

# An oxorhenium(V) Schiff-base complex: synthesis, structure, spectroscopic characterization, electrochemistry, and DFT calculations

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Reaction of the Schiff base 2-[(2-hydroxyethylimino)methyl]phenol (H<sub>2</sub>L) with *trans*-ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> in 1:1 M ratio in dichloromethane gives [ReOCl<sub>2</sub>(HL)(PPh<sub>3</sub>)] (1) in substantial yield. The compound has been characterized by C, H, and N microanalyses, IR, UV–Vis, <sup>1</sup>H NMR, and ESI-MS spectra. The X-ray crystal structure of the title compound has been determined. The structure reveals that it is an octahedral *cis-Cl*, *Cl* oxorhenium(V) complex where the relative positions of the two chlorides are *cis*. 1 crystallizes in the monoclinic space group *P*<sub>2</sub>/n with *a*=14.198(2), *b*=10.970(1), *c*=18.258(1) Å, *β*=111.83(1)°, *V*=2640.0(3) Å<sup>3</sup>, and *Z*=4. Electrochemical studies in dichloromethane show Re(V) to Re(VI) oxidation at 1.51 V along with two successive reductions – Re(V) to Re(IV) and Re(IV) to Re(III) at –0.66 V and –1.03 V *versus* Ag/AgCl, respectively. Geometry optimization of 1 vis-à-vis its *trans* analog, *trans-Cl*, *Cl* complex 2, has been performed at the level of density functional theory; **2** is more stable than 1 by 2 kcal M<sup>-1</sup>.

Keywords: Oxorhenium(V) complex; Schiff-base ligand; Electrochemistry; DFT calculation

# **1. Introduction**

Coordination chemistry of rhenium and technetium is of considerable interest due to the use of  $^{186/188}$ Re and  $^{99}$  mTc as therapeutic agents and diagnostic imaging agents, respectively, in nuclear medicine [1–5].  $^{99}$  mTc is widely used in nuclear medicine, while  $^{186/}$  mtc is widely used in nuclear medicine, while  $^{186/}$  mtc is widely used in nuclear medicine, while  $^{186/}$  mtc is widely used in nuclear medicine, while  $^{186/}$  mtc is widely used in nuclear medicine, while  $^{186/}$  mtc is widely used in nuclear medicine, while  $^{186/}$  mtc is widely used in nuclear medicine, while  $^{186/}$  mtc is widely used in nuclear medicine, while  $^{186/}$  mtc is widely used in nuclear medicine, while  $^{186/}$  mtc is a prerequisite step in the catalytic cycle of oxygen atom transfer (OAT) [6]. The catalytic aspects of mono- and dinuclear methyloxorhenium(V) complexes as prospective candidates for OAT reactions have been extensively investigated [7, 8]. Thus, there is continuing interest in fundamental knowledge about the structure, spectroscopic properties, and redox

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behaviors of Re(V) complexes. This aspect of rhenium chemistry has kindled our interest to develop the chemistry of rhenium specifically in this +V oxidation state.

One approach for development of diagnostic imaging agents of technetium and to generate potential rhenium-based therapeutic reagents is the use of Schiff-base ligands to stabilize the  $[MO]^{3+}$  core for M(V) [M=Tc(V) and Re(V)] [9–14]. Thus, tailor-made Schiff bases are often employed to stabilize the  $[MO]^{3+}$  core in *in vivo* applications [7].



In this context, 2-[(2-hydroxyethylimino)methyl]phenol (H<sub>2</sub>L), a Schiff base, is promising. H<sub>2</sub>L can adopt different binding modes, chelating or bridging, in tridentate mono-anionic (HL<sup>1-</sup>) form or in tridentate bi-anionic (L<sup>2-</sup>) form. HL<sup>1-</sup> and L<sup>2-</sup> have been employed to stabilize Cu(II), Ni(II), Fe(III), Mn(II), Mn(III), and Zn(II) [15–20]. Thus, coordination chemistry of first-row transition metal ions with H<sub>2</sub>L is vast. Tetranuclear Cu (II), Ni(II), and Fe(II) with cubane structures are examples [21, 22]. There is no such report with rhenium. Herein, we report the synthesis, characterization, structural elucidation, and redox behavior of an oxorhenium(V) complex of H<sub>2</sub>L. Calculations at the level of density functional theory (DFT) were also performed to rationalize the structure and spectral observations.

## 2. Experimental

#### 2.1. Materials and physical measurements

Ammonium perthenate (Sigma–Aldrich Chemicals) was used as received. The precursor [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] was prepared and characterized following the method of Chatt and Rowe [23]. Ethanolamine and salicylaldehyde were obtained from Sigma–Aldrich and used without purification. Microanalyses were performed with a Perkin–Elmer 2400II elemental analyzer. FTIR spectra in the solid phase were recorded as KBr pellets with a Perkin–Elmer FTIR-100 spectrophotometer. UV–Vis absorption spectra of the ligand and 1 were recorded on a Perkin–Elmer Lambda 25 spectrophotometer and NMR spectra (in CDCl<sub>3</sub>) with a Bruker DPX300 spectrometer. Electrospray ionization mass spectra in the positive ionization mode were recorded on a Waters Qtof Micro YA263 spectrometer. Electrochemical experiments were performed on a BAS Epsilon electrochemical workstation (Model CV-50) under nitrogen in dry and degassed dichloromethane at 293 K. The supporting electrolyte is tetra-n-butylammonium perchlorate (0.1 M). The conventional three-electrode system is comprised of a glassy carbon (GC) working electrode, a platinum wire counter electrode and a Ag/AgCl reference electrode. All potentials reported here are referenced to Ag/AgCl.

## 2.2. Synthesis of $H_2L$

 $H_2L$  was synthesized by reacting 1 mL (10 mM) of salicylaldehyde with 0.6 mL (10 mM) of ethanolamine in the absence of solvent. The resulting yellow reaction mixture was

stirred for 2 h at room temperature. After stirring, the dark yellow liquid obtained was purified by distillation under reduced pressure. Yield: 1.56 g (85%), b.p. 137 °C Anal. Calcd (%) for C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub>: C, 65.44; H, 6.71; N, 8.48. Found (%): C, 65.10; H, 6.30; N, 8.74%. FTIR (KBr/cm<sup>-1</sup>): v(O-H<sub>alcoholic</sub>) 3488(br *versus.*); v(PhO–H) 3320(br *versus.*), v(C=N) 1612(*versus.*); v(C–O<sub>phenolic</sub>) 1280(*versus.*);  $\delta$ (C–H) 1480(*versus.*). UV–Vis (CHCl<sub>3</sub>),  $\lambda_{max}$  ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 242 (22 246); 345 (6 523). <sup>1</sup>H NMR ( $\delta$ , ppm): 3.70 (t, 2H, J=5 Hz, – CH<sub>2</sub>–); 3.87 (t, 2H, J=8.7 Hz, –CH<sub>2</sub>–); 6.84 (t, 1H, J=7.5 Hz, Ar–H); 6.92 (d, 1H, J=8.3 Hz, Ar–H); 7.22 (d, 1H, J=7.6, Ar–H); 7.29 (t, 1H, J=8.1 Ar–H); 8.34 (s, 1H, imine–H).

## **2.3.** Synthesis of $[ReO(HL)PPh_3Cl_2]$ (1)

To a suspension of *trans*-ReOC1<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.208 g, 0.25 mM) in chloroform (15 mL) was added H<sub>2</sub>L (0.041 g, 0.25 mM) dissolved in 10 mL of chloroform dropwise with stirring. The resulting reaction mixture was heated under reflux for 5 h. During reflux, the color changes from yellow-green to dark green. After refluxing, the resulting solution was cooled to room temperature and allowed to evaporate in the air to dryness to get a gummy green mass. This gummy green mass was washed thoroughly with diethyl ether to get a green powder. Yield: 128 mg 73%; m.p. 145 °C. Anal. Calcd (%) for C<sub>27</sub>H<sub>25</sub>NRePO<sub>3</sub>Cl<sub>2</sub>: C, 46.32; H, 3.60; N, 2.00. Found (%): C, 46.09; H, 3.65; N, 2.10. FTIR (KBr/cm<sup>-1</sup>):  $\nu$ (O–H) 3468(*versus.*);  $\nu$ (Re=O) 961(*versus.*);  $\nu$ (C=N) 1605(*versus.*);  $\delta$ (C–H) 1480 (*versus.*),  $\delta$ (C–P) 692(*s*). UV–Vis (CHCl<sub>3</sub>),  $\lambda_{max}$  ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 446sh (665), 405 (1 298), 355 (5 693), 242 (20 153). <sup>1</sup>H NMR ( $\delta$ , ppm): 1.25 (1H, *s*, –O–H), 3.43 (2H, *t*, *J*=10 Hz, –CH<sub>2</sub>–); 3.72 (1H, *d*, *J*=12 Hz, –CH<sub>2</sub>–); 4.46 (1H, *dt*, *J*=3 Hz, *J*t=12 Hz, –CH<sub>2</sub>–); 6.59 (1H, *d*, *J*=8 Hz, Ar–H); 6.95 (1H, *d*, Ar–H); 7.32–7.62 (17H, *m*, 15H of PPh<sub>3</sub> & 2H of Ar–H); 8.46 (*s*, 1H, imine–H). Mass spectra requires for the molecular ion peaks C<sub>27</sub>H<sub>25</sub>NRePO<sub>3</sub>Cl<sub>2</sub> 699.57, found 700.59 [M+H]<sup>+</sup>, 717.89 [M+H<sub>3</sub>O]<sup>+</sup>, 738.69 [M+K]<sup>+</sup>.

## 2.4. X-ray crystal structure analysis

Single crystals of 1 suitable for X-ray analysis were selected from those obtained by slow direct diffusion of petroleum ether (40-60 °C) into a moderately concentrated solution of 1 in dichloromethane at 298 K. An appropriate single crystal of 1 was mounted on a Bruker SMART APEX II CCD area detector diffractometer at 298(2) K using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Intensity data of 1 were reduced using SAINT [24], and the empirical absorption corrections were performed with SADABAS [25]. The structure of 1 was solved by direct methods and refined by full-matrix least-squares based on |F|<sup>2</sup> using SHELXL-97 [26]. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions and constrained to ride on their parent atoms. Even the best single crystal selected for data collection gave diffuse diffraction spots, indicating a large mosaic spread; a few of the diffraction spots were overlapping and the integration of these spots could not be carried out properly by the processing software. Consequently, a small portion of the reflections collected was rejected and the structure was refined using the available data ( $1.6 < \theta < 25.0^{\circ}$ ), which was adequate to give a precise structure. All calculations were carried out using SHELXS-97 [26], SHELXL-97, and SHELXTL [26] programs. The crystallographic data for 1 are summarized in Table 1.

Parameter	Complex 1		
Formula	C <sub>27</sub> H <sub>25</sub> Cl <sub>2</sub> NO <sub>3</sub> PRe		
Formula weight	699.56		
Crystal system	Monoclinic		
Space group	$P2_1/n$		
Unit cell dimensions			
a (Å)	14.198(2)		
b (Å)	10.970(1)		
<i>c</i> (Å)	18.258(1)		
α (°)	90.00		
β (°)	111.83(1)		
γ (°)	90.00		
Volume (Å <sup>3</sup> )	2640.0(3)		
Ζ	4		
Temperature (K)	293		
$\rho_{\rm calc}  ({\rm g}{\rm cm}^{-3})$	1.753		
$\mu$ (Mo- $K_a$ ) (mm <sup>-1</sup> )	4.895		
$F(0 \ 0 \ 0)$	1356		
Crystal size (mm)	$0.17 \times 0.20 \times 0.24$		
$\lambda$ (Mo- $K_a$ ) (Å)	0.71073		
$\theta$ ranges (°)	$1.6 < \theta < 25.0$		
Total reflection	24,179		
Reflection independent $(R_{int})$	4639 (0.036)		
h/k/l	-16, 16/-13, 12/-21, 21		
Reflection observed $(I > 2\sigma)$	3922		
$R_1$	0.0225		
$wR_2$	0.0515		
Goodness of fit	1.06		
Largest difference peak and hole $(e Å^{-3})$	0.72  and  -0.47		

Table 1. Crystal data and structure refinement for 1.

 $R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, \ \text{w} R_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}, \ \text{calcd.} w = 1 / [\sigma^{2} (F_{o}^{2}) + (0.0276\text{P})^{2} + 3.4910\text{P}], \ \text{where } \mathbf{P} = (F_{o}^{2} + 2F_{c}^{2}) / 3.$ 

## 2.5. Computational details

All geometries and energies in the present work were computed using the gradient-corrected DFT level with three-parameter fit of exchange and correlation functionals of Becke (B3LYP) [27], which include the correlation functional of Lee et al. (LYP) [28]. The Xe core electrons of Re were replaced by a relativistic effective core potential (ECP) and associated valence double  $\xi$  basis set of Hay and Wadt [29, 30] (LANL2DZ) were employed for Pt. This includes electrons in the 6s, 6p, and 5d orbitals. The calculations were performed by using ECP basis set on rhenium, the standard 6-31+g(d) basis for chlorine, phosphorus, and nitrogen, 6-31g(d) basis for carbon, hydrogen, and oxygen [31, 32]. All computations in this study were performed using Gaussian 09, Revision A.02 program package [33]. All the computed vibrational frequencies corroborate with the experimental vibrational spectrum of 1 in terms of identical modes but with shifted positions. This is quite natural since our computations are only compatible in the gas phase. However, this can be regarded as a genuine signature of the closeness of the two structures, one as determined by X-ray crystallography (minimum energy) cis-Cl, Cl 1 and the other, trans-Cl, Cl 2 as obtained from the geometry optimization process (global minimum energy structure). Thus, there is a genuine rationale between our experimental findings and our adapted theoretical computations at the DFT level.

## 3. Results and discussion

#### 3.1. Synthesis

 $H_2L$  is a 1:1 Schiff-base condensate of ethanolamine and salicylaldehyde [34–37]. From the earlier reports use of an organic solvent like benzene, toluene, methanol, or THF is necessary. Here, for the first time, we have generated it in absence of solvent. Subsequently, we have attempted to explore its metal binding aspects particularly with Re(V). ReO(HL)(PPh<sub>3</sub>)Cl<sub>2</sub> (1) has been obtained from ligand exchange reaction of ReO(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> with 2-[(2-hydroxyethylimino)methyl]phenol (H<sub>2</sub>L) in equimolar proportion in dichloromethane. The compound is green and soluble in common organic solvents.

## 3.2. Spectroscopic properties

Infrared spectra of H<sub>2</sub>L and its oxorhenium(V) complex, **1**, have been studied and assignments made on the basis of data in the literature [38]. A strong band at  $1280 \text{ cm}^{-1}$  present in the IR spectrum of H<sub>2</sub>L is due to the phenolic (C–O) stretch. However, the shifted frequency of this is not discernable in the spectrum of 1, suggesting covalent bonding between phenolic oxygen and rhenium. A strong band at  $1612 \text{ cm}^{-1}$  for H<sub>2</sub>L is assigned to the azomethine (>C=N–) vibration. This value shifts to lower frequency ( $1605 \text{ cm}^{-1}$ ) in **1**, indicating coordination through the azomethine nitrogen to rhenium in **1**. The IR spectrum of 1 exhibits a sharp band at  $961 \text{ cm}^{-1}$ , assignable to v(Re=O) [4, 39].

The experimental vibrational spectrum of 1 has been compared with the calculated (nonscaled) one (Supplemental material). The experimental and calculated IR spectra of 1 are similar in terms of their band positions, band intensity, and shape. The calculated v(Re=O)frequency value (1008 cm<sup>-1</sup>) for 1 is higher than its experimental value only by ~5%. Often the computed gas phase data are at variance with the experimental one [40]. The calculated v(Re=O) value was exactly at the same value as found by experiment (633 cm<sup>-1</sup>).

The electronic absorption spectra of  $H_2L$  and 1 in CHCl<sub>3</sub> were recorded at room temperature and the characteristic absorption spectral data are given in the experimental section. The weak yet characteristic absorption of oxorhenium(V) complex at 446 and 405 nm is due to the presence of relatively strong ligand to metal charge transfer band [41].

The well-resolved <sup>1</sup>H NMR spectrum of the complex was studied, and a representative <sup>1</sup>H NMR spectrum of **1** is given in Figure 1. The spectral peaks in <sup>1</sup>H NMR of **1** are the same as for  $H_2L$  with downfield shifts, except methylene (-CH<sub>2</sub>-) protons. The observed signals corresponding to -CH<sub>2</sub>- peaks are discernable at position 8 as endo (facing toward the oxygen of Re=O core) and exo (far from the oxygen of the Re=O core) [42]. The endo proton is more strongly deshielded than the exo proton. Thus, the <sup>1</sup>H NMR signal of an endo proton should appear at much lower-field compared to the exo one. Therefore, signals at 4.46 and 3.72 ppm are assigned as the endo methylene proton and the exo methylene proton, respectively. The difference in chemical shifts between the endo and exo methylene groups is comparable with the literature [43].

# 3.3. X-ray crystal structure

Shining dark green cuboidal single crystals for X-ray structure determination were obtained by slow diffusion of petroleum ether (40–60 °C) into a moderately concentrated solution of 1 in dichloromethane at room temperature. An ORTEP view of the asymmetric unit, along



Figure 1. A representative <sup>1</sup>H NMR spectrum of  $[ReO(HL)Cl_2]PPh_3]$  in CDCl<sub>3</sub>. The peak marked with 'S' is due to the residual proton in CDCl<sub>3</sub>.

with the atom numbering scheme, is shown in figure 2. The structure exhibits a twofold disorder in C50 and O7 that refined to 70/30 occupancy. A figure depicting this disorder is available in the Supplementary Material. Selected bond lengths and angles are given in table 2. The rhenium is at the center of a distorted octahedral environment. The basal plane is defined by the neutral imido of  $HL^{-1}$ , two chlorides and PPh<sub>3</sub>. The Re is displaced 0.138(2) Å toward O(1) from this mean plane. The mono-anionic phenolate oxygen is *trans* to Re=O. This is a normal mode of coordination of salicylaldimine-derived ligands where the relatively hard phenoxide occupies the *trans* position relative to Re=O,



Figure 2. ORTEP diagram of 1 showing the atom-labeling scheme and 30% probability ellipsoids.

Bond lengths/bond angles	Experimental (1)	Optimized (1)	Optimized (2)	
Re1-O1	1.679(2)	1.695	1.688	
Re1-06	1.941(2)	1.975	1.994	
Re1-N1	2.130(3)	2.187	2.132	
Re1–P1	2.457(1)	2.552	2.539	
Re1-Cl3	2.418(1)	2.420	2.467	
Re1-Cl4	2.354 1)	2.409	2.456	
Cl3-Re1-Cl4	89.68(4)	88.81	170.79	
Cl3-Re1-P1	176.02(4)	172.49	95.06	
Cl3-Re1-O1	96.27(9)	100.45	91.04	
Cl3-Re1-O6	87.33(8)	88.19	83.58	
Cl3-Re1-N1	85.32(9)	86.94	86.65	
Cl4-Re1-P1	89.80(4)	89.23	90.42	
Cl4-Re1-O1	98.75(9)	99.76	95.92	
Cl4-Re1-O6	89.28(8)	90.69	89.56	
Cl4–Re1–N1	170.59(9)	171.72	86.43	
P1-Re1-O1	87.71(9)	87.03	94.44	
P1-Re1-O6	88.72(8)	84.59	84.81	
P1-Re1-N1	94.63(9)	94.07	167.59	
O1-Re1-O6	171.20(10)	166.51	174.48	
O1–Re1–N1	89.74(12)	88.00	97.83	
O6–Re1–N1	82.54(12)	82.08	83.16	
Re1-06-C51	140.1(2)	140.00	136.68	
Re1-N1-C3	127.6(3)	127.14	126.64	
Re1-N1-C15	117.9(3)	117.30	115.82	
N1-C3-C2	127.3(4)	127.96	127.52	
N1-C15-C50	112.6(6)	112.35	111.60	

Table 2. Selected experimental and optimized bond lengths (Å) and angles (°) for 1 and 2.

regardless of the denticity of the ligand [44–47]. However, there are several structures with different coordination modes [48, 49].

Some selected metrical parameters are given in table 2. The two chlorides are coordinated *cis* with a Cl(3)–Re–Cl(4) angle of 89.67(5). Clear difference exists between Re(1)–Cl(3) and Re(1)–Cl(4) bond lengths with Re(1)–Cl(3) distance *trans* to PPh<sub>3</sub> slightly longer than Re(1)–Cl(4) *trans* to imino nitrogen. A similar type of *trans* effect was observed in other [ReOCl<sub>2</sub>(O–N)(PPh<sub>3</sub>)] chelates [40, 46, 50, 51].

## 3.4. Geometry optimizations

To elucidate the bonding properties of *cis-Cl, Cl* 1 and *trans-Cl, Cl* 2, calculations at the DFT level were undertaken. The geometries were optimized in the singlet state using the DFT method with the B3LYP functional. The optimized geometry parameters of both the conformers are given in table 2. From the geometry optimizations of the conformers *trans-Cl, Cl* 2 is 2 kcal more



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stable than *cis-Cl, Cl* **1**. We have been only able to isolate the *cis-Cl, Cl* conformer **1** in the solid state. Predicted bond lengths and angles are in agreement with values based on X-ray crystal structure data and the general trends observed in the experimental data are well reproduced in the calculations. The largest difference is for the Re-P bond distance. It may come from the basis sets which are approximated to a certain extent or may indicate the influence of the crystal packing on the values of the experimental bond lengths [40, 52, 53]. Theoretical calculations do not consider the effects of the chemical environment.

#### 3.5. Electrochemistry

The electrochemical behavior of 1 in CH<sub>2</sub>Cl<sub>2</sub> has been studied by using cyclic voltammetry at GC electrode under N<sub>2</sub> atmosphere. The resulting cyclic voltammogram (CV) is shown in Supplementary Material and the peak potentials are tabulated in table 3. On the positive side of the Ag/AgCl reference electrode, 1 exhibits one anodic wave (Couple I) with a peak potential of 1.51 V versus Ag/AgCl. The associated peak current,  $i_{pa}$  is 29.4 µA. The corresponding cathodic response is discernable in the subsequent reverse cycle with a peak potential value of 1.33 V versus Ag/AgCl having a peak current,  $i_{pc}$  of 25.0 µA. H<sub>2</sub>L is electrochemically inert in the potential range of interest here. Thus, this oxidation can be assigned as metal centered. Comparison of the voltammetric peak currents with those of the ferrocene–ferrocenium couple (0.44 V versus. Ag/AgCl) under the same experimental condition establishes that the present oxidative response in 1 involves one electron. Oxidation at +1.51 V versus Ag–AgCl corresponds to Re(V) to Re(VI) oxidation. The ratio of  $i_{pc}$  to  $i_{pa}$  is 0.85, a value close to unity. Thus this oxidative response is quasi-reversible. This observed value of the Re(VI)/Re(V) redox couple is comparable to the value reported earlier [54].

Our oxorhenium(V) complex shows two consecutive electrochemical responses at  $E_{0.5}$  values of -0.73 V (Couple II) and -1.06 V (Couple III) on the negative side of the Ag/AgCl electrode. Comparison of the voltammetric peak currents of the couples II and III with those of the ferrocene–ferrocenium couple (0.44 V *versus* Ag/AgCl) under the same experimental condition establishes that the present reductive responses in 1 involve one electron in each step. Thus the two reductive responses can be assigned as Re(V) to Re (IV) and Re(IV) to Re(III) sequential reductions. The cathodic peak current,  $i_{pc}$  of couple II is 23.1 µA. Subsequent anodic response in the reverse cycle is at -0.66 V *versus* Ag/AgCl with an anodic peak current,  $i_{pa}$ , of only 18.8 µA. The ratio of  $i_{pc}$  to  $i_{pa}$  is 1.229, considerable deviation from unity. The cathodic peak current,  $i_{pc}$ , increases with the square root of the scan rate ( $v^{1/2}$ ), but not in proportionality. Again, the cathodic peak potential,  $E_{pc}$ , shifts more negatively with increase in sweep rate, *versus*. Judged on these criteria, the metal centered reduction in 1 at peak II is said to be quasi-reversible [54]. The second reductive response (Couple III) can also be said to be quasi-reversible in nature. The following plausible redox steps might be operative here:

Table 5.	Cyclic	vonammetric	data	01	1.	

Table 2 Carolia vialtemanatria data of 1

Entry	$E_{\rm pa}~({ m V})$	$E_{\rm pc}$ (V)	$\Delta E$ (V)	$E^{o}{}_{\!$	i <sub>pc</sub> (μA)	i <sub>pa</sub> (μA)
Couple I Couple II Couple III	$1.51 \\ -0.66 \\ -1.03$	$     \begin{array}{r}       1.33 \\       -0.80 \\       -1.09     \end{array} $	0.18 0.14 0.06	$1.42 \\ -0.73 \\ -1.06$	25.0 23.1 5.9	29.4 18.8 6.3

 $E_{\rm pa}$  is the peak potential for the anodic wave,  $E_{\rm pc}$  is the peak potential for the cathodic wave,  $E_{1/2}=0.5$  ( $E_{\rm pa}+E_{\rm pc}$ ),  $i_{\rm pa}$  is the peak current for the anodic wave,  $i_{\rm pc}$  is the peak current for the cathodic wave.

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$$[\text{Re}^{\text{VI}}O(\text{HL})(\text{PPh}_3)\text{Cl}_2]^+ + e^- \rightarrow [\text{Re}^{\text{V}}O(\text{HL})(\text{PPh}_3)\text{Cl}_2] \quad E_{\frac{1}{2}} = 1.42\text{V}$$
$$[\text{Re}^{\text{V}}O(\text{HL})(\text{PPh}_3)\text{Cl}_2] + e^- \rightarrow [\text{Re}^{\text{IV}}O(\text{HL})(\text{PPh}_3)\text{Cl}_2]^- \quad E_{\frac{1}{2}} = -0.73\text{V}$$
$$[\text{Re}^{\text{IV}}O(\text{HL})(\text{PPh}_3)\text{Cl}_2]^- + e^- \rightarrow [\text{Re}^{\text{III}}O(\text{HL})(\text{PPh}_3)\text{Cl}_2]^{2-} \quad E_{\frac{1}{2}} = -1.06\text{V}$$

The electrochemical reductions in oxoRe(V) to Re(III) with two one-electron transfer processes have also been proposed in previously reported oxorhenium(V) complexes with reported mechanisms [55–59] similar to our proposed mechanism. The current heights of the individual couples II and III are not the same, even though in each process only one electron is involved. Process II holds more current than process III (table 3), likely due to instability of the electro-generated Re(IV) from couple II that subsequently undergoes further reduction to Re(III) in couple III. This instability of Re(IV) within the electrochemical time scale owes to its dissociation which might have occurred immediately after its *in situ* electro-generation. Dissociation of such Re(IV) intermediates is not unprecedented in sequential redox events of an oxorhenium(V) complex [58].

### 4. Conclusion

We have synthesized and characterized an oxorhenium(V) complex from 2-[(2-hydroxyethylimino)methyl]phenol (H<sub>2</sub>L). The X-ray crystal structure of  $[\text{Re}^{V}O(\text{HL})(\text{PPh}_3)\text{Cl}_2]$  (1) reveals that the rhenium(V) center is a distorted octahedral "NO<sub>2</sub>Cl<sub>2</sub>P" coordination chromophore. The two chlorides are *cis*. However, DFT calculations in the gas phase reveal that the *trans-Cl*, *Cl* oxorhenium(V) complex, **2** is more stable than **1** by 2 kcal/M<sup>-1</sup>. The electrochemical studies show Re(V) to Re(VI) oxidation along with two consecutive oneelectron reductions – Re(V) to Re(IV) and Re(IV) to Re(III) for **1** in dichloromethane.

### Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 879742). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336,033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc. cam.ac.uk).

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