

Synthesis and Structural Characterization of a Novel Ligand-bridged Dimer of Oxorhenium(V)

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Rhenium(V) complexes of potentially tetradentate ligands have been well studied during the last three decades.¹ These ligands were mainly of the amine-phenol and amine-acetylacetonate type with the ONNO donor atom set, and monomeric complexes of the general formula [ReOCl(ONNO)] were isolated if air and moisture were excluded from the reaction mixtures. However, if the reactions were carried out in air and wet solvents, so that some water was present, dimeric oxo-bridged complexes of the type [Re₂O₃(ONNO)₂] were formed, with a linear O=Re-O-Re=O axis.¹ As a matter of fact, multidentate ligand-bridged dimers of oxorhenium(V) are very rare in the literature, and dimers of the ReO³⁺ core are mainly of the oxo-bridged type. In fact, the coordination chemistry of dinuclear and polynuclear oxo complexes have received increased attention recently, since these species exhibit structures, reactions and properties which are unusual for mononuclear complexes.² Also, these compounds are important in catalysis, electron-transfer reactions, biological mimicry and metal-metal interactions.³

Described here is the detail of the synthesis of the molecule 1,3-di(pyridin-2-yl)but-1-ene-1,3-diol (H₂dbd), and the synthesis and crystal structure of a novel dbd-bridged dimeric complex (μ-dbd)[ReOCl₂(PPh₃)₂], prepared from H₂dbd and *trans*-[ReOCl₃(PPh₃)₂].

Experimental Section

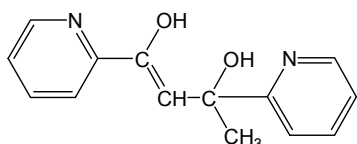
General procedures. All manipulations were carried out in air. Solvents were purified and dried by standard procedures. (NH₄)[ReO₄], 2-bromopyridine and 2-acetylpyridine were purchased from Aldrich. *trans*-[ReOCl₃(PPh₃)₂] was synthesized by a literature procedure.⁴ Common laboratory chemicals were of reagent grade and were used without further purification. Infrared spectra were recorded on a Digilab FTS 3100 Excalibur HE spectrophotometer as KBr disks (for solids) or between NaCl disks (for oils). ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as

solutions in CDCl₃ or *d*₆-DMSO using TMS as an internal standard. Elemental analysis was performed by the Chemistry Department of the University of the Western Cape in Cape Town.

X-ray structural characterization. X-ray diffraction data were collected on an Oxford XCalibur CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073). Multi-scan absorption corrections were made with SADABS.⁵ The structure was solved by direct methods using SHELXS-97.⁶ Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on *F*² using SHELXL-97.⁶ Hydrogen atoms were first located in the difference map, the positioned geometrically and allowed to ride on their respective parent atoms. ORTEP3 was used for diagram generation.⁷

Preparation of H₂dbd. To 0.308 g of magnesium in 20 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added dropwise 1.2 mL of 2-bromopyridine (12.6 mmol). After the addition was completed, the solution was heated under reflux for 2 h, after which it was cooled to 0 °C, before 1.5 mL of 2-acetylpyridine (13.3 mmol) was added dropwise. Stirring was continued at 0 °C for 15 h, followed by the addition of a saturated ammonium chloride solution (20 mL). The aqueous layer was separated and extracted with ether (4 × 10 mL). The combined extracts were dried over anhydrous Na₂SO₄. The removal of the ether under reduced pressure yielded 1.77 g of a yellow oil (yield 58%). Anal. Calcd for C₁₄H₁₄N₂O₂: C, 69.40; H, 5.82; N, 11.56. Found: C, 69.12; H, 5.92; N, 11.91%. ¹H NMR (CDCl₃) δ 2.49 (s, 3H, CH₃), 3.11 (s, 1H, H(8)), 6.94 (t, 1H, *J* = 5 Hz), 7.14 (m, 2H), 7.24 (t, 1H, *J* = 7 Hz), 7.50 (t, 1H, *J* = 7 Hz), 7.68 (d, 1H, *J* = 7.5 Hz), 8.02 (d, 1H, *J* = 4 Hz), 8.35 (d, 1H, *J* = 4 Hz). ¹³C NMR (CDCl₃) δ 26.14 (C(7)), 30.11 (C(6)), 49.01 (C(8)), 119.75 (C(9)), 120.77 (C(2)), 121.70 (C(11)), 122.11 (C(13)), 122.40 (C(4)), 137.09 (C(3)), 137.50 (C(12)), 146.60 (C(1)), 146.88 (C(5)), 148.32 (C(14)), 149.19 (C(10)).

Preparation of (μ-dbd)[ReOCl₂(PPh₃)₂]. A mixture of 180 mg (216 μmol) of *trans*-[ReOCl₃(PPh₃)₂] and 26 mg (107 μmol) of H₂dbd in 20 mL of acetonitrile was heated under reflux for 3 h. The original light green solution gradually turned to a dark green colour, and after heating was stopped, the solution was cooled to room temperature and filtered. No precipitate formed. After standing at ambient temperature for 3 days, dark green needles, suitable for X-ray analysis, were collected by filtration. They were washed with ethanol and



Scheme 1. Schematic drawing of H₂dbd.

diethyl ether, and dried under vacuum. Yield: 89% (131 mg), based on H₂dbd. Anal. Calcd for C₅₀H₄₂N₂O₄P₂Cl₄Re₂. 1.5-CH₃CN: C, 46.38; H, 3.41; N, 3.57. Found: C, 46.19; H, 3.28; N, 3.91. IR (KBr, cm⁻¹) ν (Re=O) 937(s), ν (Re-N) 500(m), 528(m). ¹H NMR (*d*₆-DMSO) δ 2.05 (s, 3H, CH₃), 5.01 (s, 1H, H(8)), 6.87 (t, 1H), 7.06 (t, 1H), 7.21-7.55 (m, 33H), 7.61 (t, 1H), 7.70 (d, 1H), 7.95 (d, 1H).

Results and Discussion

The treatment of *trans*-[ReOCl₃(PPh₃)₂] with H₂dbd in a 2:1 molar ratio in acetonitrile led to the isolation of the ligand-bridged dimer (μ -dbd)[ReOCl₂(PPh₃)₂]. The same product was isolated even at equimolar quantities of reactants, and all effort to synthesize the monomer [ReOCl₂(PPh₃)₂-(Hdbd)] were unsuccessful.

The elemental analysis of the complex is in good agreement with its formulation. The infrared spectrum displays the Re=O stretching frequencies as a single peak at 937 cm⁻¹, which falls in the observed region of 906-948 cm⁻¹ for neutral six-coordinate monooxorhenium(V) complexes with an alcoholate oxygen atom coordinated *trans* to the oxo group.⁸ Deformation vibrations of the pyridine rings occur at 1603 and 1626 cm⁻¹. Two medium intensity bands at 500 and 528 cm⁻¹ are assigned to ν (Re-N). The lack of paramagnetic broadening or shifts of resonances in the ¹H NMR spectrum of the complex confirms its diamagnetic character. Due to the similarity of the coordination environment of the two pyridyl rings in the complex, the proton signals could not be assigned with certainty. Several signals in the spectrum of the complex moved upfield from their positions in the spectrum of the free ligand H₂dbd. This phenomenon shows that these protons are

particularly sensitive to their environment in the complex, probably originating from anisotropic effects. With the ligand orientation observed in the crystal structure, anisotropy from the Re=O bond is likely to be felt by H(1) and H(14). At the same time, these protons can be influenced by the anisotropy of the adjacent phosphine ligands. Coordination of dbd will also introduce significant structural modifications in its conformation/orientation from what it was in the free ligand, thereby altering the magnetic environment of the protons.

A perspective view of the asymmetric unit of (μ -dbd)-[ReOCl₂(PPh₃)₂] is shown in Figure 1. The complex displays a dinuclear structure in which two rhenium(V) ions are bridged by the dbd ligand. Each rhenium ion is in a distorted octahedral geometry. The basal plane is defined by a phosphorus atom of the PPh₃ group, two chlorides *cis* to each other, and a pyridyl nitrogen atom of dbd. The oxo group and alcoholate oxygen of dbd lie in *trans* axial positions. Distortion of an ideal rhenium-centred octahedron results in a non-linear O(1) = Re(1)-O(2) axis of 161.1(2)° [162.2(2)° for O(4) = Re(2)-O(3)] and Cl(1)-Re(1)-N(1) and Cl(2)-Re(1)-P(1) of 169.1(2)° and 178.86(6)° respectively [Cl(4)-Re(2)-N(2) = 166.4(2)°; Cl(3)-Re(2)-P(2) = 170.50(7)°]. The metal is shifted out of the mean equatorial plane formed by Cl₂NP by 0.098 Å for Re(1) towards O(1) [by 0.225 Å for Re(2) towards O(4)], with angles O(1)-Re(1)-Cl(1) = 105.0(2)° [O(4)-Re(2)-Cl(4) = 104.3(2)°], O(1)-Re(1)-Cl(2) = 93.6(4)° [O(4)-Re(2)-Cl(3) = 98.5(2)°], O(1)-Re(1)-N(1) = 85.5(3)° [O(4)-Re(2)-N(2) = 88.9(2)°] and O(1)-Re(1)-P(1) = 85.9(4)° [O(4)-Re(2)-P(2) = 90.4(2)°]. The Re(1)=O(1) axis is inclined by 10.92° with respect to the equatorial plane [by 9.15° for Re(2)=O(4)]. The two bite angles of the dbd ligand are very similar [N(1)-Re(1)-O(2) = 75.9(2)°; N(2)-Re(2)-O(3) = 74.4(2)°].

The Re=O bond lengths [average = 1.674(6) Å] are within the range expected with an alcoholate oxygen *trans* to the oxo group.⁸ There is a significant difference in bond length between Re(1)-O(2) [1.913(6) Å] and Re(2)-O(3) [1.987(5) Å], which is also reflected in the difference between the Re(1)-O(2)-C(6) [127.3(4)°] and Re(2)-O(3)-C(9) [121.1(4)°] bond angles. These bond lengths are substantially shorter than 2.04 Å, which is considered to be representative of a Re(V)-O single bond.⁹ The average Re-N bond length of 2.146(6) Å is typical of the rhenium(V)-pyridyl bonds.¹⁰ On average, the two pyridyl rings make a dihedral angle of 83.26° with the mean equatorial planes, and 64.69° with each other. The

Table 1. Crystallographic Data for (μ -dbd)[ReOCl₂(PPh₃)₂].1.5-CH₃CN

Empirical formula	C ₅₃ H _{46.50} Cl ₄ N _{3.50} O ₄ P ₂ Re ₂
Fw	1372.63
Space Group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	17.0472(4)
<i>b</i> , Å	16.9667(3)
<i>c</i> , Å	24.5031(6)
β , deg	132.945(1)
<i>V</i> , (Å ³)	5187.8(2)
<i>Z</i>	4
ρ (calc), Mg/m ³	1.755
<i>T</i> , K	200(2)
λ , Å	Mo K α (0.71073)
θ range (deg)	3.7-25.3
<i>hkl</i> ranges	-21 20, -21 21, -22 15
Reflections collected	25017
Independent reflections	9374
μ , mm ⁻¹	4.978
GOF	0.85
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0309
<i>wR</i> ₂	0.0631

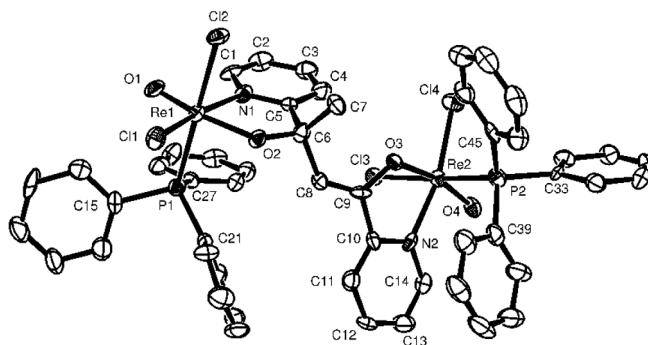


Figure 1. ORTEP plot of (μ -dbd)[ReOCl₂(PPh₃)₂] showing the atom labelling; thermal ellipsoids are drawn at 40% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg)

Re(1)-Cl(1)	2.362(2)	Re(2)-Cl(3)	2.435(2)
Re(1)-O(1)	1.675(6)	Re(2)-O(4)	1.672(5)
Re(1)-O(2)	1.913(6)	Re(2)-O(3)	1.987(5)
Re(1)-N(1)	2.148(6)	Re(2)-N(2)	2.144(5)
C(8)-C(9)	1.33(1)	C(6)-C(8)	1.51(1)
O(1)-Re(1)-O(2)	161.2(2)	O(4)-Re(2)-O(3)	162.2(2)
O(1)-Re(1)-Cl(1)	105.0(2)	O(4)-Re(2)-Cl(4)	104.3(2)
N(1)-Re(1)-O(2)	75.9(2)	N(2)-Re(2)-O(3)	74.4(2)

N-C-C angles at the ring junctions deviate significantly from 120° [N(1)-C(5)-C(6) = 116.0(7)°, N(2)-C(10)-C(9) = 112.8(6)°], and the rhenium atoms lie off the lone-pair directions of 120° [C(5)-N(1)-Re(1) = 115.0(4)°, C(10)-N(2)-Re(2) = 116.9(5)°]. The Re(1)-Cl(2) bond length [2.457(2) Å] is significantly longer than the Re(1)-Cl(1) one [2.362(2) Å], due to the larger *trans* effect of phosphorus compared to the pyridyl nitrogen.

There is a remarkable difference between the O(2)-C(6) bond length [1.43(1) Å], with C(6) sp³ hybridized [O(2)-C(6)-C(7) = 107.7(5)°], and the O(3)-C(9) length of 1.367(9) Å, with C(9) being sp² hybridized [C(8)-C(9)-C(10) = 123.3(7)°]. The C(8)-C(9) bond is double [1.33(1) Å].

The rigidity of the dimeric structure is strengthened by a comprehensive network of nine hydrogen bonds. The CH⁺⋯O interactions vary in the range 2.38-2.59 Å, and those of CH⁺⋯Cl in the range 2.59-2.79 Å.

Although oxo-bridged dimers of rhenium(V) are common, ligand-bridged species are rare in the literature. Among ligands capable of forming dinuclear complexes are pyrazoles, which can act as *exo*- or *endo*-bidentate ligands. The treatment of [ReOCl₃(PPh₃)₂] with 3,5-dimethylpyrazole (3,5-Me₂pzH) in acetone led to the isolation of the dinuclear complexes [{ReOCl(PPh₃)₂ }₂(μ-O)(μ-3,5-Me₂pz)₂] and [{ReOCl(PPh₃) }₂(μ-O)(μ-3,5-Me₂pz)₂{ReOCl(3,5-Me₂pzH)}].¹¹ The rhenium(V) μ-phosphito(1-) bridged dimeric compounds [ReOCl{μ-OP(OR)₂}(P~O)]₂ (R = Me, -CMe₂; P~O = (OCMe₂CMe₂O)-POCMe₂CMe₂O) were synthesized from the reaction of [ReOCl₂(P~O)L] (L = py, PPh₃) with P(OMe)₃ or spiroposphorane [HP(OCMe₂CMe₂O)₂].¹² In addition, the reaction of [ReN(PMe₂Ph)(Et₂dtc)₂] with an excess BH₃ in THF led to the isolation of [Re(NBH₂SBH₃)(PMe₂Ph)(Et₂dtc)]₂, in which

two rhenium(V) atoms are linked by two (NBH₂SBH₃)⁴⁺ units, which act as tridentate ligands.¹³

Supplementary Material. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 709832). A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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