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Novel Rhenium(III, IV, and V) Tetradentate N₂O₂ Schiff Base Mononuclear and Dinuclear Complexes

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Abstract

Reaction of (Bu₄N)[ReOCl₄] with the tetradentate Schiff base ligand , '-(1,1-dimethylethylene)dinitrilo]di-*o*-cresol (sal₂ibnH₂) yields *cis*-[Re^VOCl(sal₂ibn)], which quickly forms *trans*-[μ-O(Re^VO(sal₂ibn))₂] in solution. The dinuclear complex can also be isolated by the addition of base (Et₃N) to the reaction mixture. Conversely, the mononuclear complex can be trapped as *cis*-[Re^VO(NCS)(sal₂ibn)] by addition of (Bu₄N)SCN to the reaction mixture. Reduction of *cis*-[Re^VO(NCS)sal₂ibn] with triphenylphosphine gives the unique *trans*-[Re^{III}(NCS)(PPh₃)(sal₂ibn)] and rare μ-oxo Re(IV) dimer *trans*-[μ-O(Re^{IV}(NCS)(sal₂ibn))₂]. All of the complexes were characterized by ¹H and ¹³C NMR, FT-IR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), cyclic voltammetry and single crystal X-ray diffraction.

Introduction

Technetium-99m remains the workhorse of diagnostic nuclear medicine despite the recent shortages and the increased availability of positron emission tomography (PET) imaging systems and radionuclides (e.g., ¹⁸F).¹ Technetium is well-known for both its diagnostic imaging applications (^{99m}Tc; t_{1/2} = 6.01 h; E_γ = 140 keV) and its environmental impact as a long-lived, mobile fission product (6.1% yield) produced during the nuclear fuel cycle (⁹⁹Tc; t_{1/2} = 2.12 × 10⁵ y; E_βmax = 0.292 MeV).² Rhenium has two radioisotopes (¹⁸⁶Re: t_{1/2} = 90 h; E_βmax = 1.071 MeV; E_γ = 137 keV (9%) and ¹⁸⁸Re: t_{1/2} = 17 h; E_βmax = 2.118 MeV; E_γ = 155 keV (15%)) suitable for theranostics, emitting both beta particles and gamma rays, and is often considered the radiotherapeutic “matched pair” for technetium in radiopharmaceutical development.^{1, 3, 4}

In addition, rhenium, the third row congener of Tc, is often used as a non-radioactive analogue for developing Tc chemistry. Differences in their redox chemistry and substitution kinetics however may lead to “non-matched pair” behavior, requiring careful investigation of their fundamental inorganic chemistry. A major challenge for the development of potential Re radiopharmaceuticals is the kinetic and redox stability of the radiotracer complexes under the high dilution experienced *in vivo*. Instability leads to release of rhenium and oxidation to perrhenate.

The tetradentate N₂O₂ Schiff base ligands have shown very interesting chemistry with technetium, particularly in the field of nuclear medicine. The ^{99m}Tc “Q-series” (*trans*-[^{99m}Tc^{III}(PR₃)₂(N₂O₂-Schiff base)]⁺) has been investigated for use as single photon emission computed tomography (SPECT) imaging agents.^{26, 27} Translation of the “Tc-Q” chemistry to Re has highlighted some of the differences in chemistry between these two congeners, including redox chemistry and substitution kinetics.^{19, 20, 22, 25} Efforts have led to a variety of potential Re(III) and Re(V) Schiff base the ranostic agents with and without coordinated phosphines and with very few examples of Re(III) analogues of the Tc-Q complexes.^{20, 25}

The chemistry of rhenium with Schiff base ligands has been extensively investigated.^{5–9} Methyltrioxorhenium(VII) Schiff base complexes have been evaluated as potential catalysts for epoxidation reactions^{6, 7} while Re(V) salen complexes are being probed as potential oxidation and epoxidation catalysts.^{5, 8, 9} Various rhenium Schiff base complexes have also been explored for potential applications to diagnostic and therapeutic nuclear medicine.^{10–25}

Mononuclear, dinuclear, and trinuclear complexes of Re(V) with tetradentate Schiff base ligands were first reported by Wilkinson.^{10, 12–17, 19–22, 25, 28, 29} Mononuclear complexes ([ReOXL]) are generally isolated under dry, inert conditions using excess ligand as the proton scavenger.^{10, 15, 19} Dinuclear (μ-O[ReOL]₂) and trinuclear ((μ-O)₂O₂[ReL]₃) species are a result of reactions performed open to the atmosphere or in the presence of basic proton scavengers, and have also been isolated as conversion products from mononuclear species that have been left in solutions exposed to water and/or base.^{10, 14, 15, 19} Isolation of crystalline mononuclear species has proven difficult in past work since dinuclear and trinuclear species form under standard aerobic conditions from mononuclear species, likely due to the presence of water, and may preferentially crystallize.²⁰ Indeed, *trans*-[ReO(X)(aca₂en/pn)] (X = OH₂ or Cl[−]) converted to the dinuclear complexes *trans*-[μ-O-(ReO(aca₂en/pn))₂] over time when left exposed to the atmosphere. The addition of base (NaOH) to mononuclear complexes instantaneously converted them to the dinuclear complexes.¹⁹ Conversion back to the mononuclear complexes has only been successful when dinuclear complexes are treated with two equivalents of [Et₃Si]⁺. In these reactions, the bridging oxo ligand is successfully abstracted by the trialkylsilyl cation yielding Et₃SiOSiEt₃ and leaving a vacant coordination site on the resulting mononuclear complexes to be filled by solvent molecules.^{23, 24, 30}

Many N₂O₂ Schiff base mononuclear complexes of the type *cis/trans*-[ReOX(L)], where L is an N₂O₂ Schiff base ligand, have a site *cis* or *trans* to the oxo group available for substitution. Reaction with π-backbonding ligands may lead to complexes that are kinetically more inert.^{20, 22} Addition of thiocyanate to *trans*-[ReO(X)(aca₂en/pn)] (X = OH₂ or Cl[−]) led to the formation of *cis*-[ReO(NCS)aca₂en/pn]. A cyanide complex was also reported for the acac₂en complex.^{20, 22} Interestingly, the dinuclear complex was not observed as in previous studies in the absence of NCS[−] or CN[−], suggesting a method of trapping and stabilizing the mononuclear species.

Our efforts to understand and develop Re Schiff base chemistry suitable for translation to potential theranostic agents have led to the isolation of a novel Re(IV) Schiff base dimer complex and an unusually aqueous stable Re(V) Schiff base monomer complex. We previously reported on using a rigid Schiff base ligand (sal₂phen) to generate the Re analog of the “Q-compounds”.²⁵ Now we report on using a sterically more hindered Schiff base to investigate the factors that might lead to *trans*-[Re(PR₃)₂(Schiff base)]⁺. The reaction of (Bu₄N)[ReOCl₄] with a salicylaldehyde based N₂O₂ Schiff base ligand derived from 1,2-diamino-2-methylpropane (, ' -[(1,1-dimethylethylene)dinitrilo]di-*o*-cresol, sal₂ibnH₂) under various conditions led to several products (Scheme 1). Reaction of ReOCl₄[−] with the

ligand gave the mononuclear Re(V) complex *cis*-[Re^VOCl(sal₂ibn)] and the dinuclear Re(V) complex *trans*-[μ-O(Re^VO(sal₂ibn))₂]. Addition of thiocyanate to the mononuclear chloro complex led to *cis*-[Re^VO(NCS)(sal₂ibn)], an unusually stable mononuclear Re(V) complex. Subsequent reduction of *cis*-[Re^VO(NCS)(sal₂ibn)] with triphenylphosphine generated the mononuclear *trans*-[Re^{III}(NCS)(PPh₃)(sal₂ibn)] and the novel dinuclear *trans*-[μ-O(Re^{IV}(NCS)(sal₂ibn))₂].

Results and Discussion

Synthesis of Re(V) Mono- and Dinuclear Complexes 1, 2, and 3

Reaction of sal₂ibnH₂ with (Bu₄N)[ReOCl₄] in ethanol in the absence of a proton scavenger and under dry, inert conditions, gave the mononuclear complex *cis*-[ReOCl(sal₂ibn)]·3 CHCl₃, **1**, as green cubic crystals. The dinuclear complex *trans*-[μ-O(ReO(sal₂ibn))₂]·4CHCl₃, **2**, was isolated as dark green cubic crystals from reaction in ethanol in the presence of a proton scavenger. Single crystals of compound **1** were difficult to isolate because dimerization to **2** readily occurs. The conversion from mononuclear to the dinuclear species is so favourable that a pure sample of **1** slowly converts to **2** while NMR spectroscopy is performed as observed by the growth of signals from the dinuclear species in the spectrum. This was confirmed by lack of any Re–O–Re stretch prior to sample dissolution for NMR measurements and subsequently observing the Re–O–Re stretch in the IR spectrum. Several other products were also observed in the NMR spectrum of **1** (*vide infra*).

Interestingly, the mononuclear complex is readily isolated or “trapped” as *cis*-[ReO(NCS)(sal₂ibn)], **3**, by the addition of (Bu₄N)SCN. The SCN[−] must be added after the mononuclear complex is formed but before the dinuclear complex forms. The yield of **3** decreases and the yield of **2** increases the longer sal₂ibnH₂ is allowed to react with (Bu₄N)[ReOCl₄]. Once SCN[−] was added to the reaction mixture, a kelly green solid quickly formed and the green color of the solution faded. Recrystallization by slow evaporation of acetonitrile open to the atmosphere yielded **3** as the only product.

After confirmation of a single mononuclear species by IR and ¹H NMR analysis, the stability of compound **3** was investigated. Most Re(V) Schiff base complexes undergo hydrolysis in the presence of water. Compound **3** was dissolved in a 1:1 CH₃CN:H₂O solution and left for over a week, after which time the sample was dried and analysed by IR and ¹H NMR. The complex was virtually unchanged demonstrating this compound's extraordinary water stability.

Synthesis of the Mononuclear Re(III) Complex 4 and Novel Dinuclear Re(IV) Complex 5

Complexes of technetium(III) and rhenium(III) are numerous, which can be attributed to the fact that the *d*⁴ configurations are readily stabilized by ligands with pronounced donor and -acceptor properties. However, Tc(IV) and Re(IV) are much rarer, owing to their tendency to hydrolyze to the thermodynamically favored MO₂.³¹ The Tc(V) Schiff base complexes that were reduced with trialkyl phosphines to the corresponding *trans*-[Tc^{III}(PR₃)₂(Schiff base)]⁺ (i.e., the Tc–Q series) were evaluated for radiopharmaceutical applications.^{2, 32} The use of hydrophilic substituents on the Schiff base or phosphine (e.g., ethers) can increase *in vivo* stability by reducing protein binding. Translation of this chemistry to Re to form the analogous *trans*-[Re^{III}(PR₃)₂(Schiff base)]⁺ has proven challenging.^{10, 16, 18} The mononuclear Re(V) chloro complex (**1**) dimerizes readily to **2**, especially in the presence of water (or base); thus, the mononuclear Re(V) thiocyanate complex (**3**) was reacted with triphenylphosphine. Unfortunately, disubstitution to yield *trans*-[Re^{III}(PPh₃)₂(sal₂ibn)]⁺ did not occur most likely due to the steric requirements of the backbone *gem*-dimethyl groups,

although the monosubstituted *trans*-[Re^{III}(NCS)(PPh₃)(sal₂ibn)] (**4**) formed, along with a novel dimeric μ -oxo Re(IV) complex (**5**) in 16.6% and 6.78% yields, respectively.

Previously reported reactions of monooxorhenium(V) Schiff base complexes with phosphines yielded either the reduced *trans*-[Re^{III}(PR₃)₂(Schiff base)]⁺ or the monosubstituted *cis*-[Re^VO(PR₃)(Schiff base)]⁺ complex, depending on the particular Schiff base and phosphine used.^{16, 18} The Re(III) complex, **4**, represents a rare case in which a single tertiary phosphine coordinates and reduces the metal center with a simultaneous rearrangement of the sal₂ibn Schiff base ligand to purely equatorial coordination sites and the phosphine and thiocyanate groups positioned *trans* to each other. A sterically less bulky phosphine(PR₂R' where R = Ph, Et, or Me; R' = Et, Me, or H) may yield the disubstituted product and this is currently under investigation.

The Re(IV) complex, **5**, containing a linear SCN–Re–O–Re–NCS moiety, is the first of its kind of which we are aware. Of the few non-Re(V) dinuclear complexes with a bridging oxo group, most contain additional bridging ligands, a terminal oxo, or are mixed-valent, but none have terminal NCS groups.^{33–35} The mechanism for the formation of **5** is unclear. We postulated that complex **5** may have been a disproportionation product of **3** to ReO₄[−] and complex **5**, however refluxing complex **3** in CH₃CN for over a week showed no observable reaction. The IR spectrum of the dried product from this reaction gave signals consistent with **3**, and no signals corresponding to **5** or any other dinuclear species were observed. Furthermore, ¹H NMR analysis of the refluxed sample gave signals corresponding only to compound **3**.

General Characterization

Electrospray ionization mass spectrometry (ESI-MS) of compounds **1** – **5** confirmed the identities of the products. The molecular ions with the expected rhenium isotope pattern were observed in the positive mode of ESI-MS for compounds **2** and **4**. Compounds **1** and **3** were observed as [M – Cl]⁺ and [M – NCS]⁺ in the positive mode, respectively. Compound **5** was observed as the radical cation [M – e]⁺ in the positive mode and as the radical anion [M – e][−] in the negative mode. Fragments of dimer **5** with m/z values corresponding to [M – NCS – ReSC₁₉H₁₈N₃O₂]⁺ and [M – ReOC₁₈H₁₈N₂O₂]⁺, where [M] = [C₃₈H₃₆O₅N₆S₂Re₂], were also observed. The FT-IR spectra of all complexes showed the expected Schiff base C=N stretches between 1597 – 1603 cm^{−1}. The spectra of the monomeric oxo-rhenium(V) complexes showed the presence of the Re=O stretches near 950 cm^{−1}, and absence of the Re–O–Re stretch at 694 cm^{−1}. All dinuclear compounds exhibited the Re–O–Re stretch at 694 cm^{−1}. A signal at 980 cm^{−1} for the Re=O stretch, typical for multinuclear oxorhenium complexes,^{10, 13, 19, 20, 25, 36} was observed for compound **2** and was absent in compound **5**. The thiocyanate containing complexes exhibited SCN stretches from 2050 – 2090 cm^{−1}, consistent with literature values.^{22, 37} The elemental analyses of compounds **1** – **5** verified the chemical makeup of the dried complexes albeit compound **4** included an extraneous solvent molecule. In addition, the sulfur content in compound **4** was higher than theoretically expected, possibly the result of free NCS[−].

NMR Analyses

The mononuclear and dinuclear complexes can be easily distinguished based on their ¹H-NMR chemical shifts (Table 1). The asymmetry associated with the sal₂ibn ligand makes every carbon atom and virtually all protons unique. The ¹H and ¹³C NMR spectra of the mononuclear compounds **1** and **3** are consistent with the coordination of the chloro and thiocyanate *cis* to the Re(V) oxo group, respectively, and are very similar to one another. The proton NMR spectra of **1** and **3** showed two singlets for the ligand backbone geminal methyl groups, separate doublets for each methylene proton, and unique singlets for each

imine proton. The aromatic protons were observed as expected between 6.8–7.6 ppm. The ^1H and ^{13}C NMR spectra of **1** also showed the presence of at least one other related species. We suspect that this species may be $[\text{ReO}(\text{X})\text{sal}_2\text{ibn}]$ ($\text{X} = \text{OREO}_3^-, \text{OH}^-, \text{OH}_2$, or solvent) in which X has displaced the coordinated chloride.¹⁹ The ^1H NMR spectrum of this unknown species is almost unchanged with the exception of a new signal at 8.9 ppm for the imine proton. Rearrangement of the ligand from *cis* to *trans* occurs with the imine as the pivot point, which would account for the shift observed by NMR. The ^{13}C NMR spectrum showed double the signals expected for **1** and **3** with the additional chemical shifts very similar to both those assigned to **1** and to those found for compound **2**.

The dinuclear complex **2** exhibited chemical shifts and splitting patterns similar to the monomeric complex **1**, with the exception of the methyl groups. Three different chemical shifts at 1.31, 1.95, and 2.04 ppm were observed for the geminal dimethyl protons. The resonance at 1.2 ppm integrates for six protons, and is likely indicative of the pseudo-equatorial methyl protons directed away from the coordination centers, corresponding to C17A (Figure 4), which is furthest from the influence of the rhenium. The two axially directed methyl groups are observed with two different chemical shifts, 2.0 and 1.9 ppm, integrating for 4 and 2 protons, respectively.

The ^1H NMR spectra for complexes **4** and **5** are much more complex due to the paramagnetic Re center. The ^1H NMR spectra exhibited sharp peaks with no evident peak broadening due to paramagnetism as observed in the literature,^{38–44} but each complex had distinctly different chemical shifts for the protons on the Schiff base ligand. For example, the aromatic protons from the ligand in complex **4** range from 3 to 11 ppm, whereas the same protons for complex **5** range from –21 to 27 ppm. As observed in the literature, ^1H NMR shifts for paramagnetic Re(III) complexes are unpredictable.^{20, 45, 46} Two dimensional NMR techniques were used to help assign the protons to the appropriate chemical shifts. The ^{13}C NMR spectrum displayed only minor shifts for compounds **4** and **5** relative to the diamagnetic complexes. Additionally, the NMR spectra of **5** demonstrates that some paramagnetic Re(IV) (d^3) complexes allow characterization by ^1H - and ^{13}C -NMR although few are reported.

Initially, the NMR studies of compound **5** showed that the sample was not “clean” and another species was present. Purification on a second silica gel column pre-equilibrated with CH_2Cl_2 slowly eluted a faint green band, which was determined to be *trans*- $[\text{Re}^{\text{IV}}(\text{NCS})_4(\text{PPh}_3)_2]$, analogous to Re(IV) phosphine halogen complexes of the type *trans*- $[\text{ReX}_4(\text{PR}_3)_2]$.^{47–49} Compound **5** was then displaced with $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ (1:9) as a purple band and determined to be pure by NMR and ESI-MS studies.

Electrochemistry

The various Re Schiff base complexes were evaluated electrochemically by cyclic voltammetry. All of the complexes showed chemically, but not electrochemically, reversible couples (Table 2) under the conditions used. The five complexes were initially evaluated with a window of +1.00 to –2.00 V. No reversible couples were observed in the positive region for any of the complexes. However, a single anodic signal was observed in the positive region for compounds **3**, **4**, and **5**. This signal could be attributed to an impurity or an irreversible oxidation of the compound itself. In the cathodic region of the CV, the complexes showed redox couples with cathodic-anodic peak separations of 0.160 to 0.230 V rather than the 0.059 V expected for Nernstian behavior. The three Re(V) complexes (**1**, **2**, and **3**) all exhibited Re(V) to Re(IV) reduction waves at about –0.63 V (Table 2), which were chemically reversible; however scanning beyond the Re(V)/Re(IV) reduction wave resulted in irreversible behaviour. Bottomley et al. reported reduction waves for monomeric

and dimeric Re(V) Schiff base complexes however the solvent (1,2-dichloroethane) and electrode (SCE) were different; they observed irreversibility suggestive of chemical reactions following reduction.¹⁶ We cannot directly compare our values to their reduction potentials since the electrochemical systems were quite different, however they appear to be in the same region (near -0.6 V). Additionally they observed oxidation waves, which would have been outside of our redox window.¹⁶ The Re(III) complex (**4**) and Re(IV) dimer (**5**) exhibited chemical reversibility regardless of scan window with reduction waves at about -0.6 V. The repetitive cyclic voltammograms (CV) of compounds **4** and **5** are shown in Figures 1 and 2, respectively. The electrochemical potentials are significantly more negative than those observed for other Re and Tc III/II and IV/III couples.^{12, 16, 20, 50, 51}

X-ray Crystal Structures

The Re(V) complexes *cis*-[ReOCl(sal₂ibn)] · 3 CHCl₃, **1**, *trans*-[μ-O(ReO(sal₂ibn))₂] · 4 CHCl₃, **2**, and *cis*-[ReO(NCS)(sal₂ibn)], **3**, and Re(III) complex *trans*-[Re(NCS)(PPh₃)sal₂ibn], **4**, and the Re(IV) complex *trans*-[μ-O(Re(NCS)sal₂ibn)₂] · 2 CH₃CN, **5**, were characterized by X-ray crystallography (Figures 3–7, respectively). All five complexes exhibit distorted octahedral geometry around the metal center. The ligand occupies the equatorial plane in the two dinuclear complexes (**2** and **5**), and this is also observed for the Re(III) complex, **4**. The mononuclear complexes **1** and **3** have a chloride and a thiocyanate ligand, respectively, coordinated *cis* to the oxo, while the *trans* position is occupied by a phenolic oxygen from sal₂ibn. Space group, lattice parameters, and other relevant information are given in Table 3. Relevant bond lengths and angles are given in Table 4.

cis-[ReOCl(sal₂ibn)] · 3 CHCl₃, (**1**)

The X-ray crystal structure of **1** shows a Re(V)-sal₂ibn complex with a chloride coordinated in the *cis* position relative to the oxo group (Figure 3). Both nitrogen donors and one phenolic oxygen donor from the Schiff base ligand coordinate the rhenium in the equatorial plane along with the chloride, with the rhenium lying about 0.2 Å above the plane toward the oxo group. The second sal₂ibn phenolic oxygen donor is coordinated *trans* to the oxo group. No lengthening of the Re–O single bond *trans* to the oxo group is observed compared to the phenolic Re–O bond *cis* to the oxo group. The two Re–O bond distances are similar, which is typical for these complexes, and fall within the range of similar Re(V) complexes (1.973–2.079 Å).^{15, 20–22, 25} The Re=O bond distance of 1.693 Å also falls within the range of similar structures (1.679–1.697 Å).^{15, 20–22, 25} The O=Re–O angle is close to linear at 169.97°, which is common for these complexes.^{15, 20–22, 25} The bite angles made by the ligand and the Re atom (*i.e.*, the N–Re–N and O1–Re–N1 angles) tend to vary from 78.5–91.9°,^{15, 20–22, 25} with those here just outside of this range, most likely due to the constraints of the backbone, which reduced the N–Re–N angle and expanded the O2–Re–N5 angle.

trans-[μ-O(ReO(sal₂ibn))₂] · 4CHCl₃, (**2**)

Three different crystal forms of **2** were isolated, all in the same space group with different unit cell dimensions due to variations in the included solvent molecules (*i.e.*, *trans*-[μ-O(ReO(sal₂ibn))₂] · 3CHCl₃ and *trans*-[μ-O(ReO(sal₂ibn))₂] · 2CH₂Cl₂ also crystallized) and only minor differences in bond lengths and angles. The structure of **2** shows a neutral μ-oxo dimer, centrosymmetric about the bridging oxo group (Figure 4). The rhenium atoms are in an octahedral coordination environment, with the sal₂ibn ligand in the equatorial plane around the rhenium center and a capping oxo group *trans* to the bridging oxo. The two sal₂ibn ligands are oriented with the backbone methyl groups on opposite sides (*i.e.*, two N's of one ligand are situated above two O's of the other) to minimize steric crowding. The ligand itself is chemically unchanged aside from deprotonation of the phenolic groups. The imine bonds are intact, with an average C=N bondlength of 1.272(8), typical for a C=N

double bond. Each of the Re atoms is situated about 0.16 Å above the plane of the ligand toward their respective capping oxo group. The angles between bonds formed by the chelating ligand are within the having a range of 1.964–2.12 Å, and the Re–N bond having a range of 1.99–2.131 Å.^{13, 19–21, 25, 28} The bond lengths and angles of **2** are listed in Table 4.

The planes of the ligands are approximately 3.5 Å apart. The isobutylene backbone of the ligand is in a conformation placing the methyl group corresponding to C18A in a pseudo-axial position, parallel to the capping oxo, and the second methyl (C17A) in a pseudo-equatorial position, directed away from the complex. The complex is packed together in such a way that the axis of every other complex is offset by 50°, with pseudo-equatorial methyl and aryl hydrogen contacts of 2.9 Å.

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***cis*-[ReO(NCS)(sal₂ibn)], (**3**)**

Crystallographic data of **3** shows a Re(V)-sal₂ibn complex with a thiocyanate ligand coordinated *cis* relative to the oxo group (Figure 5). The geometry around the Re center is similar to that observed in **1**, where the nitrogen donors and one of the oxygen donors from the Schiff base ligand coordinate the rhenium in the equatorial plane along with the thiocyanate. The rhenium is about 0.2 Å above the equatorial plane toward the oxo group. All bond lengths between the Re and the sal₂ibn ligand are similar to literature values. The Re=O bond distance is 1.698 Å, which falls within the range of literature values.^{15, 20–22, 25} The thiocyanate ligand is close to linear, with an N–C–S bond angle of 179.9°. The Re–C–N bond angle of the thiocyanate ligand is also close to linear (174.7°) as typically observed for transition metals.²² The Re–NCS (2.087 Å) bond is slightly longer than the Re–N bonds associated with the sal₂ibn ligand, but is typical for Re(V) complexes with a coordinated thiocyanate.^{22, 52}

***trans*-[Re(NCS)(PPh₃)(sal₂ibn)], (**4**)**

Complex **4** displays a distorted octahedral coordination environment with the triphenylphosphine coordinated *trans* to the thiocyanate (Figure 6). The bond angles about the Re(III) center are near expected values, with angles for the *cis* and *trans* ligands approximately 80–99 and 171°, respectively. The metal center itself is pulled slightly out of the equatorial plane towards the phosphine by 0.05 Å. The Re–O (2.011–2.012 Å) and the Re–N (2.030–2.042 Å) bond distances from the sal₂ibn are consistent with other Re(III) Schiff base complexes.^{15, 20–22, 25, 53, 54} The thiocyanate ligand is close to linear, with an N–C–S bond angle of 179.2°. The Re–N–C bond angle is further from linear (166.9°) and angles towards the pseudo-equatorial methyl group; it is typical for similar Re and Tc systems reported in the literature. The Re–NCS (2.097 Å) bond is within typical ranges for Re(V) complexes with a coordinated thiocyanate and is on the long end of the reported Re–NCS and Tc–NCS bond distances for Re(III) complexes.^{22, 55–59} The Re–P (2.424 Å) bond distance is comparable to those observed in other Re(III) complexes.^{20, 25, 38, 40, 60, 61}

***trans*-[μ-O(Re(NCS)(sal₂ibn))₂] · 2 CH₃CN, (**5**)**

The structure of **5** (Figure 7) is of similar geometry to **2**, where two identical Re structures are bonded to a bridging oxo. Of the rare Re(IV) dinuclear complexes, this unusual compound is the first to not have terminal oxo groups, but rather thiocyanate ligands *trans* to

the bridging oxo.^{33, 34, 62} As in **4**, the thiocyanate ligands are near linear with N–C–S bond angles of 175.79°, the Re–NCS bond length (2.151 Å) is slightly longer than typically observed, and the Re–NCS bond angle (Re–N–C) deviates from linear (163.64°).^{22, 56, 63, 64} The two sal₂ibn ligands are positioned with the backbone methyl groups on opposite sides as in **2**. The planes of the ligands are on average 3.8 Å apart and are canted up or down on either side of the Re–O–Re bond. The Re metal center is pulled slightly out of the plane of the Schiff base ligands and toward the bridging oxo by 0.033 Å. The Re–μ-oxo (1.838 Å) bond distance is slightly longer than normal ranges for Re(V) complexes^{13, 19, 21, 25, 28} and shorter than dinuclear Re(IV) complexes with bridging ligands other than an oxo moiety.^{33, 34, 62} The Re–NCS bond distance of 2.13(1) is longer than average literature values but still falls within the reported range albeit literature values are from mixed metal complexes and NCS saturated Re coordination environments.^{53, 54, 63–65}

Experimental Section

General Considerations

Unless noted, all common laboratory chemicals were of reagent grade or better. Absolute ethanol was degassed prior to use and experiments using ethanol were performed under an argon atmosphere, using standard Schlenk techniques for inert syntheses. ¹H and ¹³C NMR spectra (including HMQC ¹H–¹³C correlation) were recorded on a Bruker DRX300 WB or DRX500 at 25°C in CDCl₃, CD₂Cl₂, CD₃CN, or DMSO-d₆ with TMS as an internal standard. Infrared spectra were obtained as KBr pellets on a Thermo Nicolet Nexus 670 FT-IR spectrometer. Electrospray Ionization Mass Spectroscopy (ESI-MS) was performed on a Thermo Finnigan TSQ7000 triple-quadrupole mass spectrometer. Elemental analysis was performed by Quantitative Technologies Inc. (QTI; Whitehouse, NJ).

Materials—Salicylaldehyde and 1,2-diamino-2-methylpropane were purchased from Sigma Aldrich and used as received. Triethylamine was purchased from Sigma Aldrich and distilled from CuSO₄ prior to use. Absolute ethanol, acetonitrile, toluene, dichloromethane, chloroform, and diethyl ether were used as purchased unless otherwise noted. (*n*-Bu₄N)[ReOCl₄] was prepared by the literature method.⁶⁶ The ligand , '-[(1,1-dimethylethylene)dinitrilo]di-*o*-cresol (sal₂ibnH₂) was prepared as previously reported through condensation of two equivalents of salicylaldehyde with one equivalent of 1,2-diamino-2-methylpropane in absolute ethanol.⁶⁷ The purity of the starting materials was verified by ¹H NMR and FT-IR spectroscopies. The sal₂ibn was recrystallized from absolute ethanol prior to use.

cis-[Re^VOCl(sal₂ibn)]·3 CHCl₃, (1)—Sal₂ibnH₂ (0.1075 g, 0.363 mmol) and (*n*-Bu₄N)[ReOCl₄] (0.213 g, 0.363 mmol) were combined in a Schlenk flask and the flask evacuated and backfilled with argon three times. The solids were dissolved in absolute ethanol (20 mL), with a green solution forming quickly upon dissolution. The solution was stirred at room temperature under argon for 1 hour, after which the solution was brought to dryness *in vacuo*. The oily material was reconstituted in a minimal volume of CHCl₃ and filtered. X-ray quality crystals were obtained by allowing the solution to sit tightly capped at room temperature for several days. Yield 8.6 % (0.0278 g). ¹H NMR [500 MHz, CD₂Cl₂, r.t., (ppm)]: 8.60 (s, 1H, –CH=N–); 7.90 (s, 1H, –HC=N–); 6.89 – 7.65 (m, 8H, ArH); 4.39 (d, *J* = 10 Hz, 1H, –NCH₂–C(CH₃)); 4.28 (d, *J* = 10 Hz, 1H, –NCH₂–C(CH₃)); 1.66 (s, 3H, C(CH₃)); 1.01 (s, 3H, C(CH₃)). ¹³C NMR [500 MHz, CD₂Cl₂, r.t., (ppm)]: 175.94, 174.93 (–HC=N–); 174.81, 166.48 (Ar–O); 139.35, 138.40, 137.54, 134.60, 122.24, 121.70, 120.68, 119.71, 118.65, 118.60 (Ar); 80.22 (–NCH₂–C(CH₃)₂); 75.87 (–NCH₂–C(CH₃)₂); 27.01, 22.91 (C(CH₃)). FT-IR (KBr pellet, /cm^{–1}): 1601 (C=N st); 955 (Re=O st). ESI MS (*m/z*):

497.09 (497.09 calcd for $[\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_2\text{Re}]^+ (\text{M}^+-\text{Cl})$). Elemental Anal. calcd (found) for $\text{ReC}_{18}\text{H}_{18}\text{O}_3\text{N}_2\text{Cl}$: C, 40.60 (39.95); H, 3.41 (3.11); N, 5.26 (5.07).

***trans*-[μ -O($\text{Re}^{\text{VO}}(\text{sal}_2\text{ibn})_2$)] · 4CHCl₃, (2)**—(*n*-Bu₄N)[ReOCl₄] (1.0 g, 1.2 mmol), $\text{sal}_2\text{ibnH}_2$ (0.35 g, 1.2 mmol), and triethylamine (0.5 mL, 0.689 g, 6.81 mmol) were combined in 50 mL of ethanol in air. This solution was refluxed for 1.5 hours, and then taken to dryness on a rotary evaporator. The crude product was dissolved in 50 mL of chloroform and washed three times with an equal volume of water. The organic layer was collected and evaporated to dryness with a rotary evaporator. The product was recrystallized from chloroform/hexanes. Crystals suitable for X-ray diffractometry were obtained by slow evaporation of a solution of **2** in CHCl₃ or CH₂Cl₂ resulting in differing numbers of included solvent. Yield 50% (0.43 g). ¹H NMR [500 MHz, CD₂Cl₂, r.t., (ppm)]: 8.20 (s, 2H, —HC=N—); 8.02 (s, 2H, —HC=N—); 6.52–7.54 (br m, 16H, ArH); 4.57 (m, 2H, —NCH₂—C(CH₃)); 3.75 (m, 2H, —NCH₂—C(CH₃)); 2.04 (s, 4H, C(CH₃)); 1.95 (s, 2H, C(CH₃)); 1.31 (s, 6H, C(CH₃)). ¹³C NMR [500 MHz, CDCl₃, r.t., (ppm)]: 177.0, 176.4 (—HC=N—); 172.88, 170.79 (Ar—O); 138.14, 138.04, 136.79, 136.66, 121.65, 120.68, 118.03, 117.33 (Ar); 77.58 (—NCH₂—C(CH₃)₂); 74.41 (—NCH₂—C(CH₃)₂); 29.39, 21.16 (C(CH₃)). FT-IR (KBr pellet, ν/cm^{-1}): 1597 (C=N st); 980 (Re=O st); 694 (Re—O—Re st). ESIMS (*m/z*): 1010.2 (1010.17 calcd for $[\text{C}_{36}\text{H}_{36}\text{O}_7\text{N}_4\text{Re}_2]^+ (\text{M}^+)$). Elemental Anal. Calcd (found) for $\text{Re}_2\text{C}_{36}\text{H}_{36}\text{O}_7\text{N}_4$: C, 42.76 (42.38); H, 3.59 (3.27); N, 5.55 (5.31).

***cis*-[Re^{VO}(NCS)(sal₂ibn)], (3)**— $\text{Sal}_2\text{ibnH}_2$ (0.051 g, 0.171 mmol) and (*n*-Bu₄N)[ReOCl₄] (0.100 g, 0.171 mmol) were combined in a Schlenk flask and the flask evacuated and backfilled with argon three times. The solids were dissolved in degassed absolute ethanol (20 mL). A green solution formed quickly upon dissolution of the solids. After 30 minutes of reaction time, (*n*-Bu₄N)SCN (0.051 g, 0.171 mmol) was added to the flask using standard Schlenk techniques. The solution was allowed to stir for 2 hours or until the formation of green precipitate ceased. The kelly green solid was isolated on a medium porosity glass fritted funnel, washed with ethanol, and then diethyl ether. X-ray quality crystals were obtained by slow evaporation of an acetonitrile solution of **3**. Yield 45.5 % (0.042 g). ¹H NMR [500 MHz, DMSO-*d*₆, r.t., (ppm)]: 8.55 (s, 1H, —CH=N—); 7.92 (s, 1H, —HC=N—); 6.92–7.66 (m, 8H, ArH); 4.33 (d, *J* = 11 Hz, 1H, —NCH₂—C(CH₃)); 4.27 (d, *J* = 11 Hz, 1H, —NCH₂—C(CH₃)); 1.66 (s, 3H, C(CH₃)); 1.00 (s, 3H, C(CH₃)). ¹³C NMR [500 MHz, DMSO-*d*₆, r.t., (ppm)]: 175.71, 174.05 (—HC=N—); 172.55, 164.27 (Ar—O); 139.25, 138.09, 134.68, 121.03, 120.18, 119.81, 119.64, 119.49, 118.36 (Ar); 146.40 (NCS); 80.09 (—NCH₂—C(CH₃)₂); 77.00 (—NCH₂—C(CH₃)₂); 26.21, 22.71 (C(CH₃)). FT-IR (KBr pellet, ν/cm^{-1}): 2086 (NCS st as); 1603 (C=N st); 953 (Re=O st). ESI MS (*m/z*): 497.09 calcd for $[\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_2\text{Re}]^+ (\text{M}^+-\text{NCS})$. Elemental Anal. calcd (found) for $\text{ReC}_{19}\text{H}_{18}\text{O}_2\text{N}_3\text{S}$: C, 41.08 (40.74); H, 3.28 (3.37); N, 7.57 (5.45); S, 5.78 (5.83).

***trans*-[Re^{III}(NCS)(PPh₃)(sal₂ibn)], (4)**—Complex **3** (0.150 g, 0.270 mmol) was placed in a Schlenk flask and the flask evacuated and backfilled with argon three times. The solid was dissolved in 20 mL of dry degassed CH₃CN added *via* cannula. To this solution, triphenylphosphine (0.501 g, 1.90 mmol) was added following standard Schlenk techniques. The green solution was refluxed for 4 days under inert atmosphere, during which time the color changed to brownish yellow. The solution was then brought to dryness *in vacuo*, and the oily substance was reconstituted in CH₂Cl₂ and purified on a silica gel column pre-equilibrated with CH₂Cl₂. Compound **4** was the third visible band (red/orange in color) eluted with CH₂Cl₂. Slow evaporation of the solvent produced X-ray quality crystals of **4**. Yield 16.6 % (0.036 g). ¹H NMR [500 MHz, CD₂Cl₂, r.t., (ppm)]: 26.58 (d, *J* = 6.9, 1H, ArH), 25.63 (d, *J* = 6.9, 1H, ArH); 17.24 (t, *J* = 6.9, 1H, ArH); 16.21 (t, *J* = 9.2, 1H, ArH); 8.29 (br s, 3H, ArH); 7.88 (br s, 9H, ArH); 7.40–7.75 (m, 3H, ArH); 2.36 (s, 1H, C(CH₃));

1.27 (s, 2H, $-\text{NCH}_2-\text{C}(\text{CH}_3)$); -3.67 (s, 3H, $\text{C}(\text{CH}_3)$); -6.43 (dd; $J = 6.9, 9.2$; 1H; ArH); -8.33 (dd; $J = 6.9, 9.2$; 1H; ArH); -18.73 (d, $J = 6.9$ Hz, 1H, ArH); -20.46 (d, $J = 6.9$ Hz, 1H, ArH); -26.69 (s, 1H, $-\text{HC}=\text{N}-$); -40.74 (s, 1H, $-\text{HC}=\text{N}-$). ^{13}C NMR [500 MHz, CDCl_3 , r.t., /ppm]: 155.81, 46.19 ($-\text{HC}=\text{N}-$); 154.42, 138.80, 134.04, 126.26, 101.65, 68.43, 63.38, -1.88 (Ar); 138.01, 132.66, 129.82 (PPh_3); 30.38 ($-\text{NCH}_2-\text{C}(\text{CH}_3)$); 60.72, 21.01 ($\text{C}(\text{CH}_3)$). FT-IR (KBr pellet, / cm^{-1}): 2072 (SCN st as); 2031 (SCN st sy); 1598 (C=N st). ESI MS (m/z): 800.96 (801.16 calcd for $[\text{C}_{37}\text{H}_{36}\text{O}_2\text{N}_3\text{PSRe}]^+$ (M^+)). Elemental Anal. calcd (found) for $\text{ReC}_{37}\text{H}_{36}\text{O}_2\text{N}_3\text{PS}\cdot\text{CH}_2\text{Cl}_2$: C, 51.55 (52.84); H, 4.08 (4.71); N, 4.78 (5.06); S, 3.6 (5.32).

trans*- $[\mu\text{-O}(\text{Re}^{\text{IV}}(\text{NCS})(\text{sal}_2\text{ibn}))_2] \cdot 2\text{CH}_3\text{CN}$, **5*—This compound was prepared as described for compound **4** and isolated as a separate band from the silica gel column. Compound **5** remained at the top of the column until yellow band **5** was removed with CH_2Cl_2 ; purple compound **5** was then eluted with an $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ (1:9) solution. Slow evaporation of the solvent gave X-ray quality crystals of **5**. Yield 6.78 % (0.020 g). ^1H NMR (500 MHz, CD_3CN , r.t., /ppm): 13.49 (s, 1H, $-\text{CH}=\text{N}-$); 8.29 (s, 1H, $-\text{HC}=\text{N}-$); 10.29 (d, $J = 8.0$ Hz, 1H, ArH); 10.23 (t, $J = 8.0$ Hz, 1H, ArH); 8.99 (t, $J = 7.5$ Hz, 1H, ArH); 8.55 (d, $J = 7.5$ Hz, 1H, ArH); 7.29 (d, $J = 7.5$ Hz, 1H, ArH); 7.24 (d, $J = 7.5$ Hz, 1H, ArH); 6.50 (t, $J = 7.5$ Hz, 1H, ArH); 3.00 (t, $J = 7.5$ Hz, 1H, ArH); 4.85, -0.36 (d, $J = 11$ Hz, 1H, $-\text{NCH}_2-\text{C}(\text{CH}_3)$); 2.32 (s, 3H, $\text{C}(\text{CH}_3)$); -1.32 (s, 3H, $\text{C}(\text{CH}_3)$). ^{13}C NMR (500 MHz, CD_3CN , r.t., /ppm): 147.42, 145.44, 143.36, 141.58, 115.54, 113.75, 110.16, 104.56 (Ar); 123.72, 73.39 ($-\text{HC}=\text{N}-$); 93.63 ($-\text{NCH}_2-\text{C}(\text{CH}_3)$); 22.91, 11.80 ($\text{C}(\text{CH}_3)$). FT-IR (KBr pellet, / cm^{-1}): 2054 (SCN st as); 1597 (C=N st); 694 (Re–O–Re st). ESI MS (m/z): 1093.27 (1094.13 calcd for $[\text{C}_{38}\text{H}_{36}\text{O}_5\text{N}_6\text{S}_2\text{Re}_2]^+$ (M^+)). Elemental Anal. calcd (found) for $\text{Re}_2\text{C}_{38}\text{H}_{36}\text{O}_5\text{N}_6\text{S}_2$: C, 41.75 (41.83); H, 3.32 (3.42); N, 7.68 (7.05).

Electrochemistry

The electrochemical data were obtained with a Bioanalytical Systems Inc. (BAS) CV-50 instrument. Tetraethylammonium perchlorate (TEAP; 0.1 M) in acetonitrile (Fisher, HPLC Grade) was used as the electrolytic solution. A non-aqueous Ag/AgCl reference electrode (BAS) (0.1 M TEAP in CH_3CN), a Pt wire auxiliary electrode (BAS), and a glassy carbon working electrode (BAS) were used for cyclic voltammetry analysis of the Re complexes (1 mM). A scan rate of 100 mV/s was used for all experiments. The results were then standardized against ferrocene.

X-ray Crystal Structures

Intensity data were obtained at -100°C on a BrükerAPEX II CCD Area Detector system using the scan technique with Mo K radiation from a graphite monochromator. Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and absorption corrections were made using the multi-scan method. Space group, lattice parameters, and other relevant information are given in Table 3. The structures were solved by direct methods with full-matrix least-squares refinement, using the SHELX package.^{68, 69} All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions and included in the refinement using a riding model, with fixed isotropic U . The final difference maps contained no features of chemical significance.

Conclusions

Mononuclear rhenium Schiff base complexes convert to dinuclear species when water or base is present. The isolated mononuclear complex *cis*- $[\text{ReOCl}(\text{sal}_2\text{ibn})]$, **1**, readily

dimerizes to form *trans*-[μ -O(ReO(sal₂ibn))₂], **2**, when exposed to the atmosphere. However, the mononuclear complex can be trapped and stabilized with thiocyanate as in **3**. Exposure of **3** to water does not result in dimerization or decomposition over more than a week, as determined by ¹H-NMR. The thiocyanate coordination to the Re center in **3** is strong enough to resist displacement under refluxing acetonitrile and even upon reduction of the Re(V) center to Re(III) and Re(IV) by triphenylphosphine. However, the reduced Re-thiocyanate monophosphine complex *trans*-[Re(NCS)(PPh₃)(sal₂ibn)], **4**, does not appear to be stable and undergoes conversion to several products. Complex **5**, *trans*-[μ -O(Re(NCS)(sal₂ibn))₂], is unique in that thiocyanates are in the terminal positions *trans* to the bridging oxo forming a linear X-Re-O-Re-X moiety, while other dinuclear Re(III) and Re(IV) complexes bridged by at least one oxo have the site that is *trans*/axial occupied by an oxo or chelating ligands or form nonlinear moieties. These studies indicate that the chemistry of rhenium with Schiff base ligands can be very complex and has implications for potential nuclear medicine applications. The aqueous stability observed for *cis*-[ReO(NCS)(sal₂ibn)], **3**, makes this Re(V) complex useful for translation to the radiotracer level for potential radiotherapy using ^{186/188}Re.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Carroll V, Demoin DW, Hoffman TJ, Jurisson SS. *Radiochim Acta*. 2012; 100:653–667.
2. Yoshihara, K.; Omori, T. *Technetium and Rhenium: Their Chemistry and Its Applications*. Vol. 176. Springer; 1996.
3. Volkert WA, Hoffman TJ. *Chem Rev*. 1999; 93:1137–1156.
4. Heeg MJ, Jurisson SS. *Accts Chem Res*. 1999; 32:1053–1060.
5. Sachse A, Mosch-Zanetti NC, Lyanshenko G, Wielandt JW, Most K, Magull J, Dall'Antonia F, Pal A, Herbst-Irmer R. *Inorg Chem*. 2007; 46:7129–7135. [PubMed: 17655288]
6. Xu Z, Zhou MD, Drees M, Chaffrey-Millar H, Herdtweck E, Hermann WA, Kuhn FE. *Inorg Chem*. 2009; 48:6812–6822. [PubMed: 19548686]
7. Altmann P, Cokoja M, Kuhn FE. *J Organomet Chem*. 2012; 701:51–55.
8. Gerber TIA, Yumata NC, Betz R. *Inorg Chem Commun*. 2012; 15:69–72.
9. Grunwald KR, Saischek G, Volpe M, Mosch-Zanetti NC. *Inorg Chem*. 2011; 50:7162–7171. [PubMed: 21736307]
10. Middleton AR, Masters AF, Wilkinson G. *J Chem Soc, Dalton Trans*. 1979:542–546.
11. Banbery HJ, McQuillan F, Hamor TA, Jones CJ, McCleverty JA. *J Chem Soc Dalton Trans*. 1989:1405–1407.
12. Tisato F, Refosco F, Mazzi U, Bandoli G, Dolmella A. *Inorg Chim Acta*. 1989; 164:127–135.
13. Banbery HJ, McQuillan FS, Hamor TA, Jones CJ, McCleverty JA. *Inorg Chim Acta*. 1990; 170:23–26.
14. Tisato F, Refosco F. *Inorg Chim Acta*. 1991; 189:97–103.
15. Herrmann WA, Rauch MU, Artus GRJ. *Inorg Chem*. 1996; 35:1988–1991.

16. Bottomley LA, Wojciechowski PE, Holder GN. *Inorg Chim Acta*. 1997; 255:149–155.
17. Brommel, KJC v; Verboom, W.; Kooijman, H.; Spek, AL.; Reinhoudt, DN. *Inorg Chem*. 1998; 37:4197–4203. [PubMed: 11670551]
18. Bereau VM, Khan SI, Abu-Omar MM. *Inorg Chem*. 2001; 40:6767–6773. [PubMed: 11735489]
19. Benny PD, Barnes CL, Piekarski PM, Lyndon JD, Jurisson SS. *Inorg Chem*. 2003; 42(20):6519–6527. [PubMed: 14514329]
20. Benny PB, Green JL, Engelbrecht HP, Barnes CL, Jurisson SS. *Inorg Chem*. 2005; 44:2381–2390. [PubMed: 15792474]
21. Gerber TIA, Luzipo D, Mayer P. *J Coord Chem*. 2005; 58:1505–1512.
22. Green JL, Benny PD, Engelbrecht HP, Barnes CL, Jurisson SS. *Synthesis and Reactivity in Inorganic, Metal-Organic and nano-Metal Chemistry*. 2005; 35:53–59.
23. Du G, Abu-Omar MM. *Organometallics*. 2006; 25:4920–4923.
24. Ison EA, Cessarich JE, Du G, Fanwick PE, Abu-Omar MM. *Inorg Chem*. 2006; 45:2385–2387. [PubMed: 16529452]
25. Lane SR, Sisay N, Carney B, Dannoon S, Williams S, Engelbrecht HP, Barnes CL, Jurisson SS. *Dalton Trans*. 2011; 40:269–276. [PubMed: 21079821]
26. Deutsch E, Vanderheyden JL, Gerundini P, Libson K, Hirth W, Colombo F, Savi A, Fazio F. *J Nucl Med*. 1987; 28:1870–1880. [PubMed: 3681444]
27. Rossetti C, Vanoli G, Paganielli G, Kwiatkowski M, Zito F, Colombo F, Bonino C, Carpinelli A, Casati R, Deutsch K, Marmion M, Woulfe SR, Lunghi F, Deutsch E, Fazio F. *J Nucl Med*. 1994; 35:1571–1580. [PubMed: 7931652]
28. de CT Carrondo MAAF, Middleton AR, Skapski AC, West AP, Wilkinson G. *Inorg Chim Acta*. 1980; 44:L7–L8.
29. Luo H, Liu S, Rettig SJ, Orvig C. *Can J Chem*. 1995; 73:2272–2281.
30. Du G, Fanwick PE, Abu-Omar MM. *Inorg Chim Acta*. 2008; 361:3184–3192.
31. McCleverty, JA.; Meyer, TJ. *Comprehensive Coordination Chemistry II*. 2. Elsevier Ltd; Amsterdam; Boston: 2003.
32. Marmion ME, Woulfe SR, Neumann WL, Nosco DL, Deutsch E. *Nucl Med Biol*. 1999; 26:755–770. [PubMed: 10628555]
33. Bartley SL, Dunbar KR, Shih KY, Fanwick PE, Walton RA. *Inorg Chem*. 1993; 32:1341–1349.
34. Shih KY, Fanwick PE, Walton RA. *Inorg Chim Acta*. 1993; 212:23–29.
35. Bartley SL, Dunbar KR, Shih KY, Fanwick PE, Walton RA. *J Chem Soc*. 1993:98–100.
36. Grove DE, Wilkinson G. *J Chem Soc (A)*. 1966:1224–1230.
37. Cotton FA, Robinson WR, Walton RA, Whyman R. *Inorg Chem*. 1967; 6(5):929–935.
38. Pearson C, Beauchamp A. *Inorg Chim Acta*. 1995; 237:13–18.
39. Randall EW, Shaw D. *Molecular Physics*. 1965; 10:41.
40. Mitsopoulou CA, Mahieu N, Motevalli M, Randall EW. *J Chem Soc, Dalton Trans*. 1996:4563–4566.
41. Gunz HP, Leigh GJ. *J Chem Soc A*. 1971:2229–2233.
42. Randall EW, Shaw D. *J Chem Soc A*. 1969:2867–2872.
43. Shaw D, Randall EW. *Chem Commun*. 1965; 5:82–83.
44. Chatt J, Leigh GJ, Mingos DMP, Randall EW, Shaw D. *Chem Commun*. 1968:419–420.
45. Chattopadhyaya S, Raya MS, Chaudhuri S, Mukhopadhyay G, Bocellid G, Cantonid A, Ghosh A. *Inorg Chim Acta*. 2006; 359(5):1367–1375.
46. Banerjee SR, We L, Levadala MK, Lazarova N, Golub VO, O'Connor CJ, Stephenson KA, Valliant JF, Babich JW, Zubieta J. *Inorg Chem*. 2002; 41:5795–5802. [PubMed: 12401085]
47. Colton R, Wilkinson G. *Chem Ind London*. 1959:1314–1315.
48. Johnson NP, Lock CJL, Wilkinson G. *J Chem Soc*. 1964:1054–1066.
49. Cariati F, Sgamellotti A, Morazzoni F, Valenti V. *Inorg Chim Acta*. 1971; 5:531–535.
50. Jurisson SS, Dancey K, McPartlin M, Tasker PA, Deutsch E. *Inorg Chem*. 1984; 23:4743–4749.
51. Lever ABP. *Inorg Chem*. 1991; 30:1980–1985.

52. Battistuzzi R, Saladini M. *Inorg Chim Acta*. 2000; 304:114–117.
53. Sugimoto H, Kamei M, Umakoshi K, Sasaki Y, Suzuki M. *Inorg Chem*. 1996; 35:7082–7088. [PubMed: 11666890]
54. Sugimoto H, Takahira T, Yoshimura T, Shiro M, Yamasaki M, Miyake H, Umakoshi K, Sasaki Y. *inorg Chim Acta*. 2002; 337:203–211.
55. Rall J, Weingart F, Ho DM, Heeg MJ, Tisato F, Deutsch E. *Inorg Chem*. 1994; 33:3442–3451.
56. Dinda S, Hazra D, RoyChowdhury S, Helliwell M, Malik KMA, Mukherjee M, Bhattacharyya R. *Inorg Chim Acta*. 2009; 362:2108–2116.
57. Cotton FA, Matusz M. *Inorg Chem*. 1987; 26:3468–3472.
58. Yoshimura T, Chen Z, Itasaka A, Abe M, Sasaki Y, Ishizaka S, Kitamura N. *Inorg Chem*. 2003; 42:4857–4863. [PubMed: 12895107]
59. Jurisson S, Halian MM, Lydon JD, Barnes CL, Nowotnik DP, Nunn AD. *Inorg Chem*. 1998; 37(8):1922–1928.
60. Rossi R, Duatti A, Magon L, Casellato U, Graziani R, Toniolo L. *J Chem Soc, Dalton Trans*. 1982:1949–1952.
61. Bhattacharyya S, Banerjee S, Dirghangi BK, Menon M, Chakracorty A. *J Chem Socs, Dalton Trans*. 1999:155–159.
62. Sokolov NM, Fedorova NE, Pervukhina NV, Peresypkina EV, Virovets AV, Patow R, Fedorov VE, Fenske D. *Russian Chemical bulletin, International Edition*. 2006; 55(1):53–61.
63. Gonzalez R, Barboza N, Chiozzzone R, Kremer C, Armentano D, Munno GD, Faus J. *Inorg Chim Acta*. 2008; 361:2715–2720.
64. Gonzalez R, Acosta A, Chiozzzone R, Kremer C, Armentano D, Munno GD, Julve M, Lloret F, Faus J. *Inorg Chem*. 2012; 51:5737–5747. [PubMed: 22574893]
65. Homolya L, Preetz W. *Zeitschrift fuer Naturforschung, B: Chemical Sciences*. 1999; 54(8):1009–1014.
66. Alberto R, Schibli R, Egli A, Schubiger A, Herrmann W, Artus G, Abram W, Kaden T. *J Organomet Chem*. 1995; 492:217–224.
67. Patel KS Jr, J. C. B. *J Inorg Nuc Chem*. 1971; 33:1399–1406.
68. Sheldrick, GM. *SHELXS-97, Crystal Structure Solution*. University of Gottingen; Gottingen, Germany: 1997.
69. Sheldrick, GM. *SHELXL-97, Crystal Structure Refinement*. University of Gottingen; Gottingen, Germany: 1997.

Fig. 1.
Repetitive cyclic voltammogram (CV) for *trans*-[Re^{III}(NCS)(PPh₃)sal₂ibn] (**4**)

Fig. 2.
Repetitive cyclic voltammogram (CV) for *trans*-[μ -O(Re^{IV}(NCS)sal₂ibn)₂] (**5**)

Fig. 3. Thermal ellipsoid plot⁷⁰ of *cis*-[ReO(sal₂ibn)Cl] (**1**) with 50% probability ellipsoids (CCDC 933550). Hydrogens and solvent molecules are omitted for clarity.

Fig. 4. Thermal ellipsoid plot⁷⁰ of $\mu\text{-O}[\text{ReO}(\text{sal}_2\text{ibn})]_2$ (2) with 50% probability ellipsoids (CCDC 933551). Hydrogens and solvent molecules are omitted for clarity.

Fig. 5. Thermal ellipsoid plot⁷⁰ of *cis*-[ReO(NCS)(sal₂ibn)] (**3**) with 50% probability ellipsoids (CCDC 933552). Hydrogens are omitted for clarity.

Fig. 6. Thermal ellipsoid plot⁷⁰ of *trans*-[Re(NCS)(PPh₃)sal₂ibn] (4) with 50% probability ellipsoids (CCDC 933553). Hydrogens are omitted for clarity.

Fig. 7. Thermal ellipsoid plot⁷⁰ of *trans*-[$μ$ -O(Re(NCS)sal₂ibn)₂] (5) with 50% probability ellipsoids (CCDC 933554). Hydrogens are omitted for clarity. O3 is labeled as O4 in Table 4 to simplify the table.

Scheme 1.
Complete reaction scheme of compounds **1** – **5**.

Table 1

¹H-NMR Chemical Shifts

	1	2	3	4	5
gem-dimethyl	1.01 (s, 3H)	1.31 (s, 4H)	1.00 (s, 3H)	2.36 (s, 3H)	2.32 (s, 3H)
	1.66 (s, 3H)	1.95 (s, 2H)	1.66 (s, 3H)	-3.67 (s, 3H)	-3.67 (s, 3H)
methylene		2.04 (s, 6H)			
	4.28 (d, 1H)	3.75 (m, 2H)	4.27 (d, 1H)	1.27 (s, 2H)	4.85 (d, 1H)
imine	4.39 (d, 1H)	4.57 (m, 2H)	4.33 (d, 1H)		-0.36 (d, 1H)
	7.90 (s, 1H)	8.02 (s, 2H)	7.92 (s, 1H)	-26.69 (s, 1H)	8.29 (s, 1H)
	8.60 (s, 1H)	8.20 (s, 2H)	8.55 (s, 1H)	-40.74 (s, 1H)	13.49 (s, 1H)
aromatic	6.89–7.65 (m, 8H)	6.52–7.54 (m, 16H)	6.92–7.66 (m, 8H)	25.63 (d, 1 H)	10.29 (d, 1H)
				25.58 (d, 1H)	10.23 (t, 1H)
				17.24 (t, 1H)	8.99 (t, 1H)
				16.21 (t, 1H)	8.55 (d, 1H)
				-6.43 (dd, 1H)	7.29 (d, 1H)
				-8.33 (dd, 1H)	7.24 (d, 1H)
				-18.73 (d, 1H)	6.50 (t, 1H)
				-20.46 (d, 1H)	3.00 (t, 1H)

Table 2 $E^{\circ'}$ Values^{a,b,c}

Complex	Redox Couple	$E^{\circ'}$ (vs. SHE)	(in V)
<i>cis</i> -[ReOCl(sal ₂ ibn)]	V/IV	−0.630 V	0.162
<i>trans</i> -[μ-O(ReO(sal ₂ ibn)) ₂]	V/IV	−0.627 V	0.210
<i>cis</i> -[ReO(NCS)(sal ₂ ibn)]	V/IV	−0.635 V	0.183
<i>trans</i> -[Re(NCS)(PPh ₃)(sal ₂ ibn)]	III/II	−0.613 V	0.175
<i>trans</i> -[μ-O(Re(NCS)(sal ₂ ibn)) ₂]	IV/III	−0.5965	0.230

^a Conditions: cyclic voltammetry in acetonitrile, 0.1 M TEAP; glassy carbon working electrode; Ag/AgCl reference electrode; Pt counter electrode; scan rate of 100 mV/s.

^b $E^{\circ'}$ values in V vs. SHE.

^c is the separation (in V) between cathodic and anodic peaks with 0.059 V Nernstian.

Table 3

X-ray Crystal Data, Data Collection Parameters, and Refinement parameters

	1	2	3	4	5
CCDC #	933550	933551	933552	933553	933554
Formula	C ₂₀ H ₂₀ Cl ₇ N ₂ O ₃ Re	C ₄₀ H ₄₀ Cl ₁₂ N ₄ O ₇ Re ₂	C ₁₉ H ₁₈ N ₃ O ₃ SRe	C ₃₇ H ₃₃ N ₃ O ₂ SPRe	C ₄₂ H ₄₂ N ₈ O ₅ S ₂ Re ₂
FW	770.73	1481.83	554.62	800.89	1175.36
crystal system	monoclinic	monoclinic	triclinic	monoclinic	Monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> - <i>1</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.1399(17)	9.602(2)	8.920(4)	39.067(8)	10.117(1)
<i>b</i> (Å)	9.4693(15)	17.819(3)	9.487(4)	8.746(2)	16.397(2)
<i>c</i> (Å)	24.716(4)	14.807(3)	11.657(5)	19.104(4)	13.168(2)
(deg)	90	90	95.882(5)	90	90
(deg)	95.913(2)	90.941(2)	96.864(5)	97.644(2)	95.155(2)
(deg)	90	90	103.701(4)	90	90
<i>V</i> (Å ³)	2593.4(7)	2533.1(7)	942.8(7)	6469(2)	2175.5(5)
<i>Z</i>	4	2	2	8	2
calcd (g/cm ³)	1.974	1.949	1.954	1.645	1.794
<i>T</i> , K	173(2)	173(2)	173(2)	173(2)	173(2)
μ , mm ⁻¹	5.433	5.458	6.580	3.909	5.708
source (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
<i>R</i> (<i>F</i>)	0.0191	0.0345	0.0302	0.0583	0.0586
<i>R</i> _w (<i>F</i>) ²	0.0422	0.0863	0.0713	0.1174	0.1282
GooF	1.119	1.096	1.058	1.174	1.157

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

Table 4

Select bond lengths (Å) and angles (deg) for compounds 1–5

	1	2	3	4	5
Re(1)-O(1)	2.009(2)	2.030(4)	1.992(3)	2.024(6)	2.004(7)
Re(1)-O(2)	1.999(2)	2.031(4)	2.014(3)	2.022(4)	2.008(7)
Re(1)-O(3) (Re=O)	1.693(2)	1.714(4)	1.689(4)	---	---
Re(1)-O(4) (Re-O-Re)	---	1.9236(3)	---	---	1.8385(4) ^a
Re(1)-N(1)	2.062(2)	2.067(4)	2.065(4)	2.025(8)	2.047(9)
Re(1)-N(2)	2.073(2)	2.057(5)	2.072(4)	2.038(7)	2.024(9)
Re(1)-Cl(1)	2.4401(6)	---	---	---	---
Re(1)-N(3) (Re-NCS)	---	---	2.087(4)	2.100(8)	2.13(1)
Re(1)-P(1)	---	---	---	2.429(2)	---
O(1)-Re(1)-O(2)	82.57(7)	88.7(2)	82.9(1)	99.0(2)	98.6(3)
O(1)-Re(1)-O(3) [O1-oxo]	169.97(8)	87.1(1)	104.1(2)	---	---
O(2)-Re(1)-O(3) [O2-oxo]	103.50(8)	89.5(1)	167.7(1)	---	---
O(1)-Re(1)-O(4) [O1-μ-O]	---	96.5(2)	---	---	91.0(2)
O(2)-Re(1)-O(4) [O2-μ-O]	---	95.8(2)	---	---	92.1(2)
O(3)-Re(1)-O(4) [oxo-μ-O]	---	173.6(2)	---	---	---
O(1)-Re(1)-N(1)	93.65(7)	95.0(2)	---	91.9(3)	91.2(4)
O(2)-Re(1)-N(1)	92.76(7)	170.8(2)	94.6(1)	167.9(3)	170.2(4)
O(3)-Re(1)-N(1) [oxo-N1]	94.01(8)	82.3(2)	95.2(2)	---	---
O(4)-Re(1)-N(1) [μ-O-N1]	92.1(2)	---	---	87.6(3)	---
O(1)-Re(1)-N(2)	80.51(7)	169.8(2)	160.1(2)	172.2(3)	171.0(3)
O(2)-Re(1)-N(2)	160.21(7)	93.3(2)	80.4(1)	88.7(3)	89.4(3)
O(3)-Re(1)-N(2) [oxo-N2]	94.74(8)	82.9(1)	94.3(2)	---	---
O(4)-Re(1)-N(2) [μ-O-N2]	---	93.2(2)	---	---	93.0(3)
N(1)-Re(1)-N(2)	78.20(7)	81.7(2)	78.3(2)	80.3(3)	80.8(4)
N(1)-Re(1)-N(3) [N1-NCS]	---	---	174.9(1)	87.8(3)	92.8(4)
N(2)-Re(1)-N(3) [N2-NCS]	---	---	98.5(2)	91.3(3)	88.7(4)
O(1)-Re(1)-Cl(1)	82.43(5)	---	---	---	---
O(2)-Re(1)-Cl(1)	89.00(5)	---	---	---	---

	1	2	3	4	5
O(3)-Re(1)-Cl(1) [oxo-Cl]	89.64(6)	---	---	---	---
N(1)-Re(1)-Cl(1)	175.46(5)	---	---	---	---
N(2)-Re(1)-Cl(1)	98.83(6)	---	---	---	---
O(1)-Re(1)-N(3) [O1-NCS]	---	---	89.4(2)	88.3(3)	87.4(3)
O(2)-Re(1)-N(3) [O2-NCS]	---	---	81.0(1)	87.2(3)	87.7(3)
O(3)-Re(1)-N(3) [oxo-NCS]	---	---	88.9(2)	---	---
O(4)-Re(1)-N(3) [μ -O-NCS]	---	---	---	---	178.3(3)
O(1)-Re(1)-P(1)	---	---	---	83.3(2)	---
O(2)-Re(1)-P(1)	---	---	---	91.7(2)	---
N(1)-Re(1)-P(1)	---	---	---	94.8(2)	---
N(2)-Re(1)-P(1)	---	---	---	97.4(2)	---
N(3)-Re(1)-P(1) [NCS-P]	---	---	---	171.2(2)	---
Re(1)-O(3)-Re(2)	---	179.9(1)	---	---	180

^aThis oxygen is labeled as O3 in Figure 5 and in the .cif file. It is labeled here as O4 to simplify the table. All μ -O are labeled in this table as O4.