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PAPER

Re(V) and Re(III) complexes with sal_2phen and triphenylphosphine: rearrangement, oxidation and reduction†

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Reactions of Re^{V}, tetradentate Schiff base complexes with tertiary phosphines have previously yielded both rearranged Re^{V} and reduced Re^{III} complexes. To further understand this chemistry, the rigid diiminediphenol (N_2O_2) Schiff base ligand sal_2phen (*N*,*N*′-*o*-phenylenebis(salicylaldimine)) was reacted with (n-Bu_4N)[$ReOCl_4$] to yield *trans*-[$ReOCl(sal_2phen)$] (**1**). On reaction with triphenylphosphine (PPh_3), a rearranged Re^{V} product *cis*-[$ReO(PPh_3)(sal_2phen^*)$]PF_6 (**2**), in which one of the imines was reduced to an amine during the reaction, and the reduced Re^{III} products *trans*-[$ReCl(PPh_3)(sal_2phen)$] (**4**) and *trans*-[$Re(PPh_3)_2(sal_2phen)$]$^+$ (**5**) were isolated. Reaction of sal_2phen with [$ReCl_3(PPh_3)_2$-(CH_3CN)] resulted in the isolation of [$ReCl_2(PPh_3)_2$(salphen)] (**3**). The compounds were characterized using standard spectroscopic methods, elemental analyses and single crystal X-ray crystallography.

Introduction

The first rhenium Schiff base complexes were reported in 1979 by Middleton and co-workers[1] and they have been studied extensively since that time for their potential applications in nuclear medicine and commercial catalysis.[2–6] High oxidation state Re-oxo complexes (Re^{VII} and Re^{V}) have found utility in catalysis.[2,4–10] Rhenium(VII) methylrhenium trioxide complexes (MTO) have proven particularly useful in oxidation catalysis.[8,11] Rhenium(V) oxo and imido phosphine complexes effect hydrogen release from organosilane and alcohol mixtures and enantioselective reduction of imines.[9,10] Multiple examples for the use of Re^{V}-oxo Schiff base complexes as potential catalysts have also been reported. For example, rhenium oxo *N*,*N*′-ethylenebis(salicylaldimine) (sal_2en) complexes have utility for oxygen atom transfer (OAT), with their reactivity stemming from rhenium's high oxidation state and the cationic charge of the complex.[7] Rhenium oxo *N*,*N*′-cyclohexan-di-yl-bis(salicylaldimine) (sal_2dach) complexes are effective catalysts for hydrosilation of alkyl and aryl ketones and silane alcoholysis of secondary alcohols.[8]

Schiff base complexes with Re^{V} and Re^{III} have been reported with salicylaldehyde (*e.g.*, sal_2en and sal_2pn) and acetylacetone (*e.g.*, $acac_2en$ and $acac_2pn$) derived tetradentate ligands.[1–3,12–21] This class of Schiff base ligands contains the N_2O_2 coordination core and upon chelation with rhenium, four configurations are possible.[22] It was suggested that the ligand will lie in the equatorial plane with respect to the rhenium oxo core when there are less than five carbons between the two imine nitrogens, resulting in the formation of three chelate rings that assist in stabilizing the rhenium complex.[22] However, there are several examples in which one oxygen of the N_2O_2 core is coordinated *trans* to the Re═O group.[2,20]

We recently reported on the reactivity of the monomeric Re^{V} oxo Schiff base complexes *trans*-[$ReO(OH_2)(acac_2en)$]Cl and *trans*-[$ReOCl(acac_2pn)$] with tertiary phosphines[20] and with thiocyanate and cyanide.[21] The reaction of the monomeric Re^{V} oxo Schiff base complexes with phosphines yielded either a rearranged Re^{V} complex with the tertiary phosphine coordinated *cis* to the oxo group or a Re^{III} complex with two tertiary phosphines coordinated *trans* to each other, with the product dependent on the phosphine and the Schiff base ligand.[20] Reaction with non-reducing nucleophiles such as thiocyanate or cyanide yielded only the rearranged Re^{V} complex with the nucleophile coordinated *cis* to the oxo group.[21]

Our interest in Re chemistry arises from the potential application of two Re radioisotopes, ^{186}Re (90 h $t_{1/2}$, 1.02 MeV β^-, 137 keV γ (7%)) and ^{188}Re (17 h $t_{1/2}$, 2.11 MeV β^-, 155 keV γ (15%)), to therapeutic radiopharmaceuticals.[23,24] Our earlier work suggested that Re^{III} Schiff base phosphine complexes, analogous to the Tc^{III} Q-series of complexes,[25–29] would result if the Schiff base was sufficiently rigid and the phosphine was not too strong of a nucleophile (otherwise the rearrangement/substitution path would dominate and a Re^{V} complex would form).[20] As Re^{III} complexes (d^4) are anticipated to be more substitutionally inert than Re^{V} complexes (d^2), our interest is in a path yielding the Re^{III} product, *trans*-[$Re(PR_3)_2(N_2O_2)$]$^+$.

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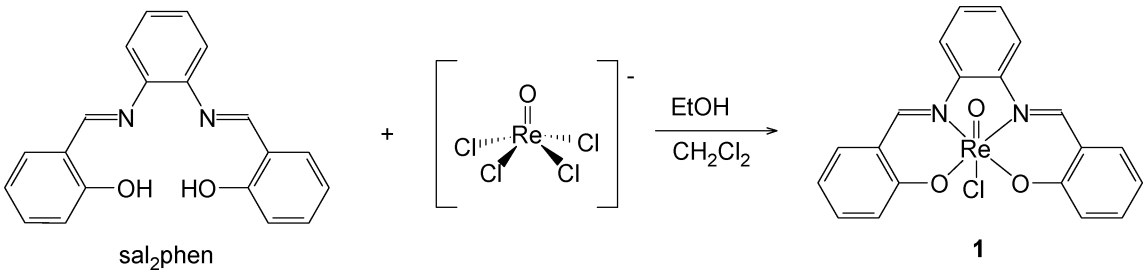

Fig. 1 Formation of the Re^{V} complex, *trans*-[ReOCl(sal_2phen)].

Here we report on Re^{V} and Re^{III} Schiff base phosphine complexes with the tetradentate Schiff base ligand *N*,*N*′-[*o*-phenylenebis(salicylaldimine)] (sal_2phen) and triphenylphosphine. Two synthetic paths were pursued, one from Re^{V} and one from Re^{III}, to probe the mechanism for forming the Re^{III} complex, *trans*-[$Re(PR_3)_2(N_2O_2$ Schiff base)]$^+$. The sal_2phen ligand was deemed a potentially rigid tetradentate Schiff base ligand with which to test our hypothesis. The mono-oxo Re^{V} complex with sal_2phen, analogous to *trans*-[ReOCl($acac_2pn$)] ($acac_2pn$ = N,N′-propylenebis(acetylacetoneimine)),[3] was synthesized, characterized, and reacted with triphenylphosphine and the Re(III) starting material [$ReCl_3(PPh_3)_2(CH_3CN)$] was reacted with sal_2phen. Several Re^{V} and Re^{III} products were isolated and characterized by their FT-IR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectra, ESI-MS spectra, elemental analyses, and single crystal X-ray structures.

Results and discussion

trans-[ReOCl(sal_2phen)] (**1**) was synthesized in 75% yield from (n-Bu_4N)[$ReOCl_4$] and sal_2phen in a manner similar to other Re^{V} Schiff base complexes (Fig. 1).[3] This synthesis is simpler and higher yielding than that previously reported without the need for column purification.[17] The product was fully characterized using a variety of spectroscopic methods. The IR band featured at 951 cm^{-1} is characteristic of the Re=O stretch and consistent with that previously reported.[17] Unique signals were observed for all sal_2phen protons in the ^{1}H NMR spectrum of **1** suggesting that the complex is slightly asymmetric. The X-ray crystal structure of **1** shows that the equatorial plane is occupied by the N_2O_2 donor atoms of the sal_2phen ligand, which is similar to our previously reported *trans*-[ReOCl($acac_2pn$)][3] but differs from Gerber *et al.* for *cis*-[ReOCl(sal_2mp)] (sal_2mp = 1,2-benzylenebis(salicylideneimine));[30] this is likely due to the rigidity of the sal_2phen backbone.

The rigidity of the sal_2phen ligand coordinated to the Re^{V} center was deemed sufficient to investigate the formation of the Re(III) species, *trans*-[$Re(PPh_3)_2(sal_2phen)$]$^+$, on reaction with the bulky triphenylphosphine. We previously reported that the rigidity of the tetradentate Schiff base ligand and the phosphine nucleophilicity and reducing power were the likely determining factors in whether a rearranged Re^{V} complex, *cis*-[$ReO(PR_3)$(Schiff base)]$^+$, or a Re^{III} complex, *trans*-[$Re(PR_3)_2$(Schiff base)]$^+$, analogous to the Tc–Q compounds was obtained.[20,27] Two synthetic approaches were used to target the desired Re^{III} complex analogous to the Tc–Q compounds (*trans*-[$Re(PR_3)_2$(Schiff base)]$^+$), substitution/reduction on *trans*-[ReOCl(Schiff base)] and substitution on [$ReCl_3(PPh_3)_2(CH_3CN)$].

The first method used to target the desired Re^{III} complex utilized the reaction of **1** with triphenylphosphine (PPh_3) in a 3.1 : 1 P : Re ratio. Depending on reaction time and solvent volume (reactant concentrations), this method resulted in the formation of three products, **2**, **4** and **5** (Fig. 2). *cis*-[$ReO(PPh_3)(sal_2phen^*)$]$^+$ (**2**) is a monosubstituted Re^{V} oxo phosphine complex in which one of the imines has been reduced to an amine. This result suggests that the ligand is reduced and rearranges faster than the metal center could be reduced.[20] *trans*-[$ReCl(PPh_3)(sal_2phen)$] (**4**) is a monosubstituted Re^{III} phosphine chloride complex. This product resulted from reduction by one triphenylphosphine *via* oxygen atom abstraction with only a single triphenylphosphine substitution. *trans*-[$Re(PPh_3)_2(sal_2phen)$]$^+$ (**5**) is the target disubstituted Re(III) phosphine complex and resulted in low yield from triphenylphosphine reduction and substitution.

A second method to target the desired Re^{III} complex involved a substitution reaction between a Re^{III} starting material, namely [$ReCl_3(PPh_3)_2(CH_3CN)$], and sal_2phen. This resulted in the isolation of a Re^{V} complex, [$ReCl_2(PPh_3)$(salphen)] (**3**), with a fragmented salphen ligand in which one salicylaldehyde unit was cleaved and the imine nitrogen had been reduced to an amine to yield a coordinated imido group (Fig. 3). This result was unexpected and may possibly be explained by rhenium's catalytic tendencies; $ReOI_3(PPh_3)_2$ is known to reduce imines to amines.[10] Organic amines have been shown to doubly deprotonate and coordinate with Re^{V} as imides.[31–33] Complex **3** is the same species reported by Gerber *et al.* from the reaction of $ReOCl_3(PPh_3)_2$ and the tridentate Schiff base ligand *N*-(2-aminophenyl)salicylideneamine), H_3apa.[31]

All Re-Schiff base-phosphine products (**2–5**) were obtained in low yield, 10–30%, and were difficult to isolate due the similarities in their chemical properties. Infrared, nuclear magnetic resonance and mass spectra assisted in determining the product formation from the various reactions. The FT-IR spectra for **1** and **2** showed a strong band at ~950 cm^{-1} corresponding to the Re=O stretch, while this band was not seen in complexes **3–5**. However, a strong absorption at 1092 cm^{-1} corresponding to the Re=N imido group in **3** is observed.

Unique ^{1}H NMR splitting patterns were observed for each of the five complexes. Proton identification was difficult in complexes **2–5** due to the multiple aromatic protons. Proton identification for the Re^{III} complex **5** was even more difficult due to the fast relaxation of the unpaired electrons,[20,34] with chemical shifts exhibited over an expanded range (–50 to 50 ppm). A single peak in the ^{31}P NMR was observed in the Re^{V} complexes **2** (24.89 ppm) and **3** (23.83 ppm). These phosphorous signals are downfield

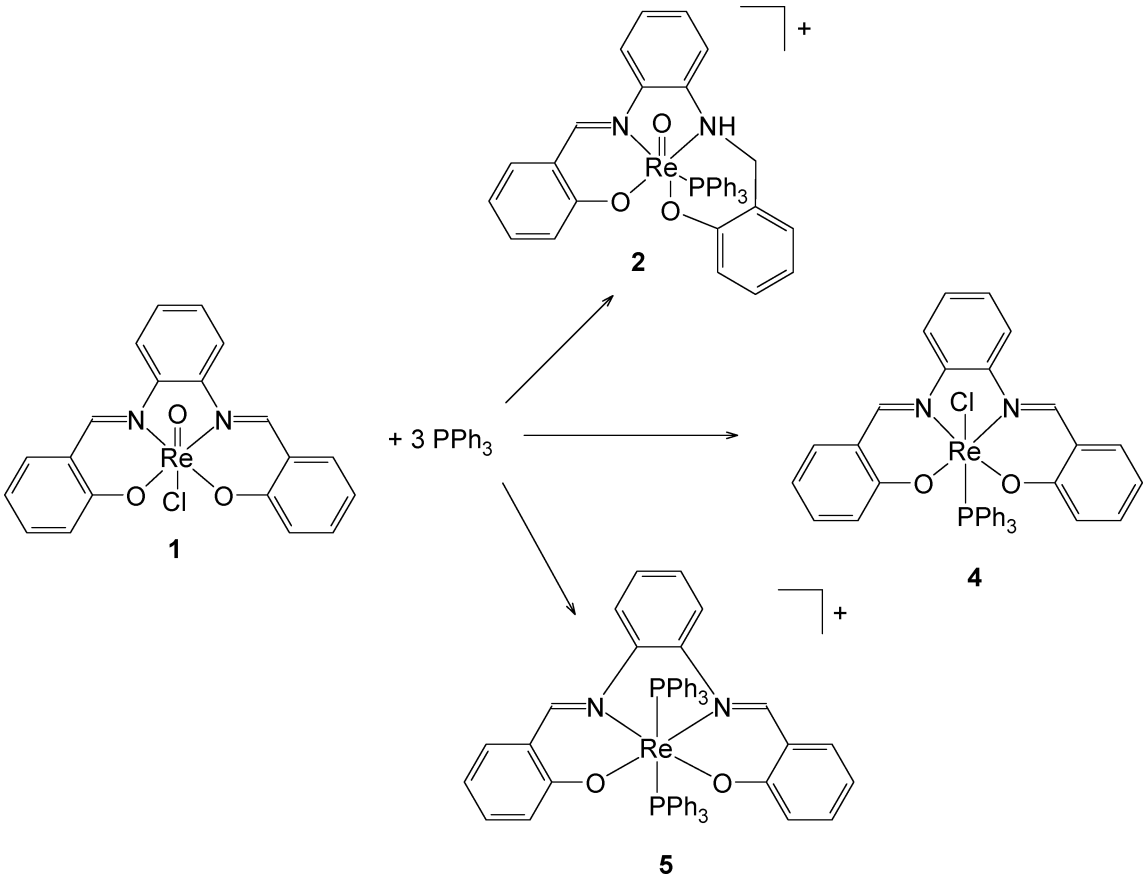

Fig. 2 Formation of Re^{V} and Re^{III} phosphine complexes on reaction of triphenylphosphine with *trans*-[ReOCl(sal_2phen)].

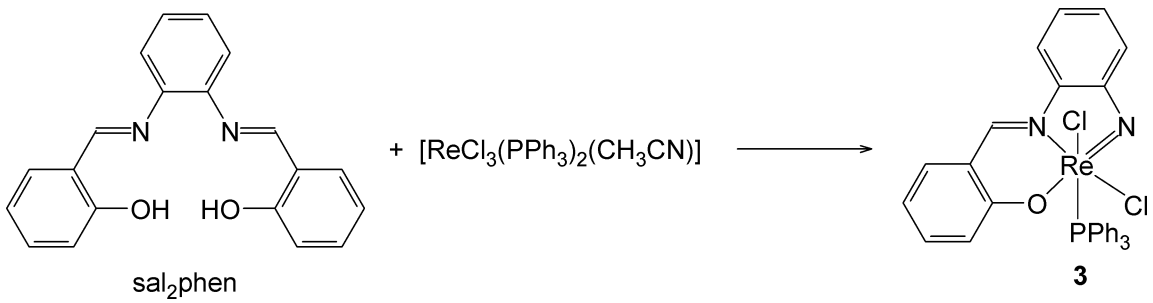

Fig. 3 Formation of Re^{V} phosphine complex on reaction of sal_2phen with $[ReCl_3(PPh_3)_2(CH_3CN)]$.

from unbound triphenylphosphine (–6 ppm) and upfield from triphenylphosphine oxide (29.8 ppm). No phosphorous signals were observed for complexes **4** and **5** due to direct coordination to the paramagnetic Re^{III} center.[20,34]

X-ray crystal structures

The Re^{V} complexes, *trans*-[ReOCl(sal_2phen)], **1**, *cis*-[ReO(PPh_3)(sal_2phen*)]PF_6, **2**, *cis*-[$ReCl_2(PPh_3)$(salphen*)], **3**, and the Re^{III} complex, *trans*-[$ReCl(PPh_3)(sal_2phen)$], **4**, were characterized by X-ray crystallography (Fig. 4–7 and Tables 1–2). All four exhibited distorted octahedral geometry and all four complexes exhibited a small (73–81.21°) bite angle for the five-membered chelate ring (NCCN) with the Re center due to the rigidity of the aromatic backbone.

trans-[ReOCl(sal_2phen)]·$CHCl_3$ (1)

Complex **1** exhibits distorted octahedral geometry with the tetradentate N_2O_2 ligand occupying the equatorial plane and a Cl coordinated in the axial position *trans* to the Re═O group (Fig. 4). The Re atom is situated 0.309(2) Å above the equatorial plane defined by the N_2O_2 donors towards the oxo group as is typically found in Re^{V} mono-oxo complexes. This structure is similar to *trans*-[ReOCl($acac_2pn$)][3] but differs from that of [ReOCl(sal_2mp)],[30] where the Re═O was *cis* to the chloride. The *trans* O═Re–Cl angle deviates slightly from linear at 174.2(1)° but falls well within the range observed for similar complexes.[3,20,27] The Re–O (1.990(3) Å), Re–N (2.054–2.061(3) Å), and Re═O (1.655(3) Å) bond distances were consistent with similar Re^{V} oxo Schiff base complexes.[2,3,12–16,18–21,30] For comparison, the *trans*

Table 1 X-ray crystal data, data collection parameters, and refinement parameters for **1**, **2**, **3** and **4**

	1	**2**	**3**	**4**
CCDC #	780136	780134	780135	780137
Formula	$C_{20}H_{14}ClN_2O_3Re{\cdot}CHCl_3$	$C_{38}H_{31}N_2O_3PRe^{+}PF_6^{-}{\cdot}0.5CH_2Cl_2$	$C_{31}H_{24}N_2OPCl_2Re{\cdot}2.5CHCl_3$	$C_{38}H_{29}ClN_2O_2PRe{\cdot}2CH_2Cl_2$
fw	671.35	968.25	1027.01	968.10
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbca*	*Pnn*2	$P\bar{1}$	*P*21/*c*
a/Å	19.4392(14)	21.0703(15)	11.1410(8)	23.0805(7)
b/Å	10.9257(8)	11.3780(8)	11.5874(8)	13.1946(4)
c/Å	21.4868(15)	15.0859(11)	17.7337(12)	25.9868(8)
α (°)	90	90	91.854(1)	90
β (°)	90	90	108.169(1)	104.447(1)
γ (°)	90	90	115.297(1)	90
V/Å^3	4563.5(6)	3616.7(4)	1929.7(2)	7663.7(4)
Z	8	4	2	8
ρ_c/g cm^{-3}	1.954	1.778	1.768	1.678
T/K	173(2)	173(2)	173(2)	173(2)
μ/mm^{-1}	5.820	3.595	3.879	3.600
λ source (Å)	0.71073	0.71073	0.71073	0.71073
Indep. Refln.	5045	7838	8290	16877
R_{int}	0.0499	0.0589	0.0251	0.0494
Obs. Refln.	30828	25028	13762	53711
R(*F*)	0.0350	0.0374	0.0515	0.0398
*R*w(*F*)^2	0.0886	0.0608	0.1139	0.0666
GoF	1.046	1.013	1.101	1.032

$R = (\Sigma \| F_O| - |F_C\|/\Sigma |F_O\|)$. $R_W = [\Sigma w(|F_O^2| - |F_C^2|)^2/\Sigma w(|F_O^2|^2]^{1/2}$.

Table 2 Selected bond angles (°) and distances (Å) for **1**, **2**, **3**, **4a** and **4b**

	1	**2**	**3**	**4a**	**4b**
Re–N1	2.061(3)	2.087(5)	2.208(7)	2.026(4)	2.024(4)
Re–N2	2.054(3)	2.199(5)	1.775(6)	2.037(4)	2.032(3)
Re–O1	1.990(3)	1.973(4)	1.891(5)	2.002(3)	1.996(3)
Re–O2	1.990(3)	1.943(3)	—	2.001(3)	2.011(3)
Re–O3	1.665(3)	1.697(4)	—	—	—
Re–P1		2.4923(16)	2.4244(16)	2.413(1)	2.422(1)
Re–Cl1	2.568(1)	—	2.4422(15)	2.455(1)	2.456(1)
Re–Cl2	—	—	2.3621(15)	—	—
N1–C3/C7	1.294(5)	1.283(8)	1.233(11)	1.318(6)	1.317(5)
N2–C6/C14	1.299(5)	1.511(7)	—	1.312(6)	1.308(5)
O1–Re–O2	85.28(12)	91.61(19)	—	97.14(12)	96.08(11)
O1–Re–N1	94.27(13)	92.08(17)	84.8(2)	90.28(13)	91.20(13)
O1–Re–N2	163.34(14)	168.84(16)	157.8(2)	170.48(13)	171.35(12)
O1–Re–O3	100.29(15)	102.69(17)	—	—	—
O1–Re–Cl1	83.04(10)	—	87.85(14)	86.85(9)	86.29(9)
O1–Re–Cl2	—	—	100.01(15)	—	—
O1–Re–P1	—	82.92(12)	87.03(14)	93.94(9)	88.85(9)
O2–Re–N1	161.21(13)	84.50(17)	—	170.81(13)	171.64(13)
O2–Re–N2	94.10(12)	80.15(19)	—	91.29(13)	91.22(12)
O2–Re–O3	102.90(14)	165.6(2)	—	—	—
O2–Re–Cl1	82.02(10)	—	—	87.88(9)	89.84(9)
O2–Re–P1	—	88.14(10)	—	87.90(9)	87.00(9)
N1–Re–N2	80.99(13)	79.72(18)	73.5(3)	80.92(14)	81.21(14)
N1–Re–O3	95.68(15)	96.48(18)	—	—	—
N1–Re–Cl1	79.29(10)	—	87.07(17)	87.13(10)	86.51(10)
N1–Re–P1	—	170.99(13)	92.61(16)	97.01(10)	97.29(10)
N1–Re–Cl2	—	—	173.39(17)	—	—
N2–Re–O3	96.08(15)	85.88(18)	—	—	—
N2–Re–Cl1	80.38(10)	—	95.20(17)	89.06(9)	89.10(10)
N2–Re–P1	—	104.15(13)	89.59(17)	90.77(9)	96.19(10)
N2–Re–Cl2	—	—	101.99(18)	—	—
O3–Re–P1	—	91.95(13)	—	—	—
P1–Re–Cl1	—	—	174.89(6)	175.77(4)	173.89(4)
P1–Re–Cl2	—	—	92.14(5)	—	—
Cl1–Re–Cl2	—	—	88.61(5)	—	—

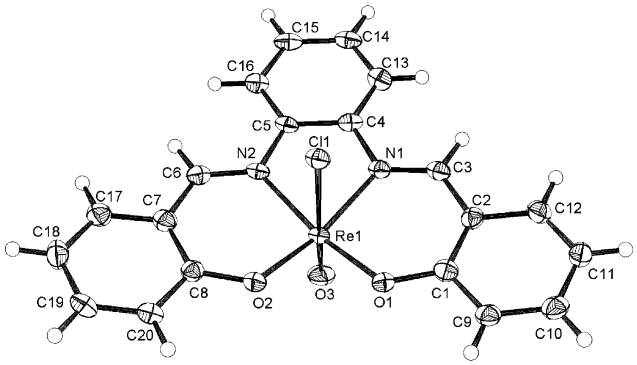

Fig. 4 ORTEP representation of *trans*-[ReOCl(sal$_2$phen)] (**1**) with 50% probability ellipsoids (CCDC# 780136). The $CHCl_3$ of solvation is omitted for clarity.

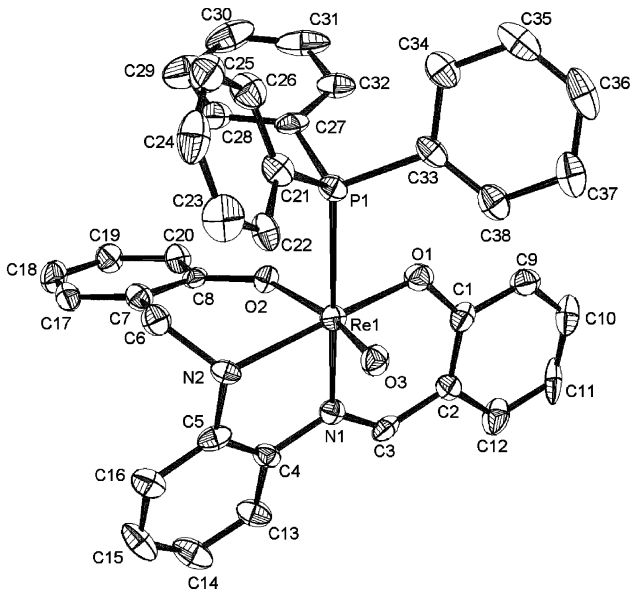

Fig. 5 ORTEP representation of *cis*-[ReO(PPh$_3$)(sal$_2$phen*)]$^+$ (**2**) with 50% probability ellipsoids (CCDC# 780134). The anion (PF_6^-) and solvent (0.5 CH_2Cl_2) are omitted for clarity.

Re–Cl bond (2.568(1) Å) was slightly longer than that of *cis*-[ReOCl(sal$_2$mp)] (2.420(1) Å) and of *trans*-[ReOCl(acac$_2$pn)] (2.468(2) and 2.464(2) Å),[3,30] and is attributed to the *trans* influence of the oxo moiety; this effect may be further enhanced by the more efficient donation of electron density to the Re atom by the sal$_2$phen ligand. The planar two carbon backbone led to a N1–Re–N2 angle of 80.99(13)° compared to 82.2(2)° in *trans*-[ReO(OH$_2$)(acac$_2$en)]Cl (also a 5-membered chelate ring).[3] Hydrogen bonding interactions (2.715–2.818 Å) are observed in the solid state between the O and/or Cl coordinated to the Re and the phenyl protons in the equatorial plane, and between the chloroform hydrogen atom (H21) (2.417–2.421 Å) and the coordinated sal$_2$phen oxygen atoms.

cis-[ReO(PPh$_3$)(sal$_2$phen*)]PF$_6$·0.5CH$_2$Cl$_2$ (2)

The X-ray crystal structure of **2** illustrates the asymmetric coordination of the sal$_2$phen ligand resulting from the coordination of triphenylphosphine *cis* to the Re^V oxo group (Fig. 5), and the reduction of one imine to an amine (from the sal fragment that

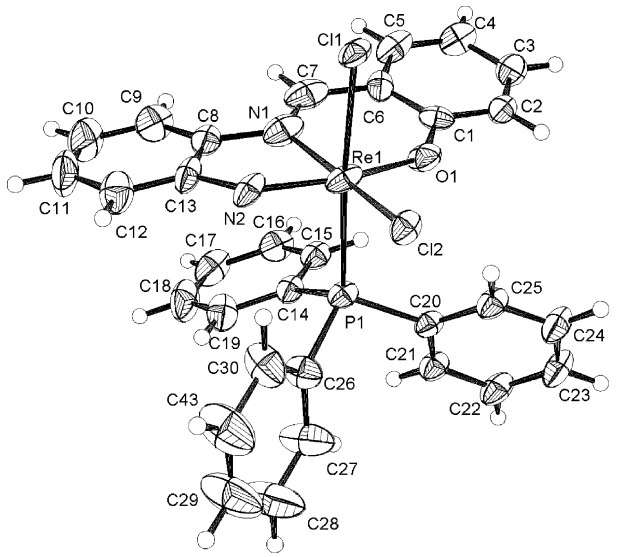

Fig. 6 ORTEP representation of [ReCl$_2$(PPh$_3$)(salphen*)] (**3**) with 50% probability ellipsoids (CCDC# 780135). The $CHCl_3$ molecules of solvation are omitted for clarity.

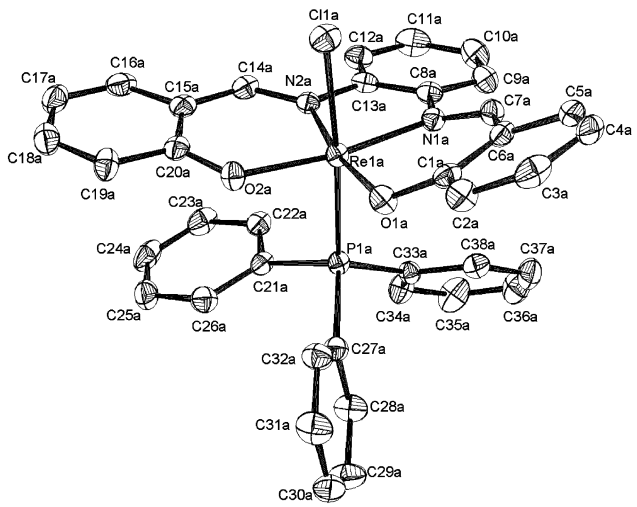

Fig. 7 ORTEP representation of *trans*-[ReCl(PPh$_3$)(sal$_2$phen)] (**4**) with 50% probability ellipsoids (CCDC# 780137). The CH_2Cl_2 molecules of solvation are omitted for clarity.

spans the equatorial and axial positions). This is very different from previous reports with the acac$_2$en and acac$_2$pn complexes, in that an imine was reduced.[20] One oxygen and two nitrogen donor atoms from sal$_2$phen* occupy three equatorial coordination sites, while the remaining phenolic oxygen donor (from the reduced sal imine fragment) coordinates in the axial position *trans* to the Re^V oxo group. This results in a distorted octahedral conformation with the Re atom situated 0.1517(20) Å above the equatorial plane (N_2OP) toward the oxo group. The Re=O bond distance of 1.697(4) Å falls within the range typically observed.[3,12–16,18–21,30] The "bite-angle" of 79.72(18)° observed for N1–Re–N2 is in line with other five-membered ring systems.[3,9,20] The Re–O and Re–N bond distances of 1.943(3)–1.973(4) Å and 2.087(5)–2.199(5) Å, respectively, are typical for Re–O and Re–N bond distances in similar complexes.[2,3,12–16,18–21,30] The longer Re–N2 bond distance of 2.199(5) Å is expected for Re-amine bonds.[35] The Re–P bond

distance of 2.4923(16) Å is within the range of Re^{V}–P bond lengths.[9,20] The Re^{V} core (O2–Re–O3) deviates from linear at 165.6(2)°, most likely due to the bulky triphenylphosphine *cis* to the oxo group and the constraints of the rearranged sal_2phen* ligand spanning an axial and three equatorial positions. An extensive hydrogen interaction network was observed in the solid state between the PF_6 anion and the complex, with distances ranging from 2.171 to 2.870 Å. The dichloromethane solvent molecule also exhibited hydrogen interactions ranging from 2.628 to 2.833 Å.

$[ReCl_2(PPh_3)(salphen)]\cdot 2.5\ CHCl_3$ (3)

Compound **3** shows a slightly distorted octahedral geometry (Fig. 6). One oxygen and two nitrogen donor atoms from the fragmented tridentate N_2O Schiff base ligand (salphen) occupy three equatorial coordination sites along with one chloride. This ligand consists of one salicylaldehyde moiety linked to one diaminobenzene and is thought to be the remnant of a reduced sal_2phen ligand in which the imine was completely reduced to an amine resulting in the loss of the second salicylic moiety. The reduction of the imine may have occurred as a result of the oxidation of Re^{III} to Re^{V} or from metal catalyzed oxidation of PPh_3; this type of reaction is not unprecedented in the literature as $ReOI_3(PPh_3)_2$ has been used in the enantioselective reduction of imines to amines.[10] The axial sites contain a PPh_3 molecule with a *trans*-coordinated chloride. The Re^{V} core (PPh_3–Re–Cl) deviates slightly from linear at 174.89(6)° and is similar to that of the Re^{V} cores (PPh_3–Re–Cl) of the tridentate phosphine complexes, *cis*-[Re(apa)$Cl_2(PPh_3)$], at 173.36(5)° and *cis*-[Re(mps)$Cl_2(PPh_3)$], at 173.15(3)°.[5,36] The *cis*-N1–Re–N2 "bite-angle" for complex **3** is 73.4(3)° and falls within the range of the similar tridentate complexes, *cis*-[Re(apa)$Cl_2(PPh_3)$], at 70.1(3)° and *cis*-[Re(mps)$Cl_2(PPh_3)$] (mps = N-(2-amino-3-methylphenyl)salicylideneimine), at 76.7(1)°.[5,30,34] The other angles (82.6(1)–87.7(3)°) around the Re center fall within the range of angles observed for similar complexes.[5,31,36] The Re–O bond distance for the equatorial oxygen atom is 1.890(5) Å, comparable to the values observed in literature of 1.866(4) and 1.928(2) Å for similar tridentate ligands.[5,31,35] The Re–N bond distances in the equatorial plane were 1.775(6) and 2.209(7) Å, indicating one imido[31,36] and one imine bond, respectively. The Re–P bond of 2.4244(16) Å is in close agreement with the Re–P bond of 2.429(2) observed in *cis*-[Re(apa)$Cl_2(PPh_3)$] by Gerber *et al.*[31] The Re–Cl bond length *trans* to the PPh_3 was longer than the *cis*-Re–Cl bond length, and is attributed to the *trans* influence of the PPh_3 moiety. Two of the three solvent chloroform molecules exhibit hydrogen bonding interactions in the solid state of 2.744–2.863 Å with the two chlorides coordinated to Re. The coordinated Cl atoms show additional hydrogen bonding interactions with hydrogen atoms on adjacent phenyl groups of 2.741–2.834 Å. The third chloroform is disordered about an inversion center.

trans-$[ReCl(PPh_3)(sal_2phen)]\cdot 2\ CH_2Cl_2$ (4)

Two independent molecules of **4** (**4a** and **4b**) were found within the unit cell. The sal_2phen ligand occupies the equatorial plane with the Re atom situated within the ligand plane, and PPh_3 and chloride occupy the axial sites. The Re^{III} core (PPh_3–Re–Cl) deviates slightly from linear at 175.77(4)° and 173.89(4)° for both molecules. The two molecules (**4a** and **4b**) have very similar bond distances and bond angles. The *cis*-N1–Re–N2 "bite-angle" was 80.92(14)° for **4a** and 81.21(14)° for **4b**. The Re–O (1.996(3)–2.011(3) Å) and Re–N (2.024(4)–2.037(4) Å) bond distances are similar to other Re^{III}–N and Re^{III}–O bond distances.[37–40] The Re–P and bond lengths in the axial positions ranged from 2.4128(11)–2.4218(12) Å and were shorter than the Re–P bonds of *trans*-$[Re(PPh_3)_2(acac_2en)]PF_6$ (2.4820(11)–2.4992(11) Å; $acac_2en$ = N,N′-ethylenebis(acetylacetoneimine)).[20] The Re–Cl bonds were 2.4550(11)–2.4563(11) Å and were within the range of Re–Cl bond lengths. The dichloromethane is involved in hydrogen bonding interactions in the solid state with the Cl atom at 2.847 Å and with the phenyl groups coordinated to phosphorus at 2.844 Å. The bound Cl atom also showed a hydrogen bonding interaction of 2.870 Å with a hydrogen atom on the phenyl group of an adjacent PPh_3.

Experimental

General considerations

All chemicals were of regent grade or better and solvents were degassed before using. All experiments were carried out under a nitrogen atmosphere unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on a Bruker 250 or 500 MHz instrument at 25 °C in deuterated solvent (d^6-DMSO or $CDCl_3$) with TMS as an internal reference. ^{31}P NMR spectra were recorded on a Bruker 250 MHz instrument at 25 °C in deuterated solvent (d^6-DMSO or $CDCl_3$) with H_3PO_4 as an external reference. FT-IR spectra were recorded in the range of 4000–400 cm^{-1} as KBr pellets on a Nicolet Magna-IR spectrometer 550. Electrospray Ionization Mass Spectra (ESI-MS) were obtained on a Thermo Finnigan TSQ7000 triple-quadrupole instrument with an API2 source. Elemental analyses were performed by Quantitative Technologies Inc. (QTI; Whitehouse, NJ).

Materials. $(n\text{-}Bu_4N)(ReOCl_4)$[41] and $[ReCl_3(PPh_3)_2(CH_3CN)]$[42] were prepared as reported in the literature. The sal_2phen ligand was synthesized according to the literature.[1]

***trans*-[ReOCl(sal_2phen)], (1).** $(n\text{-}Bu_4)[ReOCl_4]$ (186 mg, 0.318 mmol) in $CHCl_3$ (10 mL) was added to a solution of sal_2phen (207 mg, 0.653 mmol) in ethanol (15 mL). The solution was refluxed for 3 h under a nitrogen atmosphere and placed in a freezer overnight. The maroon product was collected by vacuum filtration. The product washed with hot toluene and ether to remove any remaining starting material and byproducts. The solid product was dissolved in chloroform and placed in a screw-top vial with the cap slightly opened. After several days, crystals had formed. Yield: 75%. ^1H NMR [d^6-DMSO, 500 MHz; δ (ppm)]: 7.16 (t, 1H), 7.26 (t, 1H), 7.37 (d, 1H), 7.50 (d, 1H), 7.78 (sextet, 1H), 7.82 (sextet, 1H), 7.84 (ddd, 1H), 7.95 (ddd, 1H), 8.03 (dd, 1H), 8.16 (dd, 1H), 8.53 (sextet, 1H), 8.60 (sextet, 1H), 10.41 (s, 1H), 10.42 (s, 1H). ^{13}C NMR [d^6-DMSO, 250 MHz; δ (ppm)]: 179.43, 176.28, 173.29, 172.98, 151.47, 150.02, 141.00, 140.06, 139.82, 139.59, 131.44, 131.27, 122.31, 121.54, 121.45, 120.61, 119.56. IR (KBr, ν in cm^{-1}): 951 (m, Re═O). MS (m/z): $[M–Cl]^+$ 517.04 (517.07 calcd). Anal. Found: C, 43.36; H, 2.91; N, 5.06; Cl, 6.40. Calcd for $ReC_{20}H_{14}N_2O_3Cl$: C, 43.13; H, 2.50; N, 5.27; Cl, 6.71.

***cis*-[ReO(PPh$_3$)(sal$_2$phen*)]PF$_6$·CH$_2$Cl$_2$, (2).** Triphenylphosphine (143 mg, 0.546 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **1** (100 mg, 0.181 mmol) in ethanol (10 mL). The solution was refluxed for 2.5 h under a nitrogen atmosphere, after which the solvent was removed under vacuum. The maroon-colored product was washed with hot hexane and ether to remove ligand by-products (*i.e.*, phosphine oxide, sal$_2$phen fragments). Ammonium hexafluorophosphate (NH_4PF_6) (11 mg, 0.067 mmol) was dissolved in CH_2Cl_2 (5 mL) and added to the product in CH_2Cl_2. X-ray quality crystals were obtained by the slow evaporation of $CDCl_3$ in an NMR tube at ambient temperature. Yield: 30%. ^{1}H NMR [$CDCl_3$, 500 MHz; δ (ppm)]: 3.96 (d, 2H); 6.65 (m, 2H); 6.87 (m, 2H); 6.95 (m, 2H); 7.31 (m, 3H); 7.44 (m, 7H); 7.51 (m, 6H); 7.64 (m, 6H); 7.90 (m, 2H); 8.55 (s, 1H); 9.55 (s, 1H). ^{31}P NMR [d^6-DMSO, 250 MHz; δ (ppm)]: 21.87. IR (KBr, ν in cm^{-1}): 951 (m, Re═O). MS (*m*/*z*): [M–Cl–M, Chloride bridged dimer]$^+$ 1597.78 (1597.32).

[ReCl$_2$(PPh$_3$)(salphen)]·2 CHCl$_3$, (3). [$ReCl_3(PPh_3)_2(CH_3CN)$] (50 mg, 0.063 mmol) in $CHCl_3$ (5 mL) was added to a solution of sal$_2$phen (20 mg, 0.063 mmol) in ethanol (5 mL). The orange-brown solution was refluxed for 2 h, and filtered through a medium glass frit to remove the yellow unreacted sal$_2$phen starting material. The filtrate was then dried under vacuum and sonicated in toluene to remove the green-brown unreacted [$ReCl_3(PPh_3)_2(CH_3CN)$] starting material. The purified product was then dissolved in $CDCl_3$ and placed in an NMR tube. Slow evaporation of the solvent resulted in crystal formation. Yield: 15%. ^{1}H NMR [d^6-DMSO, 500 MHz; δ (ppm)]: 5.84 (t, 1H); 6.13 (d, 1H); 6.21 (d, 1H); 7.15 (t, 1H); 7.29 (m, 9H); 7.54 (m, 1H); 7.61 (m, 2H); 7.68 (m, 6H); 8.78 (m, 1H); 13.81 (d, 1H). ^{31}P NMR [d^6-DMSO, 250 MHz; δ (ppm)]: 24.67. IR (KBr, ν in cm^{-1}): 1092 (Re═N). MS (*m*/*z*): [M+Na]$^+$ 751.16 (751.05).

***trans*-[ReCl(PPh$_3$)(sal$_2$phen)]·2 CH$_2$Cl$_2$ (4).** Triphenylphosphine (74 mg, 0.282 mmol) in CH_2Cl_2 (5 mL) was added to **1** (50 mg, 0.091 mmol) in ethanol (20 mL). The burgundy solution was refluxed under N_2 for 12 h. The brown reaction mixture volume was reduced to dryness under vacuum. The dark brown solid was washed with toluene and filtered. The dark brown solid was washed with ether and then dried in air overnight. Small, orange crystals were obtained by slow vapor deposition of dichloromethane into hexane in a scintillation vial. Yield: 10%. ^{1}H NMR [$CDCl_3$, 500 MHz; δ (ppm)]: –22.44 (d; 2H); –9.18 (t; 2H); –6.68 (d; 2H); 3.46 (m; 2H); 7.30 (m; 2H); 7.61 (b; 6H); 7.90 (t; 6H); 8.26 (t; 3H); 21.65 (t; 2H); 30.89 (d; 2H). MS (*m*/*z*): [M$^{\bullet}$]$^+$ 798.05 (798.12).

***trans*-[Re(PPh$_3$)$_2$(sal$_2$phen)]Cl (5).** Triphenylphosphine (1.47 g, 5.61 mmol) was added to **1** (1 g, 1.81 mmol) in ethanol (10 mL). The burgundy solution was refluxed for 12 h. The reaction mixture volume was reduced to dryness in vacuum. The grey solid was washed with toluene that resulted in a red-brown solid once filtered through a glass frit. The solid filtrate was washed with ether and then dried in air. Yield: 10%. ^{1}H NMR [d^6-DMSO, 250 MHz; δ (ppm)]: –22.51 (d; 2H); –8.88 (t; 2H); –7.47 (m; 2H); 6.68 (d; 12H); 7.25 (t; 12H); 7.75 (m; 4H); 8.43 (t; 6H); 20.26 (t; 2H); 30.52 (d; 2H). MS (*m*/*z*): [M$^+$] 1025.20; calcd 1025.24.

X-ray structure determinations and refinements for 1, 2, 3 and 4

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 multi-scan method. Space group, lattice parameters and other relevant information are given in Table 1. The structures were solved by direct methods with full-matrix least-squares refinement, using the SHELX package.[43,44] 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

In conclusion, the steric constraints imposed by the *o*-phenylenediimine backbone did not afford a Re^{III} complex without complications and ligand fragmentation. Obviously more than just size and rigidity of the tetradentate Schiff base ligand and nucleophilicity and reducing power of the phosphine determine the final product(s). The sal$_2$phen ligand's delocalized electron density did not assist in the reduction of Re^V to Re^{III} or afford substitution onto the Re^{III} starting material. Rhenium's catalytic tendencies, which are said to approach those of Ni and Pt, must be considered when working with rhenium compounds. One of the most versatile transition metal catalysts is methyltrioxorhenium(VII) (MTO).[8,12] Rhenium(V) oxo complexes have been reported to be involved in reduction, oxygen atom transfer, hydrosilation and silane alcoholysis reactions.[4–10] This reactivity is very different from that reported for analogous Tc complexes, and perhaps more than redox and substitution rate differences must be considered in designing radiopharmaceuticals based on Re.

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