P. Mayer, N.C. Yumata, T.I.A. Gerber and A. Abrahams,
S. Afr. J. Chem., 2010, **63**, 180–185,
<http://journals.sabinet.co.za/sajchem/>.

Coordination of the Bidentate Ligands 2,2′-Dipyridylamine, 1-Phenyl-1,3-butadione and *N*′-(Propan-2-ylidene)benzohydrazide to Rhenium(III)

Peter Mayer[1], **Nonzaliseko C. Yumata**[2], **Thomas I.A. Gerber**[2,*], **Abubak'r Abrahams**[2]

[1] *Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany.*
[2] *Department of Chemistry, Nelson Mandela Metropolitan University, 6031 Port Elizabeth, South Africa.*

Received 11 September 2010, revised 16 October, accepted 28 October 2010.

ABSTRACT

The reaction of *trans*-[ReCl$_3$(MeCN)(PPh$_3$)$_2$] with 1-phenyl-1,3-butadione (Hbat), 2,2′-dipyridylamine (dpa), and 1-(2-hydroxyphenyl)ethanone benzoylhydrazone (Hhaep) under nitrogen led to the respective complexes *cis*-[Re^{III}Cl$_2$(bat)(PPh$_3$)$_2$], *fac*-[Re^{III}Cl$_3$(dpa)(PPh$_3$)] and *cis*-[Re^{V}OCl$_2$(meb)(PPh$_3$)] (meb = *N*′-(propan-2-ylidene)benzohydrazide). All the complexes were characterized by ^{1}H NMR and infrared spectroscopy, and X-ray crystallography.

KEYWORDS

Rhenium(III) , bidentate ligands, crystal structures.

1. Introduction

There is currently considerable interest in the coordination chemistry of rhenium, mainly because of the potential applications of its $^{186/188}$Re radionuclides in radiotherapy.[1,2] The main focus is on the +I (d^6) and +V (d^2) oxidation states of the metal, since they are stabilized by a large variety of ligands and can be easily accessed by a large variety of synthons. In comparison, the coordination chemistry of rhenium(III) has received relatively little interest.[3]

Acetylacetone (Hacac) and its derivatives have been shown to be versatile ligands in coordination chemistry, and they have a propensity to stabilize metals in the +III oxidation state.[4] With rhenium, the compound [Re(acac)$_3$] has been isolated.[5] Also, the reaction of Hacac with [Re^{V}OCl$_2$(OEt)(PPh$_3$)$_2$] led to the isolation of the [Re^{III}Cl$_2$(acac)(PPh$_3$)$_2$] complex, which could also be prepared by the reaction of [Re^{IV}Cl$_4$(PPh$_3$)$_2$] with Hacac.[6]

The polypyridyl ligand 2,2′-dipyridylamine (dpa) is an important chelate due to its ability to form hydrogen-bonded networks through the active amine, and to luminescence through π-π* transitions.[7] Thus, the advantage of the amine group in dpa over polypyridines like 2,2′-bipyridine and 1,10-phenanthroline without such tailoring may lead to the formation of superstructures.[8] The ability of dpa to coordinate as a bidentate chelate to transition metal ions is well established.[9–11] The two-ring nitrogen atoms act as electron-pair donors in the most complexes, although some examples exist in which the bridging amino nitrogen also has donor properties.[12]

It is well-known that aroylhydrazone complexes of transition metal ions are known to act as models for enzyme inhibition, and are useful for their pharmacological applications.[13,14] Hydrazone complexes have also been the subject of study for many years due to their antimicrobial and anti-tumour activities.[15,16] It is especially the benzoylhydrazone complexes of copper, vanadium, ruthenium and manganese that have been extensively studied.[17–20]

In this study, the coordination behaviour of the common bidentate ligands benzoylacetone (1-phenyl-1,3-butadione; Hbat; *O,O*-donor) and 2,2′-dipyridylamine (dpa; *N,N*-donor), who both form six-membered metallocycles on coordination to metals, towards *trans*-[ReCl$_3$(MeCN)(PPh$_3$)$_2$], a useful precursor in the synthesis of rhenium(III) complexes,[21–23] was investigated. The study was extended to also include the *N,O*-donor ligand 1-(2-hydroxyphenyl)ethanone benzoylhydrazone (Hhaep). However, in the reaction Hhaep decomposed to Hmeb, and produced [Re^{V}OCl$_2$(meb)(PPh$_3$)] as product.

2. Experimental

2.1. Materials

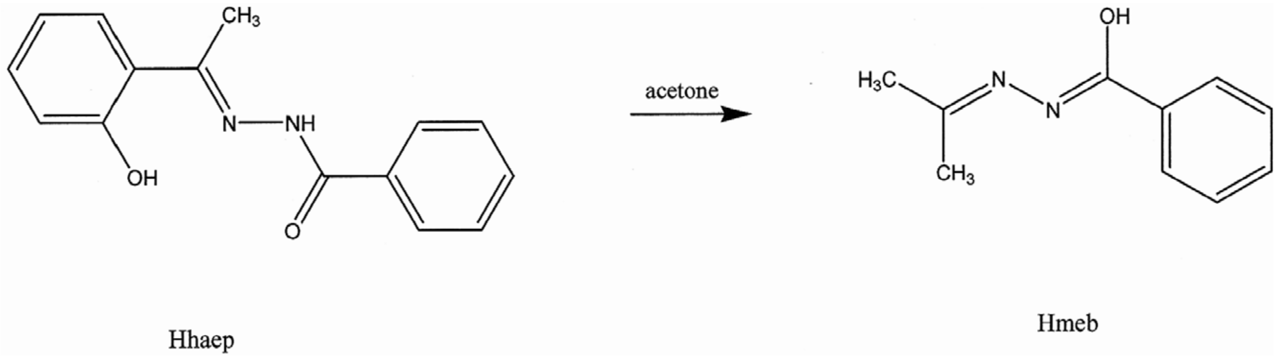
All chemicals were of reagent grade, and solvents were purified by standard techniques and drying methods. Benzoylacetone (Hbat) and 2,2′-dipyridylamine (dpa) were obtained commercially from Aldrich and were reacted without further purification after their purity was verified by ^{1}H NMR and melting point. 1-(2-Hydroxyphenyl)ethanone benzoylhydrazone (Hhaep) and *trans*-[ReCl$_3$(MeCN)(PPh$_3$)$_2$] were prepared by literature procedures.[21,24]

2.2. Physical Measurements

^{1}H NMR spectra were recorded in d_6-DMSO on a Bruker AX (300 MHz) spectrometer (Bruker, Johannesburg, South Africa) at ambient temperatures, and values are reported relative to TMS. Infrared spectra were obtained with a Digilab FTS 3100 Excalibur HE spectrophotometer (SMM Instruments, Randburg, South Africa) with solid samples prepared as KBr disks. Electronic spectra were obtained by a Shimadzu UV-3100 spectrophotometer (Labworld, Centurion, South Africa). Melting points were determined using an Electrothermal 1A-9100 melting point apparatus (Chula Vista, CA, USA). Conductivity measurements were carried out in DMF at 293 K on a Phillips PW 9509 digital conductometer (PANalytical, Randburg, South Africa). Microanalyses were obtained on a Carlo Erba EA 1108 elemental analyzer (Waltham, MA, USA).

---

* To whom correspondence should be addressed. E-mail: thomas.gerber@nmmu.ac.za



Scheme 1

2.3. Synthesis of the Complexes

2.3.1. *cis-[ReCl$_2$(bat)(PPh$_3$)$_2$]* (**1**)

A mixture of *trans*-[ReCl$_3$(MeCN)(PPh$_3$)$_2$] (200 mg, 237 μmol) and Hbat (90 mg, 555 μmol) in acetonitrile (15 cm^3) was heated at reflux for 8 hours under nitrogen. The maroon precipitate separated upon cooling, and was removed by filtration. Recrystallization from a 1:1 mixture of dichloromethane:ethanol gave maroon, diamond-shaped crystals suitable for X-ray diffraction studies. Yield = 63 %, m.p. 238–242 °C. Anal. Calc. for $C_{28}H_{24}O_2Cl_2PRe$ (%): C, 35.67; H, 2.57. Found: C, 35.59; H, 2.62. Infrared (cm^{-1}): ν(C=O) 1653, 1636 (s); ν(C=C) 1540, 1558 (s). Electronic spectrum (λ_{max}, nm/ε, M^{-1} cm^{-1}): 426 (6800); 546 (2360). Conductivity (10^{-3} M): 42 ohm^{-1}cm^{2}mol^{-1}.

2.3.2. *fac-[ReCl$_3$(dpa)(PPh$_3$)]* (**2**)

To a 200 mg (237 μmol) suspension of *trans*-[ReCl$_3$(MeCN)(PPh$_3$)$_2$] in acetonitrile (6 cm^3) was added 811 mg (492 μmol) of dpa dissolved in acetonitrile (8 cm^3) under nitrogen. The reaction mixture was heated under reflux for 2 hours, cooled to room temperature, and a brown precipitate was removed by filtration and dried under vacuum. The mother liquor was left to evaporate slowly at room temperature. After two days dark brown crystals, suitable for X-ray diffraction studies, were collected by filtration. Yield = 62 %, m.p. 217–220 °C. Anal. Calc. for $C_{28}H_{24}N_3Cl_3PRe$ (%): C, 46.32; H, 3.33; N, 5.79. Found: C, 46.27; H, 3.29; N, 5.76. Infrared (cm^{-1}): ν(N-H) 3234 (m); ν(C=N) 1660, 1631(m); ν(C=C) 1560 (m); ν(Re-N) 512 (s). ^{1}H NMR (DMSO-d_6): 8.38 (s, N*H*); 7.63–7.80 (m, 15H, P*Ph*$_3$); 7.54 (d, 2H, *H*^{1}, *H*^{6}); 7.23 (t, 2H, *H*^{3}, *H*^{8}); 7.34 (d, 2H, *H*^{4}, *H*^{9}); 7.10 (t, 2H, *H*^{2}, *H*^{7}). Electronic spectrum (λ_{max}, nm/ε, M^{-1} cm^{-1}): 257 (14000); 315 (7820). Conductivity (10^{-3} M): 44 ohm^{-1} cm^{2}mol^{-1}.

2.3.3. c*is-[ReOCl$_2$(meb)(PPh$_3$)]* (**3**)

Hhaep (579 mg, 228 μmol) was added to a solution of *trans*-[ReCl$_3$(MeCN)(PPh$_3$)$_2$] (100 mg, 119 μmol) in acetone (15 cm^3) and the mixture was stirred at reflux for 3 hours under nitrogen. The colour of the reaction mixture turned green and, after cooling to room temperature, the solution was filtered and left to evaporate slowly at room temperature. After two days green X-ray quality crystals were collected by filtration. Yield = 70 %. Anal. Found (%): C, 47.30; H, 3.67; N, 3.90. Calc (%): C, 47.33; H, 3.69; N, 3.94. Infrared (cm^{-1}): ν(Re=O) 979(s); ν(C=N) 1599(s); ν(Re-N) 527(m); ν(Re-O) 498(m). Electronic spectrum (CH_2Cl_2) [λ_{max}, nm/ε, M^{-1} cm^{-1}): 324 (12850); 458 (510); 673 (1640). Conductivity (10^{-3} M): 44 ohm^{-1} mol^{-1} cm^2.

2.4. X-ray Crystallography

Intensity data for **1–3** were collected on a Nonius Kappa CCD diffractometer at 200(2) K with Mo K$_\alpha$ radiation (λ = 0.71073 Å). The structures were solved by direct methods and were refined by full-matrix least-squares procedures using SHELXL-97.[25] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were calculated in idealized geometrical positions. The data were corrected by a numerical absorption correction[26] after optimizing the crystal structures with XShape.[27] Details of the crystal data, measurement of intensities and data processing are summarized in Table 1.

3. Results and Discussion

3.1. Synthesis and Spectral Characterization of 1 and 2

Complexes **1** and **2** were prepared in good yields by the ligand exchange reactions of [ReCl$_3$(MeCN)(PPh$_3$)$_2$]. Prolonged heating was required to form and isolate the products, and no products with sensible analyses could be isolated for heating periods less than an hour.

The complexes **1** and **2** are soluble in a variety of solvents including acetone, acetonitrile, DMF and DMSO. They are insoluble in water, alcohols and benzene, have a low solubility in chlorinated solvents, and are stable for months in the solid state and for days in solution. The conductivity values in DMF confirm that the complexes are non-electrolytes. Conductivity readings between 65 and 90 ohm^{-1} cm^{-2} mol^{-1} in DMF are consistent with 1:1 electrolytes.[28]

The infrared spectrum of **1** displays strong absorption bands in the 1630–1660 cm^{-1} region which are attributable to the C=O stretching frequency. The C=C stretching vibrations were observed in the 1540–1560 cm^{-1} region. In the electronic spectrum an absorption band at 426 nm is assigned to a ligand-to-metal charge transfer and a *d-d* transition of the complex is supported by the presence of the absorption band at 546 nm. The proton NMR spectrum consists of poorly-resolved broad peaks, showing paramagnetic shifts and line broadening of the signals.

The weak absorption band at 3234 cm^{-1} in the infrared spectrum of **2** confirms that the amino nitrogen of dpa remains protonated on complexation to the metal. The coordination of the two pyridinyl nitrogens of dpa is evidenced by the shift of ν(C=N) from 1676 cm^{-1} in the free ligand to the 1630–1660 cm^{-1} region. A broad absorption band at 512 cm^{-1} is attributed to ν(Re-N). The ^{1}H NMR signals are surprisingly sharp and well resolved. A 15-proton multiplet in the range 7.60–7.80 ppm illustrates the presence of the triphenylphoshine group. The broad singlet of the NH proton appears far downfield at 8.38 ppm. Only four signals that integrate for two protons each were observed for the eight aromatic protons of dpa, indicating that the two pyridine rings of dpa are chemically and magnetically equivalent. The expected splitting pattern of doublet-doublet-triplet-triplet is observed for these protons. The pyridinyl protons *H*^{1} and *H*^{3} are shifted upfield at 7.54 and

Table 1 Crystal and structure refinement data for **1**, **2** and **3**.

	1	**2**	**3**
CCDC	781993	778196	780531
Chemical formula	$C_{46}H_{39}Cl_2O_2P_2Re$	$C_{28}H_{24}Cl_3N_3Re$	$C_{28}H_{26}Cl_2N_2O_2Re$
Formula weight	942.86	726.05	710.604
Temperature/K	200	200	200
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	13.0553(3)	8.1956(4)	10.5768(2)
b/Å	16.9817(3)	17.6815(6)	18.4147(3)
c/Å	17.9209(4)	19.879(1)	14.7304(3)
β (°)	101.403(2)	93.844(2)	106.145(2)
Volume/$Å^3$	3894.66(14)	2874.1(2)	2755.87(9)
Z	4	4	4
Density (calc.)/g cm^{-3}	1.608	1.678	1.713
F(000)	1880	1416	1392
Crystal size/mm	0.02 × 0.13 × 0.36	0.03 × 0.03 × 0.09	0.17 × 0.18 × 0.20
θ range for data collection/°	4.2–26.3	3.3–24.4	4.2–26.3
Index ranges	$-16 \leq h \leq 16$ $-21 \leq k \leq 19$ $-20 \leq \ell \leq 22$	$-9 \leq h \leq 9$ $-20 \leq k \leq 20$ $-23 \leq \ell \leq 23$	$-12 \leq h \leq 13$ $-21 \leq k \leq 22$ $-18 \leq \ell \leq 18$
Observed data [I>2.0 $\sigma(I)$]	5308	3674	4263
Parameters	479	325	327
Goodness-of-fit on F^2	0.083	1.08	1.01
Final R indices: R	0.0293	0.0343	0.0235
$wR2$	0.0484	0.0860	0.0456
Largest diff. peak/hole/e $Å^{-3}$	1.36/–1.28	1.10/–1.02	0.99/–0.46

7.23 ppm from their expected diamagnetic positions, with upfield shifts also observed for H^4. The electronic absorption spectrum in DMF is characterized by two intense absorption bands at 257 and 315 nm. These transitions have been previously assigned to the intraligand $\pi \rightarrow \pi^*$ transitions of the pyridine rings of dpa.[7]

3.2. Crystal Structure of *cis*-[ReCl$_2$(bat)(PPh$_3$)$_2$] (1)

The X-ray structure determination reveals that the rhenium(III) atom resides in a distorted octahedral environment surrounded by the two oxygen atoms O(1) and O(2) (originating from bat), the two chlorides Cl(1) and Cl(2) and two *trans* triphenylphosphines (Fig. 1). Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear P(1)-Re-P(2) axis of 174.75(3) °, accomplished by Cl(1)-Re-O(1) and Cl(2)-Re-O(2) angles of 174.52(7) ° and 173.95(7) °, respectively (Table 2). The rhenium atom is displaced slightly out of the mean O_2Cl_2 equatorial plane by 0.0057(1) Å towards P(1), which results in the non-orthogonal angles P(1)-Re-O(1) = 88.69(8) °, P(1)-Re-O(2) = 92.00(7) °, P(1)-Re-Cl(1) = 91.77 (3) ° and P(1)-Re-Cl(2) = 87.40(3) °. The O(1)-Re-O(2) bite angle of bat equals 86.95(9) °.

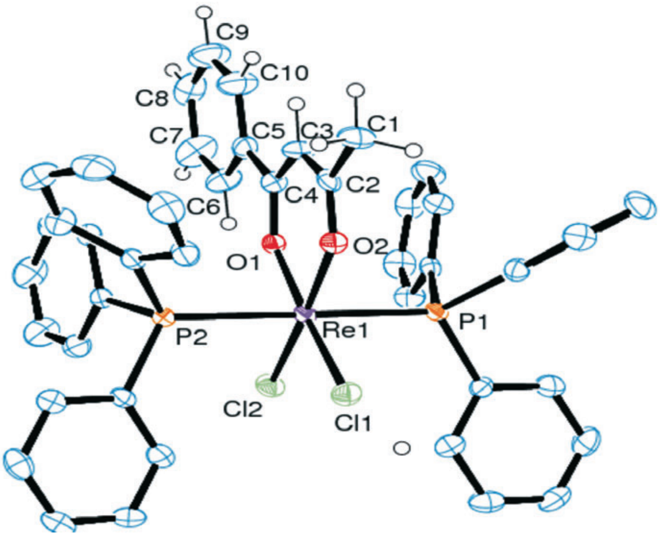


Figure 1 ORTEP diagram of the molecular structure of **1**.

The Re-Cl [average = 2.3771(9) Å] and Re-O [average = 2.024(2) Å] bond lengths are close to those observed in the rhenium complex [ReCl$_2$(acac)(PPh$_3$)$_2$] (acac = acetylacetonate),

Table 2 Selected bond lengths [Å] and angles [°] for **1**.

Re-Cl(1)	2.376(9)	Re-O(1)	2.022(2)
Re-Cl(2)	2.378(9)	Re-O(2)	2.025(2)
Re-P(1)	2.459(1)	O(1)-C(4)	1.300(4)
Re-P(2)	2.479(1)	O(2)-C(2)	1.260(4)
C(2)-C(3)	1.405(5)	C(1)-C(2)	1.497(5)
C(3)-C(4)	1.391(5)	C(5)-C(6)	1.367(5)
C(4)-C(5)	1.484(5)	C(5)-C(10)	1.375(5)
C(6)-C(7)	1.377(5)	C(7)-C(8)	1.381(7)
C(8)-C(9)	1.344(7)	C(9)-C(10)	1.378(5)
GAP			
Cl(1)-Re-O(1)	174.52(7)	Cl(2)-Re-O(1)	87.02(7)
Cl(1)-Re-O(2)	87.58(7)	Cl(2)-Re-O(2)	173.95(7)
Cl(1)-Re-Cl(2)	98.46(3)	Cl(2)-Re-P(1)	87.40(3)
Cl(1)-Re-P(1)	91.77(3)	Cl(1)-Re-P(2)	92.57(3)
Cl(1)-Re-P(2)	92.15(3)	P(1)-Re-P(2)	174.75(3)
P(1)-Re-O(1)	88.69(8)	P(2)-Re-O(1)	87.74(8)
P(1)-Re-O(2)	92.00(7)	P(2)-Re-O(2)	91.66(7)
O(1)-Re-O(2)	86.95(9)	Re-O(2)-C(2)	129.9(2)
O(1)-C(4)-C(3)	123.30(3)	C(1)-C(2)-C(3)	119.2(3)
O(2)-C(2)-C(1)	116.10(3)	C(3)-C(4)-C(5)	122.1(3)
O(2)-C(2)-C(3)	124.60(3)	C(4)-C(5)-C(6)	119.5(3)

where the corresponding average values are 2.369(4) Å and 2.03(1) Å. The Re-P lengths of 2.459(1) Å and 2.479(1) Å agree well with the average of 2.470 Å found in other rhenium(III) complexes containing two *trans* triphenylphosphine ligands.[9,30]

Bond distances and angles in the benzoylacetone ligand are normal, and show that bat acts as a monoanionic bidentate chelate. The intraligand bond lengths do not differ much from the corresponding ones of acac in [ReCl$_2$(acac)(PPh$_3$)$_2$].[31] The atoms O(1)C(4)C(3)C(1)O(2) are coplanar, which means that the ligand coordinates in the pseudo-aromatic form. The O(2)C(2)C(3)C(4) and C(2)C(3)C(4)O(1) torsion angles are –2.2(6) ° and 1.0(6) °, respectively. The bond angle C(2)-C(3)-C(4) equals 125.5(3) °, which illustrates that C(3) is sp^2 hybridized, with the angles O(1)-C(4)-C(3) [123.3(3) °] and O(2)-C(2)-C(3) [124.6(3) °] also intimating sp^2 hybridization of C(4) and C(2). The similarity of the O(1)-C(4) [1.300(4) Å] and O(2)-C(2) [1.260(4) Å] bond lengths, and the C(2)-C(3) [1.405(5) Å] and C(3)-C(4) [1.391(5) Å] lengths, illustrate delocalization in the coordination metallocycle. The C(1)-C(2) bond is single [1.497(5) Å], with the average C-C bond length in the phenyl ring equal to 1.370(5) Å, as expected for an aromatic ring.

3.3. Crystal Structure of *fac*-[ReCl$_3$(dpa)(PPh$_3$)] (2)

Figure 2 depicts the ORTEP drawing of **2**, showing the atom numbering scheme. The rhenium atom is at the centre of a distorted octahedral environment with the three chlorides arranged in a *facial* geometry. The basal plane is defined by the two nitrogen atoms N(1) and N(3) of dpa and the two *cis* chlorides Cl(1) and Cl(2). The phosphorus atom P and Cl(3) lie in *trans* axial positions. Distortion from an ideal octahedral environment results in a non-linear Cl(3)-Re-P axis of 175.89(6) °, with the remaining *trans* angles Cl(2)-Re-N(1) = 173.44(2) ° and Cl(1)-Re-N(3) = 174.80(2) ° also deviating from linearity. The rhenium atom is displaced out of the mean N$_2$Cl$_2$ equatorial plane by 0.050 Å towards P. This results in the non-orthogonal angles P-Re-Cl(1) = 86.63(6) °, P-Re-Cl(2) = 89.34(7) °, P-Re-N(1) = 92.79(2) ° and P-Re-N(3) = 96.97(2) °. The N(1)-Re-N(3) bite angle of dpa equals 83.4(2) °, which is significantly smaller than in other six-membered metallocyclic dpa complexes of copper(II) and cobalt (II), where it varies from 88.0(2) ° to 91.2(2) °.[10] The C-C-N angles at the ring junctions are close to 120 ° with bond angles of C(5)-C(4)-N(1) = 121.9(5) ° and C(9)-C(10)-N(3) = 122.6(6) °.

The bond distancs (Table 3) of rhenium with the donor atoms support its oxidation state of +III. The Re-P, Re-N and Re-Cl distances are similar to those found for other rhenium(III) polypyridyl complexes.[32] A Re-N$_{py}$ distance of 2.121(6) Å has been reported in a rhenium(III) complex, with a pyridine as part of a bidentate nitrogen-donor ligand.[33] The differences in Re-Cl bond distances are ascribed to the large *trans* effect of the triphenylphoshine group. The result is that the Re-Cl(3) distance is longer than the corresponding Re-Cl(1) and Re-Cl(2) bond lengths located in *trans* positions to the dpa ligand [2.416(2) Å *vs.* 2.397(2) Å and 2.360(2) Å]. The average C(1)-C(5) and C(6)-C(10) bond lengths are typical for aromatic systems. The chloride Cl(1) forms an intermolecular NH Cl hydrogen-bond of 3.342(5) Å with a N-H Cl(1) angle of 147 °.

3.4. Synthesis and Characterization of *cis*-[ReOCl$_2$(meb)(PPh$_3$)] (3)

The reaction of Hhaep with the rhenium (V) starting material in acetone led to the substitution of the (2-hydroxyphenyl) ethanone group by an acetone molecule to give the coordinated bidentate NO-donor chelate meb in the neutral six-coordinate monooxorhenium(V) product *cis*-[ReOCl$_2$(meb)(PPh$_3$)].

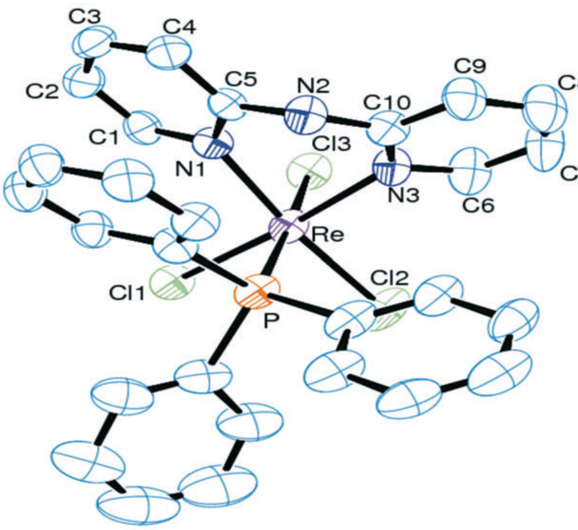


Figure 2 ORTEP diagram of the molecular structure of **2**.

Table 3 Selected bond lengths [Å] and angles [°] for **2**.

Re-Cl(1)	2.397(2)	Re-P	2.434(2)
Re-Cl(2)	2.360(2)	Re-N(1)	2.117(5)
Re-Cl(3)	2.416(2)	Re-N(3)	2.129(5)
Cl(2)-Re-P	89.34(7)	Cl(1)-Re-Cl(2)	93.57(6)
Cl(3)-Re-N(1)	87.37(2)	Cl(1)-Re-Cl(3)	89.26(6)
Cl(3)-Re-N(3)	87.14(2)	Cl(1)-Re-N(1)	92.75(1)
Cl(3)-Re-P	175.89(6)	Cl(1)-Re-N(3)	174.80(2)
N(1)-Re-P	92.79(2)	Cl(1)-Re-P	86.63(6)
N(3)-Re-P	96.97(2)	Cl(2)-Re-Cl(3)	90.95(7)
N(1)-Re-N(2)	83.4(2)	Cl(2)-Re-N(1)	173.44(2)
C(5)-C(4)-N(1)	121.9(5)	Cl(2)-Re-N(3)	90.24(2)

The infrared spectrum displays the Re=O stretching frequency at 979 cm^{-1} which is in the expected region (960–980 cm^{-1}) for similar octahedral oxorhenium(V) compounds.[34] The absence of the characteristic IR bands associated with N-H and C=O bonds of the amide functionality confirms that the ligand has coordinated to the metal in the *enolate* form. The Re-N and Re-O stretches appear at 527 cm^{-1} and 498 cm^{-1}, respectively. The ^{1}H NMR spectrum was run in the extremely polar solvent DMSO-d_6 because of its poor solubility in chloroform. This resulted in a poor spectrum and assignment of the peaks had to be approached with caution. It follows that the broad singlet centred at 8.10 ppm illustrates the presence of the PPh$_3$ group with the aromatic protons of the phenyl ring being hidden under this peak. The six-proton singlet centred at 2.65 ppm is attributable to the two magnetically equivalent methyl groups. The green colour of the complex leads to intense absorptions in the visible region, which are typical of rhenium(V) complexes containing oxo, nitrogen-donor and chloride ligands.[35] The spectra are dominated by an intense absorption (around 300 nm) due to the $\pi \rightarrow \pi^*$ transition of the aromatic ring of meb. The absorption maximum of the ligand-to-metal charge transfer band is shifted to lower energy at 458 nm. A very broad *d-d* transition band is observed at 673 nm.

A representation of the X-ray crystal structure of complex **3** is shown in Fig. 3. The complex exhibits a distorted octahedral geometry around the central rhenium(V) ion. The equatorial plane is defined by the two *cis* chlorides Cl(1) and Cl(2), the neutral imino nitrogen N(1) and the phosphorus atom P(1) of

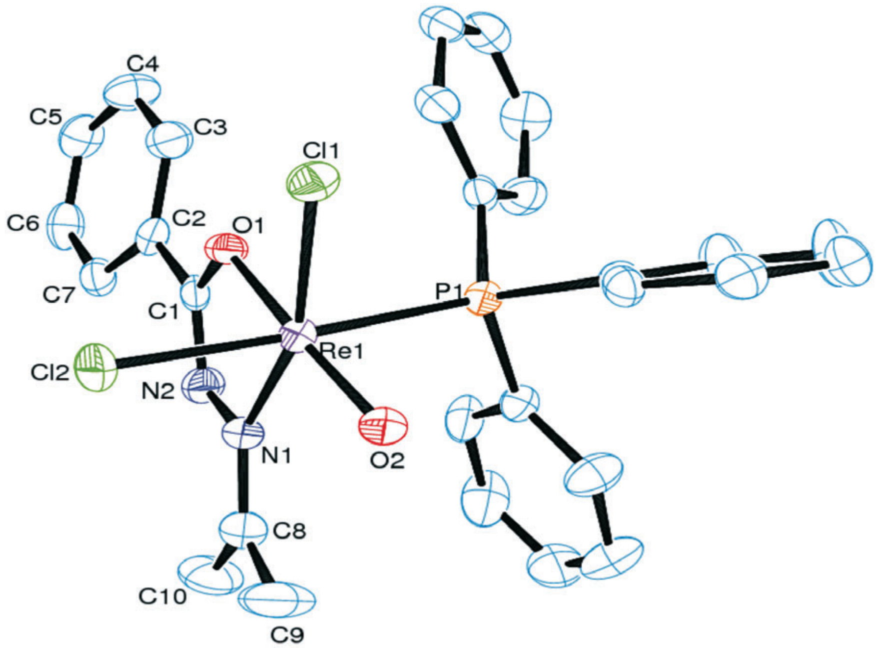


Figure 3 ORTEP diagram of the molecular structure of **3**. Thermal ellipsoids are drawn at 50 % probability, and hydrogen atoms have been omitted for clarity.

Table 4 Selected bond lengths (Å) and angles (°) for **3**.

Re(1)-O(2)	1.669(2)	Re(1)-P(1)	2.463(9)
Re(1)-O(1)	2.023(2)	C(1)-O(1)	1.317(4)
Re(1)-Cl(1)	2.344(9)	C(1)-N(2)	1.303(4)
Re(1)-Cl(2)	2.387(1)	N(1)-N(2)	1.403(4)
Re(1)-N(1)	2.152(3)	N(1)-C(8)	1.313(5)
O(1)-Re(1)-O(2)	163.00(1)	Cl(1)-Re(1)-N(1)	160.86(8)
Cl(1)-Re(1)-O(2)	104.17(8)	Cl(2)-Re(1)-P(1)	174.88(3)
Cl(2)-Re(1)-O(2)	101.16(8)	O(1)-Re(1)-N(1)	73.8(1)
N(1)-Re(1)-O(2)	94.80(1)	O(1)-C(1)-N(2)	122.0(3)
P(1)-Re(1)-O(2)	83.52(8)	N(1)-C(8)-C(9)	121.4(3)
Cl(1)-Re(1)-Cl(2)	88.29(3)	N(1)-C(8)-C(10)	121.7(3)

the triphenylphoshine group. The oxo group O(2) and the enolate-oxygen O(1) are in *trans* axial positions. The Re(1)-O(1) bond length of 2.023(2) Å is within the range expected for Re-O single bonds *trans* to the oxo group for six-coordinate rhenium(V) complexes. Distances of between 1.92–2.09 Å for Re-O single bonds *trans* to the oxo group have been reported.[36,37] The two double bonds in meb are C(1)-N(2) = 1.303(4) Å and C(8)-N(1) = 1.313(5) Å, which are confirmed by the following bond angles: O(1)-C(1)-N(2) = 122.0(3) °, N(1)-C(8)-C(9) and N(1)-C(8)-C(10) bond angles of 121.4(3) ° and 121.7(3) °, respectively (Table 4). These bond angles are close to 120 ° and are indicative of the sp^2 hybridization of the C(1) and C(8) atoms. The corresponding bond distances confirm that meb coordinates to the metal in the *enolate* form.

4. Conclusion

The reaction of *trans*-[$ReCl_3(MeCN)(PPh_3)_2$] with the potentially bidentate ligands 1-phenyl-1,3-butadione (Hbat), 2,2′-dipyridylamine (dpa), and 1-(2-hydroxyphenyl)ethanone benzoylhydrazone (Hhaep) under nitrogen led to the respective complexes *cis*-[$Re^{III}Cl_2(bat)(PPh_3)_2$] (**1**), *fac*-[$Re^{III}Cl_3(dpa)(PPh_3)$] (**2**) and *cis*-[$Re^{V}OCl_2(meb)(PPh_3)$] (**3**) (meb = *N*′-(propan-2-ylidene)benzohydrazide). X-ray crystallographic results show that all three complexes have distorted octahedral geometries. The synthesis of **3** was done in acetone, which led to the substitution of the (2-hydroxyphenyl)ethanone group in Hhaep by an acetone molecule to produce a coordinated meb ligand.

5. Supplementary Data

CCDC-781993, 778196 and 780531 contain the supplementary crystallographic data for complexes **1–3**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44)1223-336-033; or e-mail: data request@ccdc.cam.ac.uk.

References

1 J.R. Dilworth and S.J. Parrott, *Chem. Soc. Rev.*, 1998, **27**, 43–56.
2 J.C. Reubi, *J. Nucl. Med.*, 1995, **36**, 1825–1835.
3 A.R. Cowley, J.R. Dilworth, P.S. Donnelly and J. Woollard-Shore, *Dalton Trans.*, 2003, 748–754.
4 H. Kido and K. Saito, *J. Am. Chem. Soc.*, 1988, **110**, 3187–3190, and references therein.
5 R. Colton, R. Levitus and G. Wilkinson, *J. Chem. Soc.*, 1960, 4121–4125.
6 I.D. Brown, C.J.L. Lock and C. Wan, *Can. J. Chem.*, 1974, **52**,1704–1708.
7 K.-Y. Ho, W.-Y. Yu, K.-K. Cheung and C.-M. Che, *J. Chem. Soc. Dalton Trans.*, 1999, 2101–2109.
8 W.R. McWhinnie, *Coord. Chem. Rev.*, 1970, **5**, 293–311.
9 Y.S. Chung, B.K. Lee and C.E. Oh, *Bull. Korean Chem. Soc.*, 1983, **4**, 76–78.
10 E. Freire, S. Baggio, A. Mombru and R. Baggio, *Aust. J. Chem.*, 2001, **54**, 193–197.
11 C.E. Baxter, O.R. Rodig, R.K. Schlatzer and R. Sinn, *Inorg. Chem.*, 1979, **18**, 1918–1921.
12 M.F. Iskander, S.E. Zayan, M.A. Khalifa and L. Elsayed, *J. Inorg. Nucl. Chem.*, 1974, **36**, 556–560.
13 G. Clifton, S.R. Bryant and C.G. Skinner, *J. Med. Chem.*, 1970, **13**, 377–379.
14 S. Sridhar, M. Saravanan and A. Ramesh, *Eur. J. Med. Chem.*, 2001, **36**, 615–625.
15 B. Bottari, R. Maccari, F. Monforte, R. Ottana, E. Rotondo and M. Vigorita, *Bioorg. Med. Chem. Lett.*, 2000, **10**, 657–660.
16 E. Ainscough, A. Brodie, J. Ranford and M. Waters, *Inorg. Chim. Acta*, 1995, **236**, 83–88.
17 N.R. Sangeetha, S. Pal, *Polyhedron*, 2000, **19**, 2713–2717.

18 W. Plaas, A.R. Pohlmann and H.-P. Yozgatli, *J. Inorg. Biochem.*, 2000, **80**, 181–183.

19 R. Raveendran and S. Pal, *Polyhedron,* 2005, **24**, 2777–2783.

20 O. Pouralimardan, A.C. Chamayou, C. Janiak and H. Monfared, *Inorg. Chim. Acta,* 2007, **360**, 1599–1608.

21 G. Rouschias and G. Wilkinson, *J. Chem. Soc.*, 1967, 993–1000.

22 T. Maina, A. Percolate, A. Dolmella, G. Bandoli and U. Mazzi, *J. Chem. Soc. Dalton Trans.,* 1994, 2437–2443.

23 P. Ghosh, A. Pramanik, N. Bag and A. Chakravorty, *J. Chem. Soc. Dalton Trans.*, 1992, 1883–1886.

24 N. Ngah, N. Mohamad, M. Ahmad and B.M. Yamin, *Acta Cryst.*, 2005, **E61**, o969.

25 G.M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures,* University of Göttingen, Germany, 1997.

26 XRed, rev. **1.09**, STOE: Darmstadt, Germany.

27 XShape, rev. **1.02**, STOE: Darmstadt, Germany.

28 W.J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81–122.

29 I.D. Brown, C.J.L. Lock and C. Wan, *Can. J. Chem.*, 1974, **52**, 1704–1708.

30 B. Machura, M. Wolff, J. Mrozinski, R. Kruszynski and J. Kusz, *Polyhedron,* 2009, **28**, 2377–2384.

31 H. Kraudelt, U. Schilde and E. Uhlemann, *Zeitschrift Anorg. Allg. Chemie,* 1995, **621**, 1797–1799.

32 J. Rall, F. Weingart, D.M. Ho, M.J. Heeg, F. Tisato and E. Deutsch, *Inorg. Chem.*, 1994, **33**, 3442–3451.

33 T.I.A. Gerber, E. Hosten, P. Mayer and Z.R. Tshentu, *J. Coord. Chem.*, 2006, **59**, 243–253, and references therein.

34 E. Roncari, U. Mazzi, R. Rossi, A. Duatti and L. Magon, *Transition Met. Chem.,*1981, **6,** 169–174.

35 G. Bandoli, A. Dolmella, T.I.A. Gerber, D. Mpinda, J. Perils and J.G.H. du Preez, *J. Coord. Chem.*, 2002, **55**, 823–833.

36 F. Connac, Y. Lucchese, M. Dartiguenave and A. Beauchamp, *Inorg. Chem.*, 1997, **36**, 256–259.

37 H.J. Banbery, W. Hussian, T.A. Hamor, C.J. Jones and J.A. McCleverty, *J. Chem. Soc. Dalton Trans.*, 1990, 657–664.