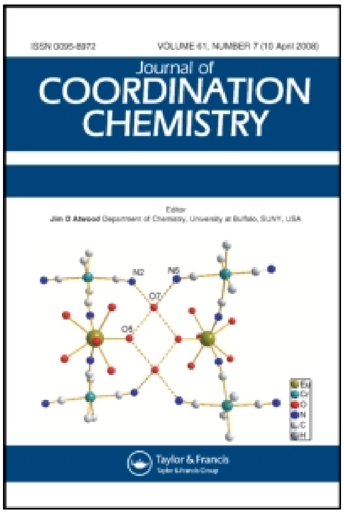


Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of rhenium(III) and (V) pyridylimidazole complexes

Thomas I. A. Gerber[a]; Eric Hosten[a]; Peter Mayer[b]; Zenixole R. Tshentu[a]
[a] Department of Chemistry, University of Port Elizabeth, 6000 Port Elizabeth, South Africa [b] Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany

To cite this Article Gerber, Thomas I. A. , Hosten, Eric , Mayer, Peter and Tshentu, Zenixole R.(2006) 'Synthesis and characterization of rhenium(III) and (V) pyridylimidazole complexes', Journal of Coordination Chemistry, 59: 3, 243 — 253

To link to this Article: DOI: 10.1080/00958970500069063

URL: http://dx.doi.org/10.1080/00958970500069063

Journal of Coordination Chemistry
Vol. 59, No. 3, 15 February 2006, 243–253

Synthesis and characterization of rhenium(III) and (V) pyridylimidazole complexes

THOMAS I. A. GERBER*†, ERIC HOSTEN†,
PETER MAYER‡ and ZENIXOLE R. TSHENTU†

†Department of Chemistry, University of Port Elizabeth, 6000 Port Elizabeth, South Africa
‡Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany

(*Received 30 November 2004*)

Reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ with 2-(2′-pyridyl)imidazole (pimH) in methanol led to the isolation of the rhenium(III) salt $[ReCl_2(pimH)(PPh_3)_2](ReO_4)$ (**1**). However, with 2-(2′-pyridyl)-1-methylimidazole (pimMe) as ligand, the complex $[ReCl_3(pimMe)(PPh_3)]$ (**2**) was obtained. The monooxorhenium(V) complexes $[ReOCl_3(pimR)]$ (R = H, Me) could only be prepared by the reduction of $[ReO_4]^-$ with an equimolar amount of PPh_3 in the presence of pimR and hydrochloric acid in acetic acid. With four equivalents of PPh_3, compounds **1** and **2** were obtained. Using (n-Bu_4N)$[ReOCl_4]$ as starting material, the μ-oxo dimers $[Re_2O_3(pimR)_2Cl_4]$ were isolated as the only products. These new compounds have been characterized by X-ray crystallography, ^{1}H NMR and IR spectroscopy. In **1** the $[ReO_4]^-$ counterion is tightly associated with the cationic complex through N–H $\cdots$ ReO_3^- hydrogen bonding. Despite being paramagnetic, ^{1}H NMR spectra for **1** and **2** could be fully assigned.

Keywords: Rhenium(III); Rhenium(V); Oxo-bridge; Crystal structure; Bidentate *N*,*N*

1. Introduction

The focus of our research group for a number of years has been the coordination chemistry of rhenium, mainly because of the possible applications of the β-emitting isotopes ^{188}Re and ^{186}Re in therapeutic nuclear medicine [1]. Recently we have become interested in the study of rhenium complexes of multidentate ligands containing the imidazole group, because of the importance of this group in biological processes [2–8].

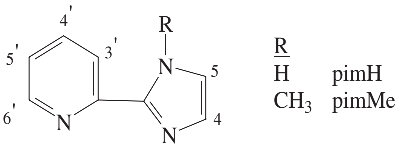
Although a number of Re(III) and (V) complexes with 2,2′-bipyridine and 2,2′-biimidazole have been prepared and studied [9–14], the reactivity of Re(V)

---

*Corresponding author. Email: thomas.gerber@upe.ac.za

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500069063

and (VII) with 2-(2′-pyridyl)imidazole (pimH) and its 1-methyl derivative 2-(2′-pyridyl)-1-methylimidazole (pimMe) have not yet been investigated. In this article we describe the syntheses and structures of Re(V) complexes of the type [ReOCl$_3$(pimR)] and



(μ-O)[ReO(pimR)Cl$_2$]$_2$, and the Re(III) compounds [ReCl$_3$(pimMe)(PPh$_3$)] and [ReCl$_2$(pimH)(PPh$_3$)$_2$](ReO$_4$). In all these complexes pimR acts as a neutral bidentate chelate.

2. Experimental

2.1. *Reactants and methods*

Reagent-grade NH$_4$ReO$_4$ and deuterated solvents were purchased from Aldrich. Solvents and other chemicals (Aldrich) were used as received. IR spectra were recorded for samples in KBr pellets on a Nicolet 20 DXC FTIR spectrophotometer in the 4000–200 cm^{-1} range. ^{1}H HMR spectra were recorded at 300 MHz on a Bruker AMX-300 spectrometer. All chemical shifts are relative to TMS, with DMSO-d_6 as solvent. Electronic spectra were obtained in DMF with a Perkin-Elmer 330 spectrophotometer. Conductivity measurements were carried out with 10^{-3} M solutions in DMF at 293 K on a Philips PW9509 digital conductometer, and the values are in units of ohm^{-1} cm^2 mol^{-1}. Elemental analyses were carried out by the Department of Chemistry at the University of the Western Cape in Cape Town.

2.2. *Synthesis*

Trans-[ReOCl$_3$(PPh$_3$)$_2$] and (n-Bu$_4$N)[ReOCl$_4$] were prepared by literature procedures [15, 16].

2.2.1. 2-(2′-Pyridinyl)imidazole (pimH). A solution of 10.70 g of pyridine-2-aldehyde (0.10 mol) in 10 cm^3 of ethanol was mixed with 20 cm^3 of a 40% aqueous glyoxal solution at 0°C. Without delay, 30 cm^3 of an ice-cold 20% aqueous ammonia solution was added, and the yellow–brown solution was stirred at 0°C for 30 min, and then allowed to stand overnight at room temperature. The ethanol was then boiled off, and the residue extracted several times with 50 cm^3 aliquots of diethylether. Removal of the ether gave a residual oil, which was distilled under vacuum to give a yellow oil that solidified under ambient conditions. This solid was recrystallized from ethyl acetate to give yellow prisms in 75% yield (10.81 g, 0.075 mol), m.p. = 133–135°C. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.15 (s, 1H, $H4$), 7.20–7.30 (m, 2H, $H5$, $H5'$), 7.83 (t, 1H, $H4'$), 8.24 (d, 1H, $H3'$), 8.55 (d, 1H, $H6'$), 11.88 (br s, 1H, NH). Anal. Calcd for C$_8$H$_6$N$_3$(%): C, 66.66; N, 29.15; H, 4.20. Found: C, 66.68; N, 29.41; H, 4.26.

2.2.2. 2-(2′-Pyridyl)-1-methylimidazole (pimMe). Some 0.9 g of sodium metal was dissolved in 50 cm^3 of dried ethanol, with the temperature being kept below 40°C. To this solution was added 5.0 g of pimH (0.0347 mol), and the mixture was stirred for 30 min, after which 4.9 g of iodomethane (0.0345 mol) was added dropwise with stirring. The solution was then heated at reflux for 15 h. After heating was stopped, the NaI precipitate was filtered off, and the volume was reduced to 5 cm^3. Then, 50 cm^3 of chloroform was added, leading to further precipitation of NaI, which was removed. The solution was then dried over anhydrous Na_2SO_4, and the chloroform boiled off to give a brown oil, which was distilled under vacuum to give a yellow oil in 64% yield (3.51 g, 0.0221 mol), bp = 119°C (5 mTorr). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.05 (s, 3H, C*H*$_3$), 6.97 (s, 1H, *H*5), 7.25–7.35 (m, 2H, *H*4, *H*5′), 7.84 (t, 1H, *H*4), 8.08 (d, 1H, *H*3), 8.58 (d, 1H, *H*6). Anal. Calcd for $C_9H_9N_3$(%): C, 67.90; N, 26.40; H, 5.70. Found: C, 67.73; N, 28.87; H, 5.92.

2.2.3. [ReCl$_2$(pimH)(PPh$_3$)$_2$](ReO$_4$) (1). [$ReOCl_3(PPh_3)_2$] (0.100 g, 0.12 mmol) and pimH (0.019 g, 0.13 mmol) were added to methanol (15 cm^3), and the mixture was heated under reflux. After 10 min, the solution changed color from yellow to purple. Heating was continued for another 50 min, and then the mixture cooled to room temperature. After standing for several hours, an orange precipitate was filtered off. The product was recrystallized from acetone/methanol (2 : 1 v/v) to give **1** · MeOH as orange crystals, which were washed with diethylether and dried under vacuum (yield 0.049 g, 0.0405 mmol, 68%, m.p. = 198°). Anal. Calcd for $Re_2C_{44}H_{37}N_3Cl_2P_2O_4 \cdot$ MeOH(%): C, 44.71; H, 3.42; N, 3.48%. Found: C, 44.66; H, 3.37; N, 3.71. ^{1}H NMR (DMSO-d_6) δ (ppm): 13.23 (d, PPh$_3$*ortho*), 8.51 (t, PPh$_3$*para*), 9.02 (t, PPh$_3$*meta*), −1.38 (s, H6′), 1.09 (br s, H4′), 3.36 (br s, H5′), 2.70 (d, H3′), 15.81 (s, NH), −1.26 (s, H5), −3.48 (s, H4). IR (ν_{max}/cm^{-1}): 3057 (N–H), 1622 (C=N), 1482 (C=C), 920, 895 (ReO_4^-), 458 (Re–N), 325, 305 (Re–Cl). UV–vis (λ_{max}, nm/ε, M^{-1} cm^{-1}): 292 (12 300), 375 (2600), 461 (1800), 555 (1300). Conductivity: 76.

2.2.4. Synthesis of 1 from [ReO$_4$]$^-$. Some 0.100 g (0.37 mmol) of $(NH_4)[ReO_4]$ and 0.34 cm^3 of concentrated HCl were added to 0.39 g (1.49 mmol) of PPh_3 and 0.108 g (0.75 mmol) of pimH in 20 cm^3 of methanol. After stirring for 10 min the mixture changed color to purple and heating was continued under reflux for 30 min. After cooling to room temperature, the purple solution was filtered to yield an orange precipitate. Recrystallization from acetone/methanol gave **1** · 0.5 MeOH. Analytical and spectroscopic data were consistent with the material synthesized from [$ReOCl_3(PPh_3)_2$], and a crystal structure determination has confirmed the formation of **1** · 0.5 MeOH.

2.2.5. [ReCl$_3$(pimMe)(PPh$_3$)] (2). The same method as for **1** was used. However, a precipitate did not form after cooling the reaction mixture to room temperature. Instead, the solvent was removed under vacuum from the purple solution, and the resulting purple oil was taken up in 10 cm^3 of acetone. After addition of 5 cm^3 of ethanol, the solution was allowed to stand at room temperature overnight. The orange crystals that formed were filtered off, washed with ethanol and diethylether, and dried under vacuum (yield 0.052 g, 0.073 mmol, 61%, m.p. = 215°C). Anal. Calcd for $ReC_{27}H_{24}N_3Cl_3P$(%): C, 45.43; H, 3.39; N, 5.89. Found: C, 45.36; H, 2.95; N, 5.78. ^1H NMR (DMSO-d_6) δ (ppm): 13.28 (d, PPh_3*ortho*), 8.79 (t, PPh_3*para*), 8.63 (t, PPh_3*meta*), 8.70 (d, H6′), 8.45 (t, H4′), 7.41 (d, H3′), 7.24 (t, H5′), 0.82 (s, H5), 1.13 (s, CH_3), −3.85 (s, H4). IR (ν_{max}/cm^{-1}): 1625 (C=N), 1481 (C=C), 459 (Re–N), 319, 298 (Re–Cl). UV–vis (λ_{max}, nm/ε, $M^{-1}\,cm^{-1}$): 306 (8800), 386 (2300), 467 (2900), 517 (1500). Conductivity: 44. Complex **2** could also be prepared from $[ReO_4]^-$ and three equivalents of PPh_3, using the same procedure as for **1** above.

2.2.6. [ReOCl$_3$(pimH)] (3). To 0.100 g (0.37 mmol) of $(NH_4)[ReO_4]$ in 0.34 cm^3 of concentrated HCl and 5 cm^3 of glacial acetic acid was added to a mixture of 0.098 g (0.37 mmol) of PPh_3 and 0.108 g (0.75 mmol) of pimH, dissolved in 10 cm^3 of glacial acetic acid. The mixture was stirred for 3 h at room temperature, during which time a bright green precipitate formed. It was filtered off and washed with glacial acetic acid and diethylether. To the green mother liquor was added 5 cm^3 of acetonitrile, and slow evaporation of this mixture at room temperature gave lime-green crystals, which were washed with diethylether before being dried under vacuum (yield 0.114 g, 0.269 mmol, 73%, m.p. = 245°C). Anal. Calcd for $ReC_8H_7N_3Cl_3O$(%): C, 22.67; H, 1.67; N, 9.92. Found: C, 22.74; H, 1.24; N, 9.51. ^1H NMR (DMSO-d_6) δ (ppm): 7.05 (1H, s, H5), 7.43 (1H, s, H4), 7.78–7.92 (2H, m, H4′, H5′), 8.40 (1H, d, H3′), 8.61 (1H, d, H6′), 14.80 (1H, br s, NH). IR (ν_{max}/cm^{-1}): 3138 (N–H), 1628 (C=N), 1499, 1483 (C=C), 983 (Re=O), 449 (Re–N), 325, 306 (Re–Cl). UV–vis (λ_{max}, nm/ε, $M^{-1}\,cm^{-1}$): 294 (20 900), 350 (2600), 421 (1200). Conductivity: 23.

2.2.7. [ReOCl$_3$(pimMe)] (4). The same method as for **3** was used (yield 0.121 g, 0.259 mmol, 70%, m.p. = 302°C). Anal. Calcd for $ReC_9H_9N_3Cl_3O$(%): C, 23.12; H, 1.94; N, 8.99. Found: C, 23.32; H, 2.12; N, 9.03. ^1H NMR (DMSO-d_6) δ (ppm): 4.18 (3H, s, CH_3), 7.04 (1H, s, H5), 7.43 (1H, s, H4), 7.77 (1H, t, H5′), 7.83 (1H, t, H4′), 8.12 (1H, d, H3′), 8.46 (1H, d, H6′). IR (ν_{max}/cm^{-1}): 1651, 1611 (C=N), 1490 (C=C), 984 (Re=O), 445 (Re–N), 326, 312 (Re–Cl). UV–vis (λ_{max}, nm/ε, $M^{-1}\,cm^{-1}$): 298 (21 100), 351 (2800), 421 (1000). Conductivity: 13.

2.2.8. (μ-O)[{ReOCl$_2$(pimH)}$_2$] (5). (n-Bu_4N)[$ReOCl_4$] (0.100 g, 0.17 mmol) and pimH (0.027 g, 0.19 mmol) were mixed in 10 cm^3 of acetonitrile. The color changed immediately to dark green. The solution was then heated under reflux for 30 min. On cooling to room temperature, a dark green precipitate that formed was removed by filtration and washed with ethanol and diethylether. The mother liquor was allowed to stand overnight in a closed vessel at room temperature, giving a crop of green crystals of **5** (yield 0.047 g, 55 µmol, 65%, m.p. = 329°C). Anal. Calcd for $Re_2C_{16}H_{14}N_6Cl_4O_3$(%): C, 22.55; H, 1.66; N, 9.86. Found: C, 22.30; H, 1.71; N, 10.19. ^1H NMR (DMSO-d_6) δ (ppm): 7.26 (1H, s, H5), 7.85 (2H, m, H4, H5′), 8.46 (2H, m, H3′, H4′), 9.10 (1H, d, H6′), 14.83 (s, 1H, NH). IR (ν_{max}/cm^{-1}): 3122 (N–H), 1620, 1592 (C=N), 1478 (C=C), 980 (Re=O), 728, 697 (Re–O–Re), 443 (Re–N), 309 (Re–Cl). UV–vis (λ_{max}, nm/ε, $M^{-1}\,cm^{-1}$): 301 (28 400), 344 (5200), 419 (1300). Conductivity: 35.

2.2.9. (μ-O)[{ReOCl$_2$(pimMe)}$_2$] (6). This compound was prepared by the same procedure as used for **5** (yield 0.053 g, 60 µmol, 71%, m.p. = 258°C). Anal. Calcd for $Re_2C_{18}H_{18}N_6Cl_4O_3$(%): C, 24.56; H, 2.06; N, 9.55. Found: C, 24.25; H, 1.88; N, 9.27. ^{1}H NMR (DMSO-d_6) δ (ppm): 4.28 (3H, s, CH$_3$), 7.16 (1H, s, H5), 7.82–7.90 (2H, m), 8.34–8.48 (2H, m), 9.23 (1H, d, H6′). IR (ν_{max}/cm^{-1}): 1611 (C=N), 1479 (C=C), 974 (Re=O), 716, 693 (Re–O–Re), 443 (Re–N), 309 (Re–Cl). UV–vis (λ_{max}, nm/ε, M^{-1} cm^{-1}): 303 (23 400), 343 (7700), 425 (900). Conductivity: 19.

2.3. *Crystallography*

Diffraction data were measured with Nonius Kappa CCD (for **1**) and STOE 1 PDS (for **2**) diffractometers with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals of **1** included 0.5 CH$_3$OH per asymmetric unit, which was disordered. Crystals of **2** were weak diffractors, and numerous attempts to grow better ones were unsuccessful. However, an acceptable data set could be obtained. Although the final *R* factor is relatively high, connectivity and other general features of the structure were confidently determined, and the molecular positional parameters of the atoms in the "inner core" are well defined. Several batches of crystals of complex **4** were obtained, but they all gave poor reflections. The best refinement factor obtained was $R = 0.199$. It was, however, possible to determine the unit cell parameters: orthorhombic, $a = 12.337(2)$, $b = 12.277(1)$, $c = 16.811(2)$ Å; $Z = 8$; $V = 2546(1)$ Å^3. Crystals of **5** also gave only poor reflections, but they allowed a determination of the unit cell: monoclinic, $a = 10.84$, $b = 18.43$, $c = 17.28$ Å; $\beta = 99.2°$; $V = 3408$ Å^3. Details of the crystal data, intensity measurements and data processing are summarized in table 1. For the structure factors, corrections for Lorentz and polarization effects and absorption were made. The structures were solved by direct methods and refined by full-matrix least-squares procedures using SHELX-97 [17]. Selected bond distances and angles are given in table 2.

Table 1. Crystallographic data for **1** and **2**.

	[ReCl$_2$(pimH)(PPh$_3$)$_2$]ReO$_4$ (**1**)	[ReCl$_3$(pimMe)(PPh$_3$)] (**2**)
Chemical formula	$C_{44}H_{37}Cl_2N_3O_4P_2Re_2 \cdot 0.5(CH_4O)$	$C_{27}H_{24}Cl_3N_3PRe$
Formula weight	1193.07	714.04
Crystal system	Monoclinic	Monoclinic
Temperature (K)	200	200
Space group	$C2/c$	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 37.1766(7)$	$a = 17.394(4)$
	$b = 9.3874(2)$	$b = 9.514(1)$
	$c = 24.1336(5)$	$c = 16.624(4)$
	$\beta = 91.706(1)$	$\beta = 104.56(3)$
Volume (Å^3)	8418.7(3)	2662(1)
Z	8	4
Density (calc.) (Mg m^{-3})	1.882	1.781
Crystal size (mm)	0.02 × 0.05 × 0.14	0.02 × 0.06 × 0.08
μ (mm^{-1})	5.998	4.947
$F(000)$	4612	1392
Theta min–max	3.2–24.1	3.6–23.2
Observed data	5034 [$I > 4\sigma(I)$]	2582 [$I > 4\sigma(I)$]
N_{ref}, N_{par}	6648, 521	4535, 166
R, $wR2$, S	0.0504, 0.1335, 1.06	0.1331, 0.1960
Min./max. resd. density (e Å^{-3})	0.00/0.00	–6.883/3.855

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

*[ReCl$_2$(pimH)(PPh$_3$)$_2$]ReO$_4$ (**1**)*			
Re–Cl(1)	2.357(3)	Re–Cl(2)	2.372(3)
Re–P(1)	2.491(2)	Re–P(2)	2.503(2)
Re–N(1)	2.127(7)	Re–N(2)	2.084(8)
C(1)–N(1)	1.35(1)	N(1)–C(5)	1.36(1)
N(3)–C(6)	1.36(2)	N(3)–C(8)	1.44(2)
P(1)–Re–P(2)	176.07(9)	N(1)–Re–N(2)	76.5(3)
Cl(1)–Re–Cl(2)	101.2(1)	Cl(1)–Re–N(2)	170.1(2)
P(1)–Re–Cl(1)	90.07(9)	Cl(2)–Re–N(1)	165.2(2)
P(1)–Re–Cl(2)	86.09(9)	P(1)–Re–N(1)	93.0(2)
C(6)–N(3)–C(8)	107(1)	P(1)–Re–N(2)	91.0(2)
Re–N(1)–C(5)	115.9(6)	Re–N(2)–C(6)	115.9(7)
*[ReCl$_3$(pimMe)(PPh$_3$)] (**2**)*			
Re–Cl(1)	2.36(1)	Re–N(1)	2.09(1)
Re–Cl(2)	2.37(1)	Re–N(3)	2.12(1)
Re–Cl(3)	2.42(1)	Re–P(1)	2.41(1)
P–Re–Cl(3)	175.9(1)	Cl(1)–Re–Cl(2)	97.1(1)
N(1)–Re–N(3)	74.9(1)	Cl(1)–Re–N(1)	167.7(1)
P–Re–Cl(1)	91.8(1)	Cl(2)–Re–N(3)	169.4(1)
P–Re–Cl(2)	87.4(3)	P–Re–N(3)	95.6(1)
P–Re–N(1)	91.0(1)	Cl(1)–Re–Cl(3)	90.0(1)

3. Results and discussion

3.1. *Synthesis*

Two new rhenium(III) complexes (**1** and **2**) with pimR (R = H, Me) as chelating ligands were synthesized by the reaction of [ReOCl$_3$(PPh$_3$)$_2$] with one equivalent of pimR in ethanol, heated at reflux in air. In both reactions, the lime-green color of the starting material was replaced by dark purple after heating for 15 min, and when heating was stopped after 1 h, orange precipitates were collected in good yields. Recrystallization from acetone (for **1**) and acetone/ethanol (for **2**) gave orange crystals that were suitable for X-ray studies. With ligand pimH the product proved to be the salt [ReCl$_2$(pimH)(PPh$_3$)$_2$](ReO$_4$) (**1**), but with pimMe the neutral complex [ReCl$_3$(pimMe)(PPh$_3$)] (**2**) was obtained as the only product. It seems therefore that N-methylation of the imidazole introduces drastic changes in reactivity because [ReO$_4$]$^-$ association with coordinated imidazole by hydrogen bonding through the NH group is a significant stabilizing factor. Reduction to Re(III) is somewhat surprising, especially in the presence of air. In **1** it is interesting to note that the counterion is [ReO$_4$]$^-$, despite the use of the Re(V) starting material, which indicates that the mechanism involves complex redox processes. In **2**, reduction of the metal center to Re(III) occurs presumably by abstraction of the oxo group by PPh$_3$ to form OPPh$_3$. Compound **1** could also be prepared by the reaction of [ReO$_4$]$^-$ with pimH in the presence of four equivalents of PPh$_3$ in methanol, acidified with a few drops of concentrated hydrochloric acid. Complex **2** could also be obtained by this procedure by using a [ReO$_4$]$^-$: PPh$_3$ molar ratio as low as 1 : 3. Complexes of the type [ReX$_2$(biimH$_2$)(PPh$_3$)$_2$]X (X = Cl, Br, I; biimH$_2$ = 2,2′-biimidazole) have been prepared by the reduction of [ReOCl$_3$(PPh$_3$)$_2$] with additional excess PPh$_3$ [13]. The complexes [ReCl$_3$(bipy)(PPh$_3$)] (bipy = 2,2′-bipyridine) and [ReCl$_3$(imMe)$_2$(PPh$_3$)] (imMe = 1-methylimidazole) have also been synthesized by the reduction of [$ReOCl_3(PPh_3)_2$] with additional excess PPh_3 [11, 18].

In attempts to isolate any rhenium(V) intermediates in the reduction process, equimolar amounts of [ReO_4]$^-$ and PPh_3 were reacted in the presence of pimR in glacial acetic acid containing a few drops of conc. HCl. The Re(V) complexes [$ReOCl_3$(pimR)] [R = H(**3**), Me(**4**)] were isolated as the only products in good yields. Furthermore, the reaction of (n-Bu_4N)[$ReOCl_4$] with pimR in acetonitrile yielded the products (μ-O)[{$ReOCl_2$(pimR)}$_2$] [R = H(**5**), Me(**6**)]. Hydrolysis of **3** in wet acetone (5% water) also led to the oxo-bridged species **5**. It was reported earlier that the reaction of *N*,*N′*-dimethylbiimidazole and bipy (N–N) with [$ReOCl_3(OPPh_3)(Me_2S)$] gives *mer*-[$ReOCl_3$(N–N)] [12]. With the nonmethylated biimidazole *trans*-O,O species, [$ReOCl_2(biimH_2)(OPPh_3)$]$^+$ was isolated as the chloride salt. Hydrolysis of [$ReOCl_3(biimMe_2)$] in wet acetone yielded (μ-O)[{$ReOCl_2(biimMe_2)$}$_2$] [12].

The conductivity of **1** in DMF ($\Lambda_M = 76\,\text{ohm}^{-1}\,\text{mol}^{-1}\,\text{cm}^2$) confirms that it is a 1 : 1 electrolyte. Conductivity readings between 65 and $90\,\text{ohm}^{-1}\,\text{mol}^{-1}\,\text{cm}^2$ are consistent with 1 : 1 electrolytes in DMF [19]. Although the value for **2** falls outside this range and it is classified as a nonelectrolyte, its conductivity value suggests that dissociation in DMF occurs to some extent.

Complexes **1** and **2** are soluble in a wide variety of solvents, including acetone, acetonitrile, dichloromethane, DMF and DMSO, but are insoluble in water, alcohols and benzene. Complexes **3**–**6** are only soluble in the most polar solvents such as DMF and DMSO, with low solubility in acetonitrile and dichloromethane. All compounds are stable for months in the solid state, and for days in solution.

3.2. *Spectroscopic characterization*

Even though **1** and **2** are paramagnetic, their ^{1}H NMR signals are surprisingly sharp and clear. Protons of the PPh_3 groups lead to the typical pattern observed previously for Re(III)–PPh_3 complexes [18]. The *ortho* protons of the phosphine phenyl rings in **1** and **2** are shifted far downfield, to around 13.2 ppm, from their normal position at ca 7.6 ppm in diamagnetic complexes. The *meta* protons of **1** are also shifted downfield, although to a lesser extent, to 9.02 ppm, while the signal of the *para* protons appear closer to their diamagnetic position at 8.51 ppm. In the spectrum of **2** the corresponding shifts are to 8.66 and 8.76 ppm, respectively. In **1** the pyridyl protons H6′ and H4′ are shifted upfield (at δ −1.38 and 1.09 ppm, respectively) by ca 6 ppm from their expected diamagnetic positions, with upfield shifts also observed for H5′ and H3′ and the imidazole protons H4 and H5. In the spectrum of **2** the signals of the pyridyl protons appear close to their diamagnetic positions, but the imidazole protons are again shifted upfield to nearly the same positions as in **1**. The NH proton in **1** (at δ 15.81 ppm) was established unambiguously by the disappearance of its signal after addition of D_2O to the solution.

As pimR consists of two different ring systems, the ^{1}H NMR data could not establish the stereochemistry of complexes **3** and **4**, that is whether they exist in the *mer* or *fac* isomers. The signals of the two imidazole ring protons (two singlets) appear at identical positions in **3** and **4** (and further upfield than the pyridine protons), while the expected splitting pattern of doublet–doublet–triplet–triplet is observed for the pyridine protons.

In the aromatic region of the ^{1}H NMR spectra of **5** and **6**, only one set of six signals was observed for the six ring protons of pimR, and these signals could be easily assigned. These data intimate that the two pimR rings (one in each [ReOCl$_2$(pimR)] half) are equivalent. In both spectra, proton H6′, on the carbon adjacent to the coordinated pyridyl nitrogen, appears the furthest downfield. The signal of the NH protons of **5** appears far downfield at δ 14.83 ppm, and only one singlet (at δ 4.28 ppm) is observed for the methyl protons of pimMe in **6**. In addition, the peaks in the spectra of **5** and **6** as a group are shifted further downfield in comparison with the corresponding signals of complexes **3** and **4**.

The infrared spectrum of **1** provides evidence for the presence of the perrhenate anion, with characteristic strong absorption bands at 920 and 895 cm^{-1} for ν[Re(VIII)=O]. The NH$\cdots$OReO$_3$ hydrogen bond (see crystal structure below) results in a weaker N–H bond, with ν(N–H) occurring at 3057 cm^{-1}, compared to about 3130 cm^{-1} in complexes **3** and **5**. Two medium intensity bands for the Re–Cl stretches indicate the presence of the two chlorides in nonequivalent *cis* positions. In the spectrum of **2**, one ν(Re–Cl) stretch occurs at a fairly low frequency of 298 cm^{-1} and is assigned to the chloride coordinated in the position *trans* to the PPh$_3$ molecule.

The presence of the Re(V)=O groups in **3** and **4** is shown by strong bands at ca 984 cm^{-1}. A Re=O stretching frequency of 985 cm^{-1} has been observed for the *mer* isomer of [ReOCl$_3$(biimMe$_2$)], and a frequency of 970 cm^{-1} was assigned in the *fac* isomer [12]. It would therefore seem that both **3** and **4** were isolated as the pure *mer* isomers, with a nitrogen atom of one of the aromatic rings coordinated in the position *trans* to the oxo oxygen atom. Two bands of medium intensity for ν(Re–Cl) were observed in the spectra of both complexes, but only one broad medium intensity band was found for ν(Re–N).

IR spectra of **5** and **6** are typical of such oxo-bridged dimers, with a peak of medium intensity at ca 977 cm^{-1}, attributed to the terminal Re=O stretch, and a very strong and broad band around 710 cm^{-1} for the Re–O–Re stretch. Only one band each for the Re–N (at 443 cm^{-1}) and Re–Cl (at 309 cm^{-1}) stretching frequencies was observed for both **5** and **6**, again supporting the equivalence of the two pimR chelates in each complex.

The orange color of complexes **1** and **2** leads to intense absorptions in the visible region of their electronic spectra. Because of their high extinction coefficients, their origin is probably due to d$_\pi$[Re(III)] $\rightarrow \pi^*$(pimR) metal-to-ligand charge-transfer (MLCT) transitions. For **2**, the absorption maxima of the MLCT bands are shifted to lower energy than for **1**. The electronic spectra of the rhenium(V) complexes **3**–**6** are very similar, and are typical of complexes containing oxo, nitrogen-donor and chloride ligands [20]. The spectra are dominated by an intense absorption (around 300 nm) due to the $\pi \rightarrow \pi^*$ transition of the aromatic rings in pimR. There are additional peaks at about 350 and 420 nm, with the former being ascribed to the oxo oxygen-to-rhenium(V) charge-transfer transition.

3.3. *Crystal structures*

Representations of the X-ray crystal structures of **1** and **2** are shown in figures 1 and 2, respectively, and pertinent crystallographic data are summarized in table 1. In both complexes the Re atom lies in a distorted octahedral environment. In **1** the two PPh$_3$ ligands lie in positions *trans* to each other, with the two *cis* chlorides, imidazole nitrogen N(2) and pyridinic nitrogen N(1), forming a square plane. Distortion from an ideal rhenium-centered octahedron mainly results in a nonlinear P(1)–Re–P(2)

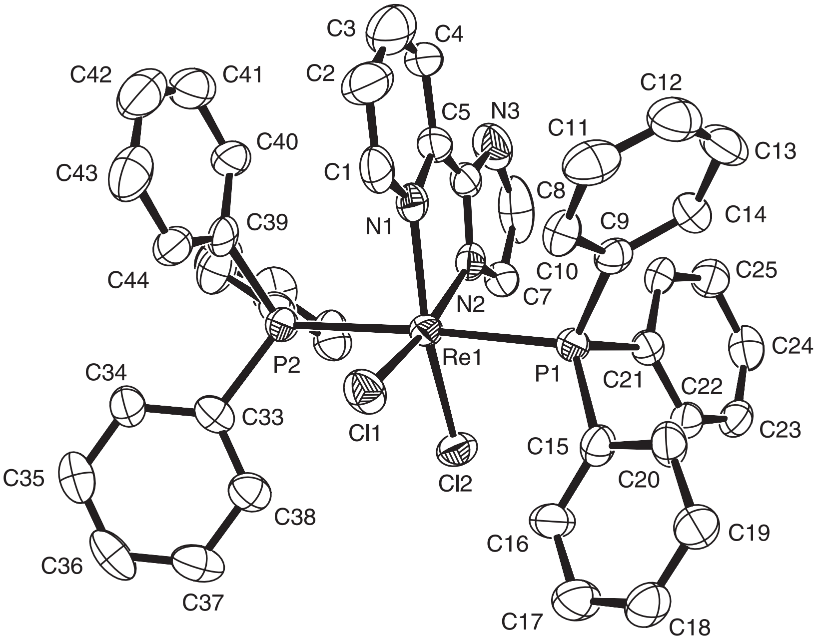


Figure 1. Structure of $[ReCl_2(pimH)(PPh_3)_2](ReO_4)$ (**1**) with the atom numbering scheme and thermal ellipsoids drawn at 50% probability. The hydrogen atoms, ReO_4^- and methanol of crystallization are omitted for clarity.

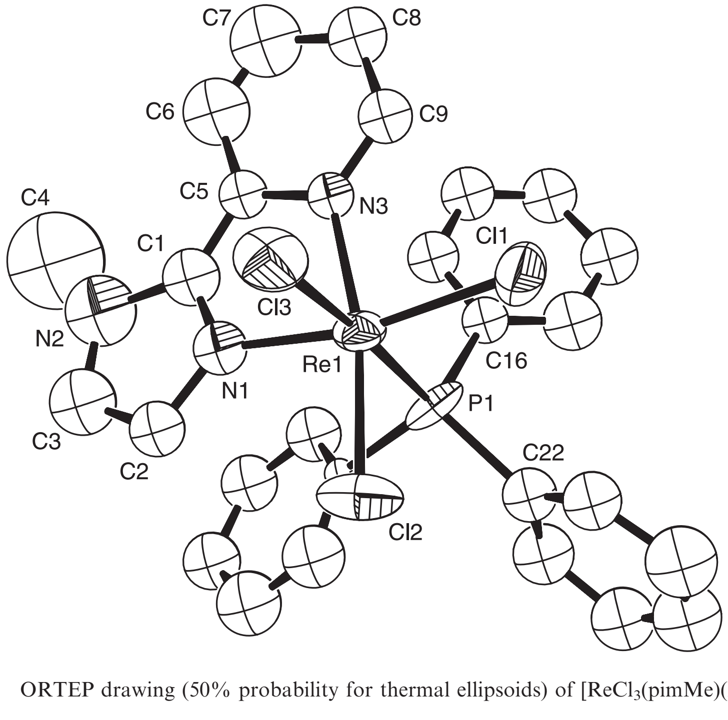


Figure 2. ORTEP drawing (50% probability for thermal ellipsoids) of $[ReCl_3(pimMe)(PPh_3)]$ (**2**).

axis of 176.07(9)°, accomplished by N(1)–Re–Cl(2) and N(2)–Re–Cl(1) angles of 165.2(2)° and 170.1(2)°, respectively. The rhenium atom is displaced slightly out of the mean equatorial N_2Cl_2 plane by 0.0057(1) Å towards P(1), the result of the nonorthogonal angles P(1)–Re–N(1) = 93.0(2)°, P(1)–Re–N(2) = 91.0(2)°, P(1)–Re–Cl(1) = 90.1(1)° and P(1)–Re–Cl(2) = 86.1(1)°. The bite angle [N(1)–Re–N(2)] of pimH equals 76.5(3)°, which is not significantly different from that of $biimH_2$ in other rhenium(III) complexes (75.2–76.0°) [13]. The smaller bite angle in **1** is the result of the Cl(1)–Re–Cl(2) angle, which is far from orthogonal [101.2(1)°]. The pyridine and imidazole rings of pimH are nearly coplanar, with a dihedral angle of 0.45° between their least-squares planes. They also make dihedral angles of only 2.69 and 2.85° with the mean equatorial plane, respectively. Both the imidazole and pyridine rings are planar, as expected. The C–C–N angles at the ring junctions deviate considerably from 120° [N(1)–C(5)–C(6) = 114.1(9)°, N(2)–C(6)–C(5) = 117.4(9)°], and the rhenium atom lie about 4° off the lone-pair directions [C(5)–N(1)–Re = 115.9(6); C(6)–N(2)–Re = 115.9(7)°]. Re–Cl distances are in the range of 2.349–2.374 Å found in other rhenium(III) complexes [13]. The average Re–P distance of 2.497(2) Å deviates little from the average of 2.483(2) Å found in other Re(III) complexes with two PPh_3 ligands *trans* to each other. The Re–N(1) bond [2.127(7) Å] is longer than the Re–N(2) bond [2.084(8) Å], reflecting the stronger basic properties of the imidazole compared to the pyridine ring. A Re–N(pyridine) distance of 2.121(6) Å has been observed previously in a Re(III) complex with a pyridine as part of a bidentate nitrogen-donor ligand. The methanol of crystallization is disordered over two equally populated orientations, with positions for C(45) being resolved. The $[ReO_4]^-$ anion has approximately regular tetrahedral geometry, and it exhibits large thermal motion as shown by the large thermal parameters of its oxygen atoms. The average Re(2)–O distance equals 1.70(1) Å. The closest contact that this counterion has with the complex is 2.533 Å, that is between O(1) and H(11) [on C(11)]. In addition, a strong hydrogen bond [2.67(2) Å] exists between N(3)H and O(2) of the nearby $[ReO_4]^-$ ion with the $N\text{–}H\cdots OReO_3$ angle (167.3°) close to linearity. In the complex $[ReCl_2(biimH_2)(PPh_3)_2]Cl$ the chloride counterion forms two $NH\cdots Cl$ hydrogen bonds of 3.13 and 3.18 Å and $N\text{–}H\cdots Cl$ angles of about 147° [13]. This bond may play a significant role in the stabilization of the complex.

Because observed reflections in the structure analysis of **2** were limited in number (crystal of poor quality, high thermal motion), anisotropic thermal parameters were assigned only to the Re, P and the three chlorine atoms. The *R* factor reached in this structure is not very low, but we think that the molecular positional parameters are well defined; we are especially interested in the "inner coordination core" of the rhenium, where the errors are probably lower.

In complex **2** the basal plane of the distorted octahedron is defined by the two nitrogen donor atoms of pimMe [N(1), N(3)] and the chlorides Cl(1) and Cl(2). The P atom and Cl(3) lie in *trans* axial positions, with the P–Re–Cl(3) angle being 175.9(1)°, and with the Cl(1)–Re–N(1) and Cl(2)–Re–N(3) angles being 167.7(1) and 169.4(1)°, respectively. The rhenium atom deviates from the mean equatorial plane by 0.050 Å towards P(1). This deviation results in the P–Re–Cl(1), P–Re–N(1) and P–Re–N(3) angles being larger than 90° (91.8, 91.0 and 95.6°, respectively). The bite angle of pimMe [74.9(1)°] is considerably smaller than that of pimH in complex **1**, and it contributes significantly to the distortion of the complex. The large Cl(1)–Re–Cl(2) angle of 97.1(1)° may contribute to the smaller bite angle of pimMe.

Pyridine and imidazole rings are coplanar within 4.2°, and the two rings make dihedral angles of 2.5° (imidazole) and 2.7° (pyridine) with the mean N_2Cl_2 equatorial plane. The Re–Cl(3) bond, *trans* to P, at 2.42(1) Å, is significantly longer than the Re–Cl bond lengths *trans* to the nitrogen-donor atoms [Re–Cl(1) = 2.36(1) Å, Re–Cl(2) = 2.37(1) Å]. Again, as was observed in **1**, the Re–N(1) bond length [2.09(1) Å] is shorter than the Re–N(3) bond length [2.12(1) Å].

Supplementary material

CCDC-252694 contains the crystallographic data for complex **1**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1 EZ, UK; fax: +44 (0) 1223-336033; email: deposit@ccdc.cam.ac.uk]. Full lists of crystallographic data for **2** are available from the authors upon request.

References

[1] J.R. Dilworth, S.J. Parrott, *Chem. Soc. Rev.*, **27**, 43 (1998).

[2] P. Cozzi, G. Cargganico, D. Fusar, M. Grossoni, M. Menichincheri, V. Pincirol, R. Tonani, F. Vaghi, P. Salvati, *J. Med. Chem.*, **36**, 2964 (1993).

[3] J. Ohmori, M. Shimizu-Sasamata, M. Okade, S. Sakamoto, *J. Med. Chem.*, **39**, 3971 (1996).

[4] T. Güngör, A. Fouquet, J.-M. Teulon, D. Provost, M. Cazes, A. Cloarec, *J. Med. Chem.*, **35**, 4455 (1992).

[5] Y.S. Lo, J.C. Nolan, T.H. Maren, W.J. Welstead, D.F. Gripshover, S.A. Shamblee, *J. Med. Chem.*, **35**, 4790 (1992).

[6] T.I.A. Gerber, E. Hosten, Z.R. Tshentu, P. Mayer, E. Pérez-Carreño, S. Garcia-Granda, J.G.H. du Preez, *J. Coord. Chem.*, **56**, 1063 (2003).

[7] T.I.A. Gerber, Z.R. Tshentu, S. Garcia-Granda, P. Mayer, *J. Coord. Chem.*, **56**, 1093 (2003).

[8] T.I.A. Gerber, Z.R. Tshentu, P. Mayer, *J. Coord. Chem.*, **56**, 1357 (2003).

[9] J.V. Caspar, B.P. Sullivan, T.J. Meyer, *Inorg. Chem.*, **23**, 2104 (1984).

[10] J.C. Bryan, R.E. Stenkamp, T.H. Tulip, J.M. Mayer, *Inorg. Chem.*, **26**, 2283 (1987).

[11] G. Rouschias, G. Wilkinson, *J. Chem. Soc.* A, 993 (1967).

[12] S. Fortin, A.L. Beauchamp, *Inorg. Chem.*, **39**, 4886 (2000).

[13] S. Fortin, A.L. Beauchamp, *Inorg. Chem.*, **40**, 105 (2001).

[14] S. Fortin, P. Fabre, M. Dartiguenave, A.L. Beauchamp, *J. Chem. Soc., Dalton Trans.*, 3520 (2001).

[15] J. Chatt, G.A. Rowe, *J. Chem. Soc.*, 4019 (1962).

[16] R. Alberto, R. Schibli, A. Egli, P.A. Schubiger, W.A. Herrmann, G. Artus, U. Abram, T.A. Kaden, *J. Organomet. Chem.*, **462**, 217 (1995).

[17] G.M. Sheldrick, *SHELXL-97: Program for Refinement of Crystal Structures*, University of Göttengen, Germany (1997).

[18] C. Pearson, A.L. Beauchamp, *Can. J. Chem.*, **75**, 220 (1997).

[19] W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

[20] G. Bandoli, A. Dolmella, T.I.A. Gerber, D. Mpinda, J. Perils, J.G.H. du Preez, *J. Coord. Chem.*, **55**, 823 (2002).