPh group were identical (2.050(3) Å).[38] The most characteristic feature of the crystal structures of **3** and **5** is the bidentate coordination of one of the ligands, yielding a free −OH group tilting away from the coordination sphere.

For **3** and **5**, the X-ray diffraction studies reveal that only one isomer is obtained. The optical activity of the rhenium center is induced by the enantiopure ligand. The refinement of the Flack absolute structure parameter[39] for **3** and **5** reveals that the reported isomer is the correct configuration. The absolute structure parameter for **3** and **5** is equal to 0. Even though the origin of diastereoselectivity in these rhenium complexes is not fully understood, one may speculate that the indenyl ring on the tridentate ligand may favor the more open space *syn* to the multiply bonded ligand (observed diastereomer) versus crowding the ligand *trans* to the oxo or imido group.

The metal-containing five-membered ring formed with the chiral amino alcohol moiety of the tridentate ligand may form in two chiral conformations, δ or λ (see the illustration below).[40−42] For the two complexes **3** and **5**, the five-membered



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ring adopts a symmetric skew conformation, δ. Conformational effects have been previously noted for other rhenium complexes with ethanediamido and ethanediolato ligands.[43−45] The six-membered ring formed by the tridentate ligand and Re remains flat, even though the other six-membered ring formed by the bidentate ligand (HL^1) adopts an asymmetric boat conformation with the Re atom and one C atom in apical positions.

Synthesis, Characterization, and Reactivity. The "3 + 2" $Re(X)(HL^{1,2})(L^{1,2})$ ($X = O$, NC_6H_5, or $NC_6H_4OCH_3$) complexes **3−6** were prepared in a one-step reaction. The bis(triphenylphosphine)oxorhenium trichloride, $Re(O)Cl_3(PPh_3)_2$, and bis(triphenylphosphine)arylimidorhenium trichloride, $Re(NR)Cl_3(PPh_3)_2$, were used as starting materials. Complex **3** can be obtained from the starting materials $[NBu_4][ReOCl_4]$ and $[NBu_4][ReOBr_4]$ in acetonitrile or ethanol according to the same procedure described in the Experimental Section using $Re(O)Cl_3(PPh_3)_2$, but at lower yield. All the syntheses were carried out in ethanol at refluxing temperature for 1−3 h. Addition of a base (2,6-lutidine or NEt_3) was necessary to neutralize the HCl produced in situ. The formation of complexes **3−6** is independent of the ligand:metal molar ratio, but the best yields of pure compounds are obtained with a 3:1 ligand:metal molar ratio for **3** and **4** and a 2:1 ratio for **5** and **6**. Complex **3** is obtained as a brown precipitate during the reflux of the reaction solution. More product is recovered by allowing the reaction solution to cool to room temperature before filtration. Pure samples of **4−6**, which are more soluble in ethanol, are only obtained by crystallization of the reaction solutions for several days at −10 °C. The yields for complexes **4−6** are lower than those obtained for **3**. All attempts to prepare the phenylimido complex $Re(NC_6H_5)(HL^2)(L^2)$,[16] an analogue of the oxo complex **4**, afforded poor yields.[46] Attempts to isolate a nitride rhenium complex from $Re(N)Cl_2(PPh_3)_2$ and H_2L^1 failed.

Elemental analyses as reported in the Experimental Section are in agreement with the proposed chemical formulations. IR spectra of the oxorhenium complexes **3** and **4** exhibit a strong characteristic $Re{\equiv}O$ stretching vibration at 960 and 956 cm^{-1}, respectively. These values are in accordance with those reported in the literature for six-coordinate monooxorhenium compounds.[47] For **3−6**, the imine groups show two different stretching frequencies: one between 1621 and 1624 cm^{-1}, and the other one between 1599 and 1604 cm^{-1}. These observations support the coordination of the imino nitrogens in two different chemical environments. These stretching vibrations appear at lower values with respect to the $\nu_{C=N}$ of the free ligand (1638 and 1616 cm^{-1} for H_2L^1 and 1624 and 1595 cm^{-1} for H_2L^2). The presence of a free hydroxyl group in the bidentate ligand $HL^{1,2}$ is characterized by the presence of a strong ν_{O-H} vibration around 3375 cm^{-1}.

The proton NMR spectra of the complexes show two signals assigned to the HC=N imino group protons, one at lower field between 8.68 and 8.87 ppm and the other one in the phenyl proton region. According to previous examples of Schiff base ligands featuring tridentate and bidentate coordination modes,[48,49] the signal at lower field is attributed to the imino group proton of the tridentate ligand L.[1,2] For **3** and **5**, the signal of the imino group proton of the bidentate ligand $HL^{1,2}$ is observed, respectively, at 7.55 and 7.45 ppm. For **4** and **6**, this signal is not detected because it is masked by the phenyl proton signals. In complex **4** the protons of the methyl substituents on the phenol ring for the two ligands HL^2 and L^2 are distinguishable and appear as singlets at 1.97 and 2.16 ppm.

Table 3. Electronic Absorption (AB) and CD Spectral Data for **3−6**

	λ_{AB}, nm (log ϵ)	λ_{CD}, nm ($\Delta\epsilon$, M^{-1} cm^{-1})
1	320 (3.8)	320 (+6.8)
	260 (4.3)	277 (−5.8)
2	339 (3.7)	336 (+4.3)
	268 (4.2)	283 (−2.1)
3	788 (2.0)	
	462 (3.5)	482 (−18.8)
	416 (3.6)	417 (+17.9)
		348 (+31.7)
	318 (4.2)	305 (−45.9)
		281 (−31.8)
	254 (4.5)	
4	815 (2.0)	
	500 (3.4)	522 (−7.6)
		451 (+7.1)
		367 (+15.3)
	339 (4.2)	326 (−51.7)
		290 (−10.5)
	263 (4.4)	263 (+17.1)
5	786 (2.0)	
		508 (−9.1)
	440 (3.9)	457 (+21.7)
		410 (−1.9)
	348 (4.2)	356 (+32.4)
	302 (4.4)	
		287 (−30.3)
	269 (4.5)	260 (+3.2)
6	795 (2.0)	
		495 (+4.9)
	427 (4.0)	428 (−34.1)
	357 (4.3)	335 (+26.1)
	285 (4.5)	282 (+55.9)

Since many rhenium(V) oxo complexes are known to transfer an oxygen atom to suitable organic substrates,[50,51] and since, to the best of our knowledge, asymmetric oxygen transfer from oxorhenium(V) has not been successful yet,[45,52] we set out to explore the potential of our chiral rhenium complexes in asymmetric oxidation. Unfortunately, complexes **3−6** were very stable toward strong organic reductants, and did not react nor decompose under harsh conditions. The reactions of compounds **3−6** with triphenylphosphine, alkanethiols, and alkylamines were investigated at room temperature and under reflux in several organic solvents. In all cases, the starting rhenium imido and oxo complexes were recovered without any evidence of

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(46) $Re(NC_6H_5)(HL^2)(L^2)$. Dark red crystals. Yield: 10%. Mp: 304 °C. ^1H NMR (ppm, CD_2Cl_2, 295 K): δ 1.55−1.76 (m, 26H), 2.04 (s, 3H), 2.16 (s, 3H), 2.89 (dd, 1H), 3.21 (dd, 2H), 3.44 (d, 1H), 4.88 (m, 1H), 4.95 (d, 1H), 5.07 (d, 1H), 5.31 (m, 1H), 5.52 (d, 1H), 6.55 (d, 1H), 6.69 (d, 1H), 6.87 (d, 1H), 7.02 (d, 1H), 7.20−7.28 (m, 9H), 8.68 (s, 1H). LRMS (FAB, NBA matrix): calcd for $(C_{60}H_{64}O_4N_3Re)^+$ 1077.38, found 1077.35 with correct rhenium 187/185 isotope ratios. IR (cm^{-1}): 1035 (w), 1286 (s, ν_{C-O}), 1602 (vbr, vs, $\nu_{C=N}$), 3379 (br, ν_{O-H}).

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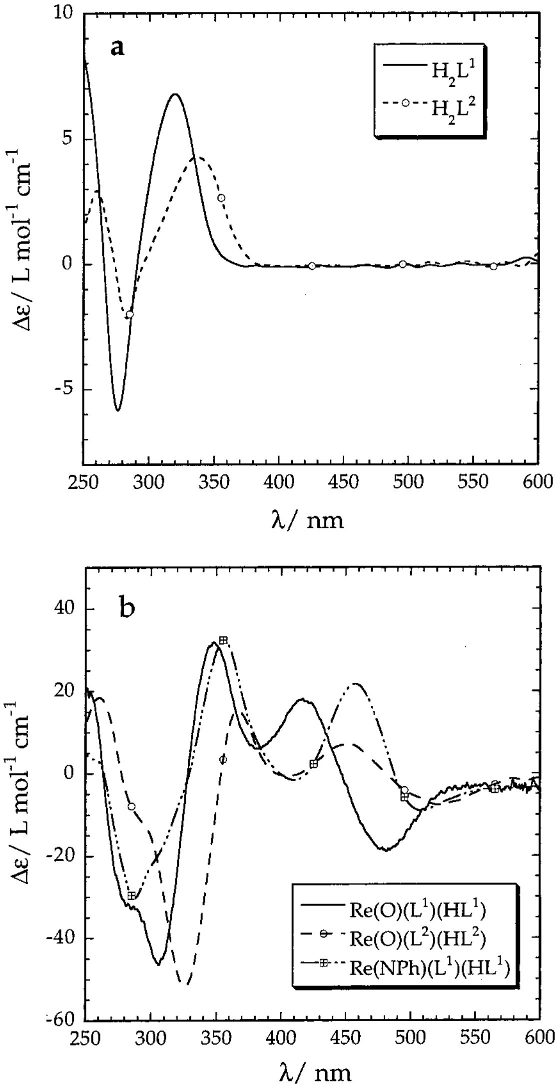


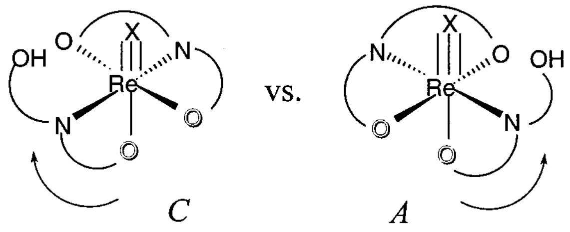
Figure 3. CD spectra of (a) ligands $H_2L^{1,2}$ and (b) complexes **3**−**5** in CH_2Cl_2 at 293 K.

reduction of the metal center nor decomposition. Complexes **3**−**6** are robust and air- and moisture-stable in solution and in the solid state. They are soluble in polar organic solvents such as acetonitrile and dichloromethane.

UV−Vis and Circular Dichroism. The electronic absorption and circular dichroism data for compounds **1**−**6** are presented and contrasted in Table 3. The spectra, obtained from methylene chloride solutions, are complex in nature. The general allures of the rhenium oxo and imido UV−vis spectra are quite similar. They exhibit intense absorption bands between 250 and 270 nm, which are attributed to the $\pi \rightarrow p^*$ transitions of the nitrogen donor organic ligands. The absorption bands between 318 and 357 nm are assigned to the oxygen to rhenium charge-transfer transitions as they were previously assigned for rhenium−Schiff base complexes.[53] The following bands at lower energy, in the visible region, are the result of other ligand to metal charge-transfer (LMCT) transitions, with extinction coefficients between 15000 and 5000 M^{-1} cm^{-1}. The approximate site symmetry of the oxo- and imidorhenium complexes **3**−**6** is C_{2v}, and the energies of the d orbitals are arranged in the order a_2 (d_{xy}) < b_1 (d_{xz}) ≅ b_2 (d_{yz}) < a_1 ($d_{x^2-y^2}$) < a_1 (d_{z^2}). All the previously mentioned transitions are symmetry allowed and concern the empty d_{xz} and d_{yz} orbitals of the metal. A very weak absorption is observed for each of the complexes at yet lower energy (around 12500 cm^{-1}) with an extinction coefficient around 100 M^{-1} cm^{-1}. This absorption is most likely due to d−d transitions, and is Laporte forbidden.

CD spectra for the two ligands H_2L^1 and H_2L^2 as well as for complexes **3**−**5** are illustrated in Figure 3. The CD spectra of the rhenium complexes in solution reveal more band multiplicity than do the corresponding UV−vis spectra. Besides the variations in the energies of the transitions, which are sensitive to the ligands (L^1 versus L^2, or Re≡O versus Re≡NR), the CD spectra of the rhenium complexes display nearly identical features (Figure 3b), indicating that the same optical isomer at rhenium is afforded. Furthermore, the supernatant solutions from which isolated solids are obtained display CD spectra comparable to those shown in Figure 3b.

The magnitudes of the Cotton effects in the visible are quite high. In fact, they are comparable to those in the UV. For example, the Kuhn anisotropy factor ($|\Delta\epsilon|/\epsilon$) is 0.0029 for the 305 nm transition in complex **3**, and it is 0.0045 for the transition at 417 nm. Furthermore, the rotational strengths of the ligand-based transitions in the UV are enhanced upon coordination to rhenium (Figure 3). The pronounced Cotton effects observed for the LMCT transitions of complexes **3**−**6** demonstrate asymmetric induction from the enantiopure organic ligand to the metal center. Thus, in agreement with the findings from X-ray crystallography (vide supra), the CD spectra of bulk products (Figure 3b) show that out of two possible rhenium enantiomers (see the illustration below), only one isomer is exclusively made and isolated. The absolute configurations for complexes **3** and **5** have been established by X-ray diffraction (Figures 1 and 2). In accordance with the Cahn, Ingold, and Prelog (CIP) rules,[54−56] and their extension to mononuclear coordination complexes,[57] the phenoxide oxygen of the tridentate $L^{1,2}$ ligand is of highest CIP priority (per the "*trans* maximum difference subrule") followed by the phenoxide oxygen of the bidentate $HL^{1,2}$ ligand (see the illustration). Thus, the optical isomer with *C* configuration at rhenium is obtained. Since CD spectra are useful in identifying absolute configurations of chiral complexes by relating similar compounds, we conclude that complexes **3**−**6** have the same stereochemical configuration, namely, *C* (see the illustration), by virtue of their nearly identical CD spectra (Figure 3b).



where, X = O or NR, and ◎ = phenolic oxygen.

Cyclic Voltammetry. Complexes **3**−**5** are electroactive in methylene chloride, Table 4. Figure S1 in the Supporting Information shows the cyclic voltammograms of **3**−**5** in methylene chloride with a scan rate of 0.050 V s^{-1}. Anodic

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Table 4. Cyclic Voltammectric Data for Complexes **3**−**5** at 298 K[a]

complex[b]	oxidation, E_{pa}, V vs $(FeCp_2)^{+/0}$	reduction, E_{pc}, V vs $(FeCp_2)^{+/0}$
3	0.892	0.792
4	0.780	0.682
5	0.502, 0.902	0.361, 0.708

[a] Scan rate 50 mV s^{-1}; reference electrode Ag/AgCl (Ag wire in 0.10 M LiCl in acetone); electrolyte 0.10 M NBu_4BF_4 in methylene chloride. [b] 3.0 mM solution in methylene chloride.

oxidation for **3** takes place via one-electron charge transfer with an irreversible interposed chemical reaction. This is affirmed on the basis of the cyclic voltammograms recorded at different potential scan rates. For scan rates smaller than 1.0 V s^{-1}, the ratio between the backward and forward peak currents is not equal to unity. However, at a fast enough potential scan rate (>1.0 V s^{-1}), the chemical reaction is prevented. It is possible then to calculate an $E^r_{1/2}$ value of 0.842 V vs ferricinium ion/ferrocene for the couple $[Re(O)(HL^1)(L^1)]^+/[Re(O)(HL^1)(L^1)]$. For complex **4**, the anodic oxidation is characterized by a reversible one-electron-transfer process. This process is not complicated by a subsequent chemical reaction. The intensities of the anodic and cathodic peak currents are equal for any potential scan rate between 0.050 and 2.0 V s^{-1}. For the couple $[Re(O)(HL^2)(L^2)]^+/[Re(O)(HL^2)(L^2)]$, the $E^r_{1/2}$ value is equal to 0.731 V (vs ferricinium ion/ferrocene). It appears that, for **4**, the oxidized species is stable on the voltammetric time scale, but this is not the case for **3**. Hence, the slow chemical reaction detected after the one-electron-oxidation step is stipulated to concern the coordinated ligands HL^1 and/or L^1 in **3**. We could assume that substituents on the phenoxide ring of H_2L^2 (a methyl group and an adamantyl group) may prevent the chemical process or render it so slow that it is not observed in the cyclic voltammogram at scan rates ranging from 0.050 to 2.0 V s^{-1}.

The cyclic voltammogram of the phenylimido complex **5** is characterized by a first anodic oxidation at 0.502 V. This oxidation step is followed by a slow chemical reaction that can be avoided at a scan rate >1.0 V s^{-1}. In this case an $E^r_{1/2}$ value of 0.431 V vs ferricinium ion/ferrocene for the couple $[Re(NC_6H_5)(HL^1)(L^1)]^+/[Re(NC_6H_5)(HL^1)(L^1)]$ can be calculated. A second oxidation, which is reversible, has been observed at 0.902 V. This second oxidation, not observed for **3** and **4**, could be attributed to a one-electron-transfer process within the phenylimido ligand. It is worth noting that the observed ease of oxidation of **5** is in line with the π-donating nature of the phenylimido ligand, which helps in stabilizing a higher oxidation state on rhenium.

Conclusion

Rhenium(V) oxo and imido complexes **3**−**6** containing "3 + 2" Schiff base ligands have been synthesized and isolated as a single isomer. Two compounds, **3** and **5**, have been subjected to single-crystal X-ray analysis, which revealed the stereochemical configuration at rhenium. All the complexes were fully characterized by ^{1}H NMR, IR, mass spectrometry, and elemental analyses. The CD spectra show that optical activity of the rhenium chromophore is induced by the chiral ligand. The absolute configuration at rhenium in all of these complexes is *C*. Due to the strengths of the Re≡O and Re≡NR bonds, reactions with organic reductants have not been observed. As such, these compounds are stable toward air, moisture, and heat. With the exception of the rhenium imido complex **5**, the metal center is difficult to oxidize as evidenced by cyclic voltammetry. Hence, these complexes are promising for therapeutic applications. Furthermore, the availability of an alcohol moiety on the bidentate ligand $HL^{1,2}$ could be exploited for tethering bioactive molecules.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-9874857-CAREER) and the Arnold and Mabel Beckman Foundation (BYI Award to M.M.A.-O.). Funds for the purchase of a diffractometer were made possible by the NSF (Grant CHE-9871332). M.M.A.-O. is grateful to Professor H. D. Kaesz for helpful discussions.

Supporting Information Available: Complete tables of crystallographic data and refinement details for complexes **3** and **5** and cyclic voltammograms for complexes **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0108033