

## Synthesis and Characterization of Novel Rhenium(V) Tetradentate N<sub>2</sub>O<sub>2</sub> Schiff Base Monomer and Dimer Complexes

Paul D. Benny, Charles L. Barnes, Pamela M. Piekarski, John D. Lydon, and Silvia S. Jurisson\*

The Chemistry Department, University of Missouri, Columbia, Missouri 65211

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Several rhenium(V) oxo complexes with tetradentate N<sub>2</sub>O<sub>2</sub> Schiff base ligands were synthesized and characterized. The general synthetic procedure involved reaction of [NBu<sub>4</sub>][ReOCl<sub>4</sub>] with a tetradentate Schiff base ligand (L<sub>1</sub> = *N,N'*-ethylenebis(acetylacetonimine), (acac<sub>2</sub>en) or L<sub>2</sub> = *N,N'*-propylenebis(acetylacetonimine) (acac<sub>2</sub>pn)) in ethanol solution to generate complexes of the form *trans*-ReOX(L) where X = Cl<sup>-</sup>, MeO<sup>-</sup>, ReO<sub>4</sub><sup>-</sup>, or H<sub>2</sub>O. The product isolated from the reaction was found to be dependent on the reaction conditions, in particular the presence or absence of water and/or base. The  $\mu$ -oxo-Re<sub>2</sub>O<sub>3</sub>(L)<sub>2</sub> dimers were synthesized and characterized for chemical and structural comparison to the related monomers. Conversion of the monomer to its dimer analogue was followed qualitatively by spectrophotometry. The complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, UV–vis, and IR spectroscopy, elemental analysis, and single crystal X-ray diffraction. The crystallographic data reported for the structures are as follows: *trans*-[ReO(OH<sub>2</sub>)(acac<sub>2</sub>en)]Cl (H<sub>20</sub>C<sub>12</sub>ClN<sub>2</sub>O<sub>4</sub>Re) **1**, triclinic (*P* $\bar{1}$ ), *a* = 7.2888(6) Å, *b* = 9.8299(8) Å, *c* = 10.8195(9) Å,  $\alpha$  = 81.7670(10)°,  $\beta$  = 77.1510(10)°,  $\gamma$  = 87.6200(10)°, *V* = 747.96(11) Å<sup>3</sup>, *Z* = 2; *trans*-[ReO(OReO<sub>3</sub>)(acac<sub>2</sub>en)] (H<sub>18</sub>C<sub>12</sub>N<sub>2</sub>O<sub>7</sub>Re<sub>2</sub>) **2**, monoclinic (*P*<sub>2</sub>/*c*), *a* = 7.5547(4) Å, *b* = 8.7409(5) Å, *c* = 25.7794(13) Å,  $\beta$  = 92.7780(10)°, *V* = 1700.34(16) Å<sup>3</sup>, *Z* = 4; *trans*-[ReOCl(acac<sub>2</sub>pn)] (H<sub>20</sub>C<sub>13</sub>N<sub>2</sub>O<sub>3</sub>ClRe) **3**, monoclinic (*P*<sub>2</sub>/*c*), *a* = 8.1628(5) Å, *b* = 13.0699(8) Å, *c* = 28.3902(17) Å,  $\beta$  = 97.5630(10)°, *V* = 3002.5(3) Å<sup>3</sup>, *Z* = 8; *trans*-[ReO(OMe)(acac<sub>2</sub>pn)] (H<sub>23</sub>C<sub>14</sub>N<sub>2</sub>O<sub>4</sub>Re) **4**, monoclinic (*P*<sub>2</sub>/*c*), *a* = 6.7104(8) Å, *b* = 27.844(3) Å, *c* = 8.2292(9) Å,  $\beta$  = 92.197(2)°, *V* = 1536.4(3) Å<sup>3</sup>, *Z* = 4; *trans*-[ $\mu$ -oxo-Re<sub>2</sub>O<sub>3</sub>(acac<sub>2</sub>en)<sub>2</sub>] (H<sub>36</sub>C<sub>24</sub>N<sub>4</sub>O<sub>7</sub>Re<sub>2</sub>) **5**, monoclinic (*P*<sub>2</sub>/*1**n*), *a* = 9.0064(5) Å, *b* = 12.2612(7) Å, *c* = 12.3695(7) Å,  $\beta$  = 90.2853(10)°, *V* = 1365.94(13) Å<sup>3</sup>, *Z* = 2; and *trans*-[ $\mu$ -oxo Re<sub>2</sub>O<sub>3</sub>(acac<sub>2</sub>pn)<sub>2</sub>] (H<sub>40</sub>C<sub>26</sub>N<sub>4</sub>O<sub>7</sub>Re<sub>2</sub>) **6**, monoclinic (*P*<sub>2</sub>/*1**n*), *a* = 9.1190(5) Å, *b* = 12.2452(7) Å, *c* = 12.8863(8) Å,  $\beta$  = 92.0510(10)°, *V* = 1438.01(14) Å<sup>3</sup>, *Z* = 2.

### Introduction

Rhenium and technetium complexes with tetradentate Schiff base ligands, of which sal<sub>2</sub>en and acac<sub>2</sub>en are classic examples, have been the focus of numerous studies.<sup>1–13</sup> The

technetium chemistry with both *N,N'*-ethylenebis(salicylaldimine) (sal<sub>2</sub>en) and *N,N'*-ethylenebis(acetylacetonimine) (acac<sub>2</sub>en) based ligands has been studied due to the importance of the isotope <sup>99m</sup>Tc to diagnostic nuclear medicine, their potential utility for imaging viable myocardium, and multidrug resistance.<sup>14–16</sup> The interest in rhenium Schiff base chemistry is driven by applications of these complexes

\* To whom correspondence should be addressed. E-mail: JurissonS@missouri.edu. Phone: 573-882-2107. Fax: 573-882-2754.

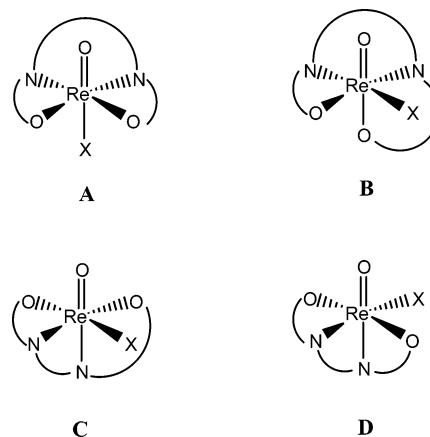
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in commercial catalysis and in therapeutic nuclear medicine.<sup>11,17–21</sup>

Re(V) oxo Schiff base complexes were first reported by Wilkinson in 1979 for both the salicylaldehyde and acetylacetonate based ligands.<sup>2</sup> Both monomeric and dimeric complexes were isolated. Characterizations, however, were limited to elemental analyses, IR, and Raman spectra. Tisato reported the chemistries of Re(V) and Tc(V) oxo complexes with propylene-bridged *N,N'*-2-hydroxypropylenebis(salicylideneimine),  $\text{sal}_2\text{pnOH}$ .<sup>7</sup> The structure of the  $\mu$ -oxo dimer of the Tc analogue was reported, and a monomer of Re(V) having the formula  $[\text{ReOCl}(\text{sal}_2\text{pnOH})]$  was identified. The analytical evidence supported a species with the *trans*  $\text{O}=\text{Re}-\text{Cl}$  arrangement.<sup>7</sup> Herrmann reported the structures and catalytic reactivities of several Re(V) oxo Schiff base complexes with the propylene bridged *N,N'*-2,2-dimethylpropylenebis(3,5-diXsalicylideneimine), where X = Cl, H, or *tert*-butyl ( $\text{sal}_2\text{pnX}_2$ ), of the form *cis*- $[\text{ReOCl}(\text{sal}_2\text{pnX}_2)]$ .<sup>11</sup> The structures showed the Re to sit in a distorted octahedral environment with a phenolic oxygen from the Schiff base ligand occupying the site *trans* to the oxo group and with the chloride *cis* to the oxo group. Reinhoudt then reported Re(V) oxo Schiff base complexes of the form  $[\text{ReO}(\text{OR})(\text{ONNO})]$  based on propylene and butylene bridged salicylaldehyde ligands.<sup>13</sup> In these distorted octahedral complexes, the alkoxide group occupies the site either *cis* or *trans* to the oxo depending on the particular alkoxide.<sup>13</sup> Clearly, the literature suggests that Re(V) oxo chemistry with sal derived tetradentate Schiff base ligands is complex, and the configuration of the ligand about the Re(V) center is dependent on the reaction conditions, as well as the nature of the ligand.<sup>7,11,13</sup> Abu-Omar recently reported the kinetics of oxygen atom transfer with two Re(V) oxo complexes containing two bidentate oxazoline-salicylaldehyde Schiff base ligands, one with a chloride bound *cis* to the oxo group and one with a water coordinated *trans* to the oxo group. Silver triflate was used to obtain the aqua bound *trans* complex.<sup>22,23</sup> Bottomley reported voltammetry studies of monomeric and dimeric Re(V) oxo complexes with tetradentate Schiff base ligands including  $\text{acac}_2\text{en}$ ; however, only elemental analysis and IR spectral characterization were reported.<sup>12</sup>

A range of Re(V) oxo complexes based on  $\text{acac}_2\text{en}$  and  $\text{acac}_2\text{pn}$  were examined for comparison with the analogous



**Figure 1.** Possible conformations of a tetradentate  $\text{N}_2\text{O}_2$  ligand in an octahedral coordination sphere relative to the rhenium oxo group.

Tc(V) Schiff base chemistry and for potential utility in therapeutic radiopharmaceuticals.<sup>4,17,18</sup> There are four possible coordination modes for a tetradentate  $\text{N}_2\text{O}_2$  ligand about a hexacoordinate Re(V) oxo core (Figure 1). The coordination geometry of the ligand relative to the rhenium oxo core is influenced by the backbone (alkyl or aryl), the carbon chain length between the nitrogens, and the type of oxygen donors present in the ligand. Although the salicylaldehyde analogues have been investigated with various backbones and derivatizations, little structural evidence (primarily elemental analyses and IR spectra) is reported for the coordination mode of Re(V) oxo complexes with acac derived tetradentate Schiff base ligands. We report here the syntheses and characterizations of several Re(V) oxo monomer complexes of type A, *trans*- $\text{ReOX}(\text{L})$ , where L is an acac based  $\text{N}_2\text{O}_2$  Schiff base ligand derived from 1,2-ethylenediamine or 1,3-propylenediamine, and X is one of a number of substituents determined by the reaction conditions. These monomer complexes are compared with the corresponding  $\mu$ -oxo dimer complexes, the previously reported Re(V) Schiff base complexes<sup>2,7,11,13</sup> and their Tc(V) analogues.<sup>4</sup> The complexes were characterized by elemental analyses,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, IR and UV–vis spectra, and single crystal X-ray diffraction structural analyses.

## Experimental Section

**General Considerations.** Unless noted, all common laboratory chemicals were of reagent grade or better. Solvents were degassed with nitrogen prior to use, and all experiments were carried out under a nitrogen atmosphere.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 250 MHz instrument at 25 °C in deuterated chloroform ( $\text{CDCl}_3$ ) with TMS as an internal reference. Infrared spectra were obtained as KBr pellets on a Nicolet Magna-FT-IR spectrometer 550. UV–vis spectra in methylene chloride (unless otherwise noted) were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Elemental analyses were performed by Quantitative Technologies Inc. (QTI, Whitehouse, NJ).

**Materials.** 2,4-Pentanedione (acac), 1,2-ethylenediamine (en), and 1,3-propylenediamine (pn) were purchased from Aldrich.

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Absolute ethanol, hexane, chloroform, and methylene chloride were used as purchased unless otherwise noted. (n-Bu<sub>4</sub>N)[ReOCl<sub>4</sub>]<sup>24</sup> and ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>25</sup> were prepared by literature methods. The ligands, **L**<sub>1</sub> = *N,N'*-ethylenebis(acetylacetonimine) [H<sub>2</sub>(acac)<sub>2</sub>en] and **L**<sub>2</sub> = *N,N'*-propylenebis(acetylacetonimine) [H<sub>2</sub>(acac)<sub>2</sub>pn], were prepared as previously reported through condensation of 2 equiv of 2,4-pentanedione with 1 equiv of the respective diamine, 1,2-ethylenediamine or 1,3-propylenediamine, in absolute ethanol.<sup>26</sup> Ligands (**L**<sub>1</sub> and **L**<sub>2</sub>) were recrystallized prior to use from either absolute ethanol or dry 2-propanol.

**trans-[ReO(acac<sub>2</sub>en)OH<sub>2</sub>]Cl, 1.** (n-Bu<sub>4</sub>N)[ReOCl<sub>4</sub>] (100 mg, 0.171 mmol) was added to a solution of H<sub>2</sub>acac<sub>2</sub>en (76.6 mg, 0.342 mmol) in 20 mL of absolute ethanol. The resultant green solution was refluxed for approximately 2 h under a nitrogen atmosphere, concentrated to 10 mL, and placed in a freezer overnight. A green product was isolated by filtration and washed with water (5 mL) and then ether (3 × 5 mL). X-ray quality crystals of **1** were obtained by solvent diffusion of hexane into a chloroform solution of **1** to yield dark green brown crystals after several days at ambient temperature. Yield 40–50% (~41 mg). <sup>1</sup>H NMR δ (ppm): 2.35, 2.45 (2 s, 12 H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 3.80–3.87, 4.26–4.32 (2 m, 4H, N–CH<sub>2</sub>); 5.45 (s, 2H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O). <sup>13</sup>C NMR δ (ppm): 23.8, 26.2 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 66.6 (N–CH<sub>2</sub>); 105.8 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 180.6 (C=N); 197.4 (C=O). UV–vis (λ (ε) in nm (cm<sup>-1</sup> M<sup>-1</sup>)): 284 (13 660), 354 (4760), 430 (3824), 614 (161). IR (ν in cm<sup>-1</sup>): 981 (Re=O). Anal. Calcd for ReClC<sub>12</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub> (Found): C, 30.1 (30.23)%; H, 3.76 (3.85)%; N, 5.86 (5.96)%.

**trans-[ReO(acac<sub>2</sub>en)OReO<sub>3</sub>], 2.** (n-Bu<sub>4</sub>N)[ReOCl<sub>4</sub>] (100 mg, 0.171 mmol) was added to a solution of 2 equiv of H<sub>2</sub>acac<sub>2</sub>en (76.6 mg, 0.342 mmol) in 20 mL of absolute ethanol. Great care was taken to exclude water from the reaction by using dry glovebox conditions and thoroughly drying the ethanol. The solution was refluxed for approximately 2 h under N<sub>2</sub>, then concentrated to approximately 2 mL, and placed in a freezer. Dark green-brown crystals formed after several days. Yield 85% (97.9 mg) based on the rhenium starting material. X-ray quality crystals of **2** were obtained by slow hexane diffusion into a solution of the green-brown solid in a minimum volume of chloroform. <sup>1</sup>H NMR δ (ppm): 2.35, 2.46 (2 s, 12 H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 3.77–3.917, 4.19–4.34 (2 m, 4H, N–CH<sub>2</sub>); 5.265 (s, 2H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O). <sup>13</sup>C NMR δ (ppm): 23.9, 26.3 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 66.7 (N–CH<sub>2</sub>); 105.9 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 180.7 (C=N), 197.5 (C=O). UV–vis (λ (ε) in nm (cm<sup>-1</sup> M<sup>-1</sup>)): 242 (14 840), 292 (10 660), 354 (5746), 432 (5417), 606 (211). IR (ν in cm<sup>-1</sup>): 908 (Re=O), 694 (Re–O–Re).

**trans-[ReO(acac<sub>2</sub>pn)Cl], 3.** **L**<sub>2</sub> (40 mg, 0.171 mmol) was dissolved in 25 mL of anhydrous ethanol and dried over 4 Å molecular sieves. (n-Bu<sub>4</sub>N)[ReOCl<sub>4</sub>] (50 mg, 0.085 mmol) was then added, and the resultant solution was refluxed for about 2 h under nitrogen. The reaction mixture was concentrated to ~5 mL and filtered to remove solid particulates of decomposed ligand. The solution was placed in a freezer overnight to yield a dark green solid, **3**. The product was washed with absolute ethanol (3 × 5 mL) followed by ether (3 × 5 mL). The solid was dried in vacuo overnight. Yield 50% (24 mg). X-ray quality crystals of **3** were obtained by solvent diffusion of hexane into a concentrated

chloroform solution of **3**. <sup>1</sup>H NMR δ (ppm): 2.04–2.12 (m, 2H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>); 2.35, 2.38 (2 s, 12H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 3.84–3.95, 4.32–4.41 (m, 4H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>); 5.35 (s, 2H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O). <sup>13</sup>C NMR δ (ppm): 24.7, 26.0 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 33.9 (N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–N); 175.6 (C=N); 189.8 (C=C–O). UV–vis (λ (ε) in nm (cm<sup>-1</sup> M<sup>-1</sup>)): 272 (11 310), 330 (5622), 686 (131). IR (ν in cm<sup>-1</sup>): 951 (Re=O). Anal. Calcd for ReClO<sub>3</sub>N<sub>2</sub>C<sub>13</sub>H<sub>20</sub> (Found): C, 32.95 (32.55)%; H, 4.25 (4.06)%; N, 5.91 (5.91)%.

**trans-[ReO(acac<sub>2</sub>pn)OMe]·MeOH·H<sub>2</sub>O, 4.** A sample of **3** (100 mg, 0.171 mmol) dissolved in a minimal volume of methylene chloride was loaded onto a basic alumina column (1 cm × 10 cm) equilibrated with methylene chloride. A methanol/methylene chloride (1:5) solvent mixture eluted two bands. The first dark green band was the μ-oxo dimer **6**, and the second blue-green band contained **4**. X-ray quality crystals of **4** were obtained by solvent evaporation. Yield 23% (24 mg) based on the initial amount of **3**. <sup>1</sup>H NMR δ (ppm): 1.92–1.97 (m, 2H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>); 2.20, 2.26 (2 s, 12H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 3.35–3.42, 3.87–3.92 (m, 4H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>); 3.40 (s, 3H, OCH<sub>3</sub>); 5.06 (s, 2H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O). <sup>13</sup>C NMR δ (ppm): 24.0, 25.3 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 33.4 (N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–N); 61.1 (N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–N); 101.9 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 173.5 (C=N); 187.5 (C=C–O). UV–vis (λ (ε) in nm (cm<sup>-1</sup> M<sup>-1</sup>)): 278 (4590), 292 (4520), 368 (1470). IR (ν in cm<sup>-1</sup>): 945 (Re=O). Anal. Calcd for ReO<sub>4</sub>N<sub>2</sub>C<sub>14</sub>H<sub>23</sub>·CH<sub>3</sub>OH (Found): C, 35.92 (41.22)%; H, 5.43 (6.63)%; N, 5.58 (6.16)%.

**trans-[μ-oxo-Re<sub>2</sub>O<sub>3</sub>(acac<sub>2</sub>en)<sub>2</sub>], 5.** The procedure for the preparation of **5** was modified from that previously reported.<sup>2</sup> To a solution of ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (1 g, 1.20 mmol) in 100 mL of toluene were simultaneously added solid **L**<sub>1</sub> (0.201 g, 1.32 mmol) and triethylamine (1 mL). The solution was refluxed for approximately 2 h and then cooled to room temperature. A dark green solid was collected by filtration, washed with toluene (3 × 5 mL) followed by ethyl ether (3 × 5 mL), and dried under vacuum. Further purification of the dark green product was accomplished using a basic alumina column. The solid was dissolved in a minimal volume of methylene chloride and loaded onto an alumina column pre-equilibrated in methylene chloride. The column was washed with methylene chloride to elute a yellow band (triphenylphosphine). When no additional bands eluted, the mobile phase was changed to a 1:10 methanol/methylene chloride solution to elute product **5** as a dark green band. This green band was collected and dried under vacuum to yield a green oil. X-ray quality crystals of **5** were obtained by slow evaporation from CH<sub>2</sub>Cl<sub>2</sub>/toluene (1:1) after dissolving the green oil in the minimum volume of methylene chloride. Yield 41% (~420 mg). <sup>1</sup>H NMR δ (ppm): 2.17, 2.21 (2 s, 12H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 3.62–3.67, 3.82–3.87 (2 m, 4H, N–CH<sub>2</sub>); 4.94 (s, 2H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O). <sup>13</sup>C NMR δ (ppm): 22.6, 27.0 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 64.5 (N–CH<sub>2</sub>); 102.5 ((CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 175.8 (C=N); 191.0 (C=C–O). UV–vis (λ (ε) in nm (cm<sup>-1</sup> M<sup>-1</sup>)): 299 (7575), 396 (1893). IR (ν in cm<sup>-1</sup>): 975 (Re=O), 720 (Re–O–Re). Anal. Calcd for Re<sub>2</sub>O<sub>7</sub>N<sub>4</sub>C<sub>24</sub>H<sub>36</sub> (Found): C, 33.33 (33.18)%; H, 4.19 (4.16)%; N, 6.48 (6.21)%.

**trans-[μ-oxo Re<sub>2</sub>O<sub>3</sub>(acac<sub>2</sub>pn)<sub>2</sub>], 6.** The preparation and the purification of **6** is analogous to the method described for **5** with the substitution of **L**<sub>2</sub> (acac<sub>2</sub>pn) for **L**<sub>1</sub> (acac<sub>2</sub>en). Dark green crystals were obtained. Yield 40–50%. <sup>1</sup>H NMR δ (ppm): 1.84–2.05 (m, 2H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>); 2.12, 2.13 (2 s, 12H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O); 3.66–3.76, 4.10–4.20 (m, 4H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>); 4.90 (s, 2H, (CH<sub>3</sub>)C–CH–C(CH<sub>3</sub>)O). <sup>13</sup>C NMR δ (ppm): 24.19,

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**Table 1.** X-ray Crystal Data, Data Collection Parameters, and Refinement Parameters of **1–6**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
formula	C <sub>12</sub> H <sub>20</sub> ClN <sub>2</sub> O <sub>4</sub> Re	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> Re <sup>+</sup> ReO <sub>4</sub> <sup>-</sup>	C <sub>13</sub> H <sub>20</sub> ClN <sub>2</sub> O <sub>3</sub> Re	C <sub>14</sub> H <sub>23</sub> N <sub>2</sub> O <sub>4</sub> Re	C <sub>24</sub> H <sub>36</sub> N <sub>4</sub> O <sub>7</sub> Re <sub>2</sub>	C <sub>26</sub> H <sub>40</sub> N <sub>4</sub> O <sub>7</sub> Re <sub>2</sub>
fw	477.95	674.69	473.96	469.54	864.98	893.02
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 1̄	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	7.2888(6)	7.5547(4)	8.1628(5)	6.7104(8)	9.0064(5)	9.1190(5)
<i>b</i> (Å)	9.8299(8)	8.7409(5)	13.0699(8)	27.844(3)	12.2612(7)	12.2452(7)
<i>c</i> (Å)	10.8195(9)	25.7794(13)	28.3902(17)	8.2292(9)	12.3695(7)	12.8863(8)
α (deg)	81.7670(10)					
β (deg)	77.1510(10)	92.7780(10)	97.5630(10)	92.197(2)	90.2853(10)	92.0510(10)
γ (deg)	87.6200(10)					
<i>V</i> (Å <sup>3</sup> )	747.96(11)	1700.34(16)	3002.5(3)	1536.4(3)	1365.94(13)	1438.01(14)
<i>Z</i>	2	4	8	4	2	2
ρ <sub>calcd</sub> (g/cm <sup>3</sup> )	2.122	2.636	2.097	2.030	2.103	2.062
<i>T</i> , K	173(2)	173	173(2)	173(2)	173	173(2)
μ, mm <sup>-1</sup>	8.315	14.46	8.280	7.926	9.02	8.460
λ source (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.0381	0.039	0.0432	0.0338	0.022	0.0349
<i>R</i> <sub>w</sub> ( <i>F</i> ) <sup>a</sup>	0.1075	0.058	0.0858	0.1108	0.030	0.0879
GOF	1.079	1.03	1.056	0.964	0.96	1.036

$$^a R = (\sum |F_o| - |F_c|) / \sum |F_o|. R_w = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)]^{1/2}.$$

25.66 ((CH<sub>3</sub>)C-CH-C(CH<sub>3</sub>)O); 32.56 (N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N); 60.88 (N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N); 101.53 ((CH<sub>3</sub>)C-CH-C(CH<sub>3</sub>)O); 171.46 (C=N); 185.77 (C=C-O). UV-vis (λ (ε) in nm (cm<sup>-1</sup> M<sup>-1</sup>)): 291 (22 400), 362 (7110), 642 (426). IR (ν in cm<sup>-1</sup>): 950 (Re=O, w), 713.0 (Re-O-Re). Anal. Calcd for Re<sub>2</sub>O<sub>7</sub>N<sub>4</sub>C<sub>26</sub>H<sub>40</sub> (Found): C, 34.70 (34.81%); H, 4.51 (4.51%); N, 6.27 (6.16%).

**Monomer to μ-oxo Dimer Conversion.** A stock solution of *trans*-[ReOCl(acac<sub>2</sub>pn)], **3** (7.1 mg, 0.0150 mmol), in 100 mL of absolute (dry) ethanol dried over molecular sieves was used in these experiments. At this concentration, the absorbance of the major charge transfer bands of **3** (278 and 352 nm) and **6** (291 and 362 nm) were observed between 0.5 and 1.2 absorbance units. Studies were conducted at 10 and 25 °C, and scans were taken every second for 30 s (unless otherwise indicated). A typical study followed the general procedure described in the following paragraph.

The *trans*-[ReOCl(acac<sub>2</sub>pn)] stock solution (3.0 mL) was transferred into a quartz UV cell and stirred, and 100 μL of aqueous solutions of NaOH (0.045 M), HCl (0.045 M), or water/ethanol (1:1) was then added and the reaction allowed to proceed. The studies were repeated several times. The reaction time of *trans*-[ReOCl(acac<sub>2</sub>pn)] with water at room temperature (25 °C) was extended to two weeks, scanning the sample once a day.

**X-ray Structure Determinations and Refinements for 1–6.** Intensity data were obtained at -100 °C on a Bruker SMART CCD area detector system using the ω scan technique with Mo Kα radiation from a graphite monochromator. Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and absorption corrections were made using the multiscan method. Space group, lattice parameters, and other relevant information are given in Table 1. Structures were solved by direct methods with full-matrix least-squares refinement, using the SHELX package.<sup>27,28</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms, except those of the waters of crystallization, were placed at calculated positions and included in the refinements using a riding model, with fixed isotropic *U*. Final difference maps contained no features of chemical significance.

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## Results and Discussion

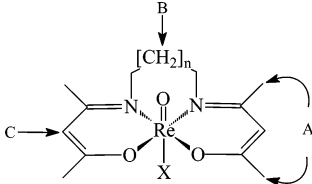
Several monomeric complexes of the formula [ReOX(L)] have been synthesized by reacting 1 equiv of tetrabutylammonium tetrachlorooxorhenate(V) (n-Bu<sub>4</sub>N [ReOCl<sub>4</sub>]) with 2 equiv of the Schiff base ligand **L**<sub>1</sub> (acac<sub>2</sub>en) or **L**<sub>2</sub> (acac<sub>2</sub>pn), with the second equivalent of ligand acting as a proton scavenger. The tetradentate ligands coordinate in the equatorial plane *cis* to the rhenium oxo group. A variety of substituents were found to occupy the position *trans* to the oxo group, the identity of which was dependent on the reaction conditions. The presence of trace amounts of water in the reaction yielded the *trans* aquo species **1** with **L**<sub>1</sub> ((acac)<sub>2</sub>en). However, when the reaction was scrupulously dried to remove all water, the product with a perrhenate anion coordinated *trans* to the oxo group, **2**, was obtained in high yield (85% based on Re). A search of the literature indicates that perrhenate coordination to rhenium is fairly common.<sup>29–47</sup> In fact, ReO<sub>4</sub><sup>-</sup> coordination to Re has been observed for a

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**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) of **1–6**

	<b>1</b>	<b>2</b>	<b>3a</b>	<b>3b</b>	<b>4</b>	<b>5</b>	<b>6</b>
Re1–O1	2.027(5)	2.036(6)	2.015(5)	2.000(5)	2.029(4)	2.087(3)	2.045(4)
Re1–O2	2.022(5)	2.019(6)	1.991(5)	2.016(5)	2.042(5)	2.090(3)	2.038(4)
Re1–O3	1.682(5)	1.682(7)	1.681(5)	1.696(5)	1.705(5)	1.711(3)	1.703(5)
Re1–O4	2.247(5)	2.271(7)			1.911(5)	1.9102(2)	1.9143(2)
Re1–N1	2.009(6)	1.996(7)	2.114(6)	2.099(6)	2.122(5)	2.031(4)	2.113(6)
Re1–N2	2.005(5)	2.018(7)	2.098(6)	2.121(6)	2.131(5)	2.036(4)	2.122(6)
Re1–Cl1			2.468(2)	2.464(2)			
Re2–O4		1.747(6)				1.9102(2)	1.9143(2)
Re2–O5		1.700(8)					
Re2–O6		1.687(9)					
Re2–O7		1.715(9)					
N1–Re1–N2	82.2(2)	83.0(3)	96.4(2)	96.2(2)	94.8(2)	83.07(14)	96.1(2)
N1–Re1–O1	92.6(2)	91.0(3)	90.8(2)	90.3(2)	90.65(19)	93.39(13)	91.2(2)
N1–Re1–O2	159.2(2)	158.0(3)	163.8(2)	162.0(2)	168.43(19)	172.63(13)	170.1(2)
N1–Re1–O3	102.0(2)	103.2(3)	91.5(2)	94.7(2)	84.15(19)	94.7(2)	91.7(3)
N1–Re1–O4(Cl)	80.2(2)	80.9(3)	80.6(2)	80.45(18)	90.7(2)	87.17(10)	85.20(15)
N2–Re1–O1	158.9(2)	158.4(3)	161.7(2)	164.3(2)	168.92(19)	172.51(14)	171.0(2)
N2–Re1–O2	93.4(2)	92.5(3)	90.7(2)	90.8(2)	91.57(19)	92.14(13)	91.3(2)
N2–Re1–O3	101.3(2)	101.7(3)	94.8(2)	91.5(2)	83.7(2)	96.9(2)	90.0(3)
N2–Re1–O4(Cl)	80.9(2)	80.0(3)	80.0(2)	80.9(2)	90.7(2)	89.11(12)	85.0(2)
O1–Re1–O2	84.19(19)	85.4(3)	78.4(2)	79.1(2)	81.52(17)	90.70(12)	80.88(16)
O1–Re1–O3	99.7(2)	99.8(3)	101.8(2)	102.2(2)	87.31(18)	89.92(14)	95.1(2)
O1–Re1–O4(Cl)	78.09(19)	78.6(3)	84.65(18)	86.1(2)	98.9(2)	84.11(9)	90.36(12)
O2–Re1–O3	98.8(2)	98.8(3)	102.4(2)	101.7(2)	86.97(19)	91.5(2)	94.8(2)
O2–Re1–O4(Cl)	78.99(19)	77.1(3)	86.4(2)	84.35(17)	98.9(2)	87.15(9)	88.91(14)
O3–Re1–O4(Cl)	177.0(2)	175.7(3)	169.9(2)	170.4(2)	172.0(2)	173.85(10)	173.82(18)
Re1–O4–Re2		146.5(4)				180.0	180.0

variety of Re oxidation states, the most common being for Re(VII) in solvates of the classic Re<sub>2</sub>O<sub>7</sub> motif where a tetrahedral Re is linked to an octahedral Re center. This differs from the Tc analogue where Tc<sub>2</sub>O<sub>7</sub> is formed from two end-on  $\mu$ -oxo bridged tetrahedra.<sup>48</sup> The literature shows perrhenates bound, predominantly as monodentate ligands, to Re(I),<sup>32,44,47</sup> Re(II),<sup>29</sup> Re(III),<sup>34</sup> Re(V),<sup>30,31,39–41,43</sup> Re(VI),<sup>37</sup> and Re(VII).<sup>35,36,38,42,45,46</sup> An interesting tendency, which may be salient to the formation of **2**, is the spontaneous generation of perrhenate (in the presence of O<sub>2</sub> and H<sub>2</sub>O) from systems involving lower oxidation state Re precursors.<sup>29,34,37,43,47</sup> The spectroscopic analyses of compound **2** (*trans*-[ReO(OReO<sub>3</sub>)-(acac<sub>2</sub>en)]), and especially its single crystal X-ray diffraction analysis, allowed us to identify/confirm its structure. The <sup>1</sup>H NMR spectrum of this complex shows the vinylic proton chemical shift at 5.26 ppm, which distinguishes it from the other reported complexes (Table 3). The Re=O stretch in the FT-IR spectrum of compound **2** was observed at 908 cm<sup>-1</sup>, at significantly lower energy than those of the other monomer or dimer complexes (945–981 cm<sup>-1</sup>). A band assigned as the  $\mu$ -oxo Re–O–Re stretch was observed at 694 cm<sup>-1</sup>, similar to the  $\mu$ -oxo Re–O–Re stretches observed for **5** and **6** at 720 and 713 cm<sup>-1</sup>, respectively. The UV–vis spectrum of compound **2** was similar to that observed for the other monomer complexes; however, an additional higher

**Table 3.** Comparisons of <sup>1</sup>H NMR Chemical Shifts for Compounds **1–6**, **L**<sub>1</sub>, and **L**<sub>2</sub>. Where the Type of *trans* Donor Directly Affects the Shielding of All Parts of the Ligand


	A	B	C
<b>1</b>	2.35, 2.45	3.80–3.87, 4.26–4.32	5.45
<b>2</b>	2.35, 2.46	3.77–3.91, 4.19–4.34	5.265
<b>5</b>	2.17, 2.21	3.62–3.67, 3.82–3.87	4.94
<b>L</b> <sub>1</sub>	1.90, 2.00	3.41–3.43	4.99
<b>3</b>	2.35, 2.38	2.04–2.12, 3.84–3.95, 4.32–4.41	5.35
<b>4</b>	2.20, 2.26	1.92–1.97, 3.35–3.42, 3.87–3.92	5.06
<b>6</b>	2.12, 2.13	1.84–2.05, 3.66–3.76, 4.10–4.20	4.90
<b>L</b> <sub>2</sub>	1.92, 1.99	1.84–1.89, 3.31–3.38,	4.98

energy band was observed at 242 nm that was not observed for the other monomer complexes. Despite the preponderance of this evidence, **2** did not yield an accurate elemental analysis.

The carbon backbone length between the imine nitrogens of **L**<sub>1</sub> and **L**<sub>2</sub> (en vs pn) also affects the identity of the ligand occupying the coordination site *trans* to the rhenium oxo group. Reaction conditions identical to those for the synthesis of **1** yielded, with **L**<sub>2</sub>, the *trans* chloride species **3**, [ReOCl(acac<sub>2</sub>pn)], as the only product rather than the *trans* aquo species. Attempts to synthesize and isolate the *trans* aquo species, *trans*-[ReO(OH<sub>2</sub>)(acac<sub>2</sub>pn)]Cl, were unsuccessful. However, this does not preclude its existence since the site *trans* to the Re oxo group is relatively labile. Attempts to prepare the pn analogue of **2** with a perrhenate anion in the

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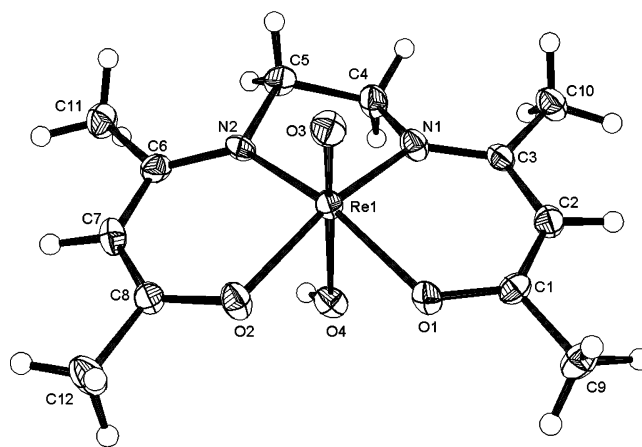
**Table 4.** UV–Vis Absorption Bands for Compounds 1–6 ( $\lambda$ , nm, ( $\epsilon$ ,  $M^{-1} \text{ cm}^{-1}$ ))

<b>1</b>	284 (13 660)	354 (4760)	430 (3824)	614 (161)
<b>2</b>	242 (14 840)	292 (10 660)	354 (5746)	432 (5417)
<b>3</b>	272 (11 310)		330 (5622)	686 (131)
<b>4</b>	278 (4590)	292 (4520)	368 (1470)	
<b>5</b>		299 (7575)	396 (1893)	
<b>6</b>		291 (22 400)	362 (7110)	642 (426)

*trans* position by carefully excluding water from the reaction were unsuccessful and produced only the *trans* chloride complex **3**. The *trans* methoxide complex **4**, *trans*-[ReO(OMe)(acac<sub>2</sub>pn)], resulted from solvolysis of **3** on a basic alumina column eluted with methanol. A byproduct of this reaction, the  $\mu$ -oxo dimer **6**, separated from the *trans* methoxide during elution. The  $\mu$ -oxo dimerization reaction (monomer to dimer) on activated basic alumina has been reported previously for *trans*-[ReOCl(sal<sub>2</sub>en)] and *trans*-[ReOCl(sal<sub>2</sub>phen)] to their respective dimers.<sup>12</sup> This synthesis of the *trans*-[ReO(OMe)(acac<sub>2</sub>pn)] complex was expanded to include other *trans* alkoxides, which were only identified by their NMR spectra. It should be noted that the *trans* alkoxide forms by solvolysis of the chloride in the presence of basic alumina, not from carrying out the synthesis in the particular alcohol. This complex (the *trans* methoxide) is not particularly stable in solution over time, especially when exposed to a humid environment, although it can be isolated in solid form from an alumina column separation. The resolution from the dimer, which elutes before the methoxide monomer, is very difficult (i.e., some tailing of the dimer into the methoxide monomer species on elution). Thus, isolation of pure complex is very difficult as evidenced by the deviation of the elemental analysis reported for this compound.

When both water (even in trace amounts) and base (such as triethylamine) are present, the  $\mu$ -oxo dimer complex is isolated from the reaction mixture as reported by Wilkinson,<sup>2</sup> regardless of starting compound (ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> or ReOCl<sub>4</sub><sup>-</sup>). The synthesis of the  $\mu$ -oxo dimers, **5** and **6**, from ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> followed the procedure reported.<sup>2</sup> However, purification was improved by separation using alumina column chromatography, which allowed the facile removal of the triphenylphosphine and other impurities. The syntheses and characterization of **5** and **6** confirm the chemical evidence presented previously and allow direct structural comparison with the related monomeric compounds.

The particular group (i.e., Cl<sup>-</sup>, H<sub>2</sub>O, ReO<sub>4</sub><sup>-</sup> or <sup>-</sup>OMe) *trans* to the rhenium oxo group influences the physical properties of these complexes. NMR proved a useful tool in the identification and characterization of complexes **1–6**. Distinctive patterns in proton chemical shifts, consistent with symmetrical coordination of the tetradentate ligand in the equatorial plane, were observed for these complexes (Table 3). Three distinct sets of <sup>1</sup>H signals (the alkyl backbone between the imine nitrogens, the methyl groups, and the vinylic proton) were used to identify the complexes. The chemical shifts of **L**<sub>1</sub> and **L**<sub>2</sub> were generally observed downfield in the complexes relative to the free ligand. The <sup>1</sup>H NMR spectra of the Re complexes appear qualitatively similar to those of the free ligand, but with more complex splitting patterns

**Figure 2.** ORTEP representation of *trans*-[ReO(acac<sub>2</sub>en)OH<sub>2</sub>]Cl, **1**, with 30% thermal ellipsoids.

in the alkyl backbone region. The <sup>13</sup>C NMR spectra of the Re complexes are consistent with the presence of the coordinated tetradentate Schiff base ligands, being qualitatively similar to the free ligands but with downfield chemical shifts.

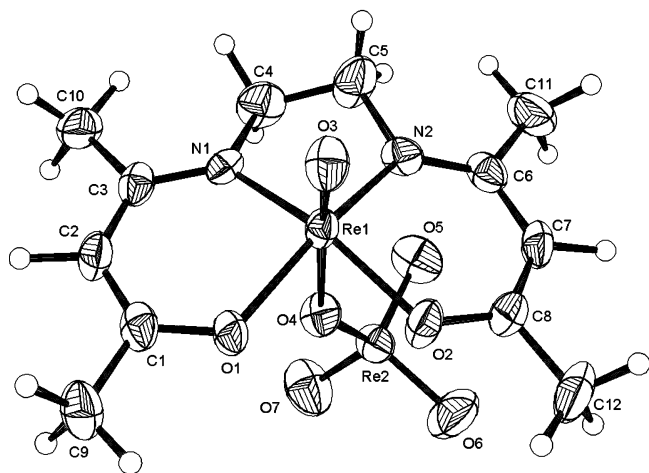
The UV–vis spectra of complexes **1–6** exhibited similar charge transfer bands (Table 4), showing intense absorbance between 270 and 430 nm ( $\epsilon$  5000–10 000  $\text{cm}^{-1} \text{ M}^{-1}$ ) and weak maxima at 600–700 nm ( $\epsilon$  < 500  $\text{cm}^{-1} \text{ M}^{-1}$ ). Differences were observed in the absorbance spectra of the monomer and dimer compounds, allowing monitoring of the conversion of monomer to dimer spectrophotometrically (vide infra). The IR spectra of compounds **1–6** exhibited the characteristic rhenium oxo (Re=O) stretches at between 900 and 1000  $\text{cm}^{-1}$ , while **2**, **5**, and **6** also showed a Re–O–Re stretch at about 700  $\text{cm}^{-1}$ , consistent with results reported for other Re(V) oxo monomer and dimer complexes.<sup>2,3,7,9–12,49,50</sup>

**X-ray Structure Analyses.** The X-ray structures of **1–6** are similar in nature, as expected with tetradentate Schiff base ligands occupying the equatorial plane of the distorted octahedral complexes. In compounds **1–6**, the rhenium lies 0.0806–0.380 Å (based on the least squares planes) above the equatorial plane of the Schiff base ligand toward the oxo group, forming distorted octahedra typical for Tc(V) and Re(V) mono-oxo complexes.<sup>1–13,49</sup> The Re atom is further above the plane of the ligand in the acac<sub>2</sub>en monomer analogues (**1** and **2**) than in the acac<sub>2</sub>pn monomer analogues (**3** and **4**), with the Re being closest to the ligand plane in the two dimers (**5** and **6**).

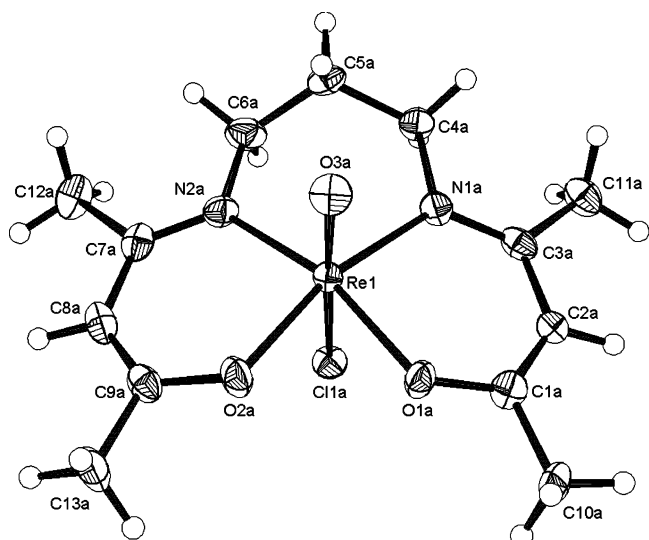
The ORTEP representations of compounds **1–6** are shown in Figures 2–7, respectively. The Re=O bond distances in these complexes range from 1.68 to 1.711 Å (Table 2), typical for mono-oxo Re(V) complexes.<sup>1,3,9–11,13</sup> The Re=O bond distances observed for the complexes with a methoxide (**4**) or  $\mu$ -oxo species (**5**, **6**) coordinated *trans* to the oxo group (Table 2) are slightly longer, but still within the range typical for these types of complexes.<sup>3,9,10,13</sup> The typical bond length

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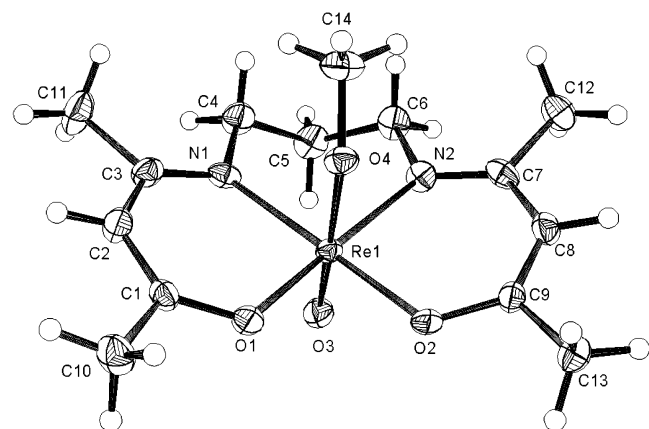
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**Figure 3.** ORTEP representation of *trans*- $\mu$ -oxo-[ReO(acac<sub>2</sub>en)OReO<sub>3</sub>], **2**, with 30% thermal ellipsoids.

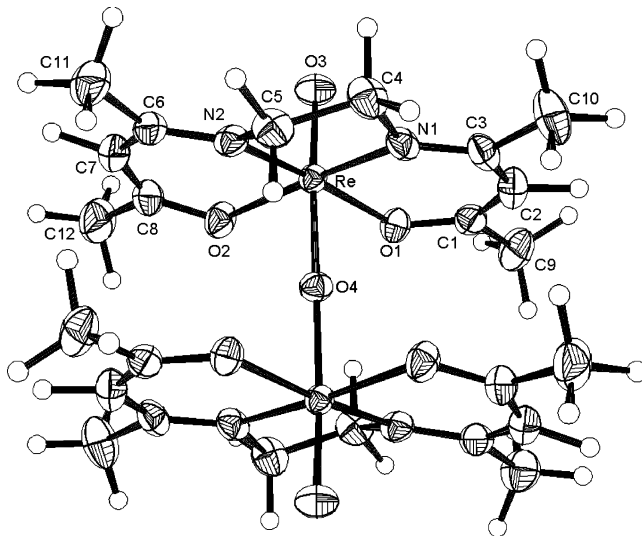


**Figure 4.** ORTEP representation of *trans*-[ReO(acac<sub>2</sub>pn)Cl], **3**, with 30% thermal ellipsoids.

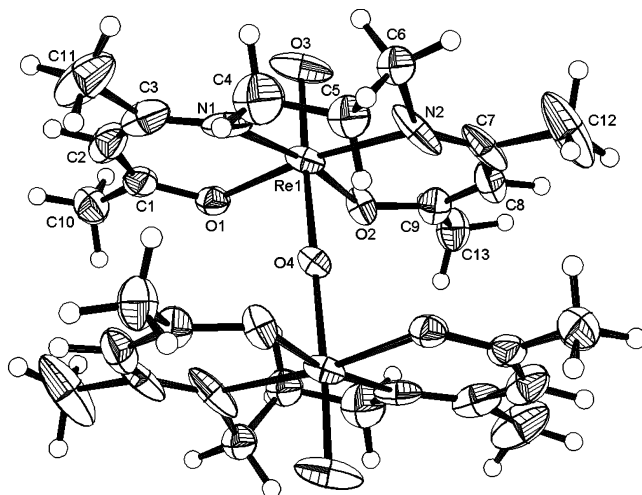


**Figure 5.** ORTEP representation of *trans*-[ReO(acac<sub>2</sub>pn)OMe], **4**, with 30% thermal ellipsoids.

for a Re(V) oxo double/triple bond is approximately 1.68–1.70 Å, whereas the *trans* rhenium dioxo bond lengths average 1.75 Å.<sup>50,51</sup> The Re–N and Re–O bond distances in the equatorial positions of the complexes are as expected (1.9–2.1 Å).<sup>1,3,9–11,13,51</sup> The group *trans* to the Re=O bond is long



**Figure 6.** ORTEP representation of *trans*-[ $\mu$ -oxo-Re<sub>2</sub>O<sub>3</sub>(acac<sub>2</sub>en)<sub>2</sub>], **5**, with 40% probability thermal ellipsoids.



**Figure 7.** ORTEP representation of *trans*-[ $\mu$ -oxo-Re<sub>2</sub>O<sub>3</sub>(acac<sub>2</sub>pn)<sub>2</sub>], **6**, with 40% probability thermal ellipsoids.

for compounds **1**, **2**, and **3**, as expected from *trans* labilization of this position and consistent with other octahedral mono-oxo Re(V) reported structures.<sup>52</sup> In general, the *trans* influence of the oxo group results in Re–X bond distances longer than a similar species in an equatorial position.<sup>1–13,49</sup>

***trans*-[ReO(OH<sub>2</sub>)(acac<sub>2</sub>en)]**, **1**. The structure of **1** is crystallographically analogous to the Tc(V) analogue, with virtually identical bond angles and distances reported in the X-ray structures.<sup>4</sup> A water coordinated *trans* to the rhenium oxo was previously thought not to exist for the tetradentate Schiff base complexes, although *trans* aquo Re(V) oxo complexes with other equatorial ligands are known.<sup>23,52,53</sup>

***trans*-[ReO(OReO<sub>3</sub>)(acac<sub>2</sub>en)]**, **2**. The structure of **2** shows a perhenate anion coordinated *trans* to the oxo group.

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Perrhenate is not typically considered as a coordinating ligand for transition metals, although this appears to occur for Re complexes more frequently than one would expect with several structures containing the Re—O—ReO<sub>3</sub> moiety reported.<sup>29–47,54,55</sup> The  $\mu$ -oxo bond (Re—O—ReO<sub>3</sub>) is bent (146.5°), and the bridging oxygen is not equidistant between the two rhenium atoms (Re(V) 2.27 Å, Re(VII) 1.75 Å). The angles and distances reported here are similar to those of the two Re(V)—oxo,  $\mu$ -oxo perrhenate structures reported in the literature, one with a porphyrin macrocycle occupying the equatorial sites<sup>30</sup> and the second with two bidentate phosphinothiols in the equatorial positions.<sup>31</sup> The structure of this mixed octahedral and tetrahedral  $\mu$ -oxo rhenium complex is also similar about the Re—O—Re bonds to the +7 oxidation state Re<sub>2</sub>O<sub>7</sub> complex.<sup>5,48,56</sup> The Re<sub>2</sub>O<sub>7</sub> structure is a composite of a regular ReO<sub>4</sub> tetrahedron and a strongly distorted ReO<sub>6</sub> octahedron linked through a  $\mu$ -oxo bridge. The bond angle between the two rhenium atoms through the bridging oxygen ranges from 146° to 152° for Re<sub>2</sub>O<sub>7</sub> (and its solvates), with inequivalent bond distances between the octahedral rhenium and the bridging oxygen (2.05–2.10 Å) and the tetrahedral rhenium bridging oxygen (1.75–1.80 Å).<sup>35,36,38,45,46,48,56,57</sup> Although this type of  $\mu$ -oxo bridged species found in **2** is similar to that observed in the Re<sub>2</sub>O<sub>7</sub> structure, it is not analogous to the technetium analogue Tc<sub>2</sub>O<sub>7</sub>, in which a complex containing two equivalent tetrahedra bridged by a linear  $\mu$ -oxo bond is observed.<sup>48</sup>

**trans-[ReOCl(acac<sub>2</sub>pn)], 3.** Two distinct crystallographic complexes (A and B) of **3** were found within the unit cell. Although molecules A and B have different orientations in the lattice, the bond angles and distances for both molecules are comparable. The linear O=Re—Cl axis of **3** shows some disorder that arises from the partial occupancy of these atoms in two orientations relative to the refined equatorial ligand. The predominant species for both A and B has the rhenium oxo group above the plane of the ligand, with the acac segments of the ligand oriented toward the chloride. This orientation was observed with 92% occupancy for A and 94% occupancy for B. The less favored orientation (8% and 6%) had the inverted arrangement with the oxo and the chloride groups transposed, along with a corresponding shift of the rhenium atom below the plane of the ligand and with the acac segments oriented toward the oxo group. Compound **3** is similar to the structure of the *trans*-[TcOCl(sal<sub>2</sub>pn)] reported by Bandoli,<sup>5</sup> but it differs from the sal<sub>2</sub>pn Re(V) oxo complexes that exhibit the *cis* configuration.<sup>2,11,13</sup> Unlike the sal derived Schiff base complexes of Re(V),<sup>11,13</sup> no evidence of the *cis* isomers was observed, even with prolonged heating.

**trans-[ReO(OMe)(acac<sub>2</sub>pn)], 4.** Although isolated in an unexpected fashion, **4** is analogous to the sal analogues with a *trans* alkoxide ligand (O=Re—OR).<sup>13</sup> The Re—O distance for the methoxide species *trans* to the oxo in **4** is typical of an equatorial Re—O single bond distance (1.911(5) versus

1.9–2.1 Å) and is similar to those reported by Reinhoudt for the *trans*-ReO(alkoxide)(sal<sub>2</sub>pn/bn) complexes.<sup>13</sup>

**trans-[ $\mu$ -oxo-Re<sub>2</sub>O<sub>2</sub>(acac<sub>2</sub>en)<sub>2</sub>], 5, and *trans*-[ $\mu$ -oxo-Re<sub>2</sub>O<sub>2</sub>(acac<sub>2</sub>pn)<sub>2</sub>], 6.** The Re— $\mu$ -oxo bond distances in **5** and **6** are typical for  $\mu$ -oxo dimers.<sup>3,9,13</sup> The two Schiff base ligands in **5** and **6** are parallel to each other, normal to the O=Re—O—Re=O axis and transposed 180° to each other such that the N atoms of one Schiff base ligand are above the O atoms of the other. This arrangement is typical of Re(V) and Tc(V) Schiff base dimer compounds.<sup>5,7,9,13</sup>

**Conversion of the Monomer to the Dimer Analogue.** The reaction conditions determine whether the monomer or dimer complexes are formed with the tetradentate Schiff base ligands. Our interest in maximizing monomer formation led us to investigate the conditions that result in formation of the dimer from a qualitative standpoint. The reactivity of the position *trans* to the oxo group of the monomer complexes is significantly greater than that of the  $\mu$ -oxo group in the dimer complexes. In fact, the dimer complexes were impossible, in our hands, to split into their monomers without decomposition. The UV—vis spectra for the monomers were sufficiently different from those of the dimers allowing spectrophotometric monitoring of the conversion (Table 4). The *trans* chloride monomer complex **3** was selected to study the formation of the dimer **6**, although the other monomer complexes exhibited similar behavior. A series of experiments were carried out to determine the effect(s) of acid, water, and/or base on an ethanol solution of **3**. The addition of 5 equiv of hydrochloric acid to a solution of **3** resulted in no spectral change. The addition of a small amount of water to an ethanol solution of **3** resulted in a spectral change consistent with the development of the *trans* aquo species. In the presence of excess water, the  $\mu$ -oxo dimer formed slowly over several days. Upon concentration of this solution, only the dimer (**6**) was isolated (<sup>1</sup>H NMR).

The addition of 5 equiv of base (NaOH) to an ethanol solution of **3** resulted in an instantaneous conversion to the dimer **6** as determined spectrophotometrically and by <sup>1</sup>H NMR of the concentrated solution from this reaction.

On the basis of these reactivity observations, it is suggested that the first step in the conversion of the monomer to the dimer is coordination of either a water molecule or a hydroxide ion *trans* to the oxo group. The *trans* aquo species appears to be stable until additional water molecules act as proton acceptors to generate the *trans* hydroxo species, which then reacts with another monomer to generate the  $\mu$ -oxo dimer. This pathway appears to be quite slow and dependent on the water concentration. The *trans* hydroxo species rapidly reacts to form the  $\mu$ -oxo dimer, which is very stable to additional base (i.e., no decomposition was noted by NMR or UV—vis spectroscopy). Attempts to regenerate the monomer from the  $\mu$ -oxo dimer through protonation of the bridging oxo by treatment with acid (HCl(g) or HCl(aq)) in ethanol were unsuccessful.

**Re(V) Oxo Schiff Base Complexes.** Complexes **1–4** showed equatorial coordination of L<sub>1</sub> and L<sub>2</sub> with a monodentate ligand occupying the position *trans* to the rhenium oxo group, as previously predicted by Wilkinson and

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analogous to the Tc(V) complexes.<sup>2,4</sup> The Tc(V) and Re(V) oxo compounds both exhibit distorted octahedral coordination geometry with the metal sitting above the equatorial plane of the Schiff base ligand. The acac complexes seem to favor a hard monodentate donor group (i.e., Cl<sup>-</sup>, <sup>-</sup>OR, OH<sub>2</sub>) *trans* to the oxo group rather than a rearrangement of the Schiff base ligand to yield the *cis* configuration with a *trans* coordinated Schiff base oxygen, as has been reported for many of the sal analogues.<sup>11</sup>

Compounds **1–6** represent several novel rhenium complexes. The syntheses of several similar Re(V) oxo N<sub>2</sub>O<sub>2</sub> Schiff base monomer complexes with sal and acac based ligands of the type *trans*-[ReO(ligand)Cl] (ligand = sal<sub>2</sub>en, acac<sub>2</sub>en, sal<sub>2</sub>pn, or sal<sub>2</sub>phen) were originally reported by Wilkinson.<sup>2</sup> These complexes were prepared from 1 equiv of ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, 1 equiv of the ligand, and 2 equiv of triethylamine in either toluene or acetonitrile under stringently dry conditions. The corresponding  $\mu$ -oxo dimer complexes were also reported, with the main synthetic product dependent on the degree of dryness. Wilkinson suggested the monomer compounds were *trans*-[ReOCl(ligand)] complexes; however, characterization was limited to IR and Raman spectra.<sup>2</sup> Since this initial study, the sal based compounds have been reinvestigated for other potential applications, and it has been demonstrated that the reaction conditions and nature of the ligands can lead to different coordination geometries.<sup>11,13</sup>

## Conclusions

Several symmetrical *trans*-[ReOX(Schiff base)] complexes with acac<sub>2</sub>en or acac<sub>2</sub>pn ligands were synthesized and characterized with various substituents (X = H<sub>2</sub>O, Cl<sup>-</sup>, ReO<sub>4</sub><sup>-</sup>, or MeO<sup>-</sup>) occupying the sixth coordination site *trans*

to the oxo group. The reaction conditions and the backbone length of the ligand (en vs pn) determined which species coordinated in the *trans* position. The presence of water (even in trace amounts) influenced the product isolated, with the presence of base rapidly generating the  $\mu$ -oxo dimer species. The acac derived Schiff base ligands coordinate in the equatorial plane of Re(V) oxo complexes with an ancillary ligand occupying the site *trans* to the oxo group. This chemistry is different from that reported for the Re(V) oxo complexes with sal based Schiff base ligands, where an asymmetric rearrangement of the N<sub>2</sub>O<sub>2</sub> Schiff base is observed such that the ancillary ligand occupies the site *cis* to the oxo group. The chemistry of the Re(V) oxo monomer complexes is relevant for extension to the radiotracer level. At the nanomolar Re-188 radiotracer level, dimer formation will not be an issue.

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**Supporting Information Available:** Crystallographic data for *trans*-[ReO(OH<sub>2</sub>)(acac<sub>2</sub>en)]Cl (**1**), *trans*-[ReO(OReO<sub>3</sub>)(acac<sub>2</sub>en)] (**2**), *trans*-[ReOCl(acac<sub>2</sub>pn)] (**3**), *trans*-[ReO(OCH<sub>3</sub>)(acac<sub>2</sub>pn)] (**4**), *trans*-[ $\mu$ -oxo-Re<sub>2</sub>O<sub>3</sub>(acac<sub>2</sub>en)<sub>2</sub>] (**5**), and *trans*-[ $\mu$ -oxo-Re<sub>2</sub>O<sub>3</sub>-(acac<sub>2</sub>pn)<sub>2</sub>] (**6**) in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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