



Short communication

Formation of a methine carbon-to-rhenium σ bond in an oxorhenium(V)-benzothiazole complex



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ABSTRACT

The reaction of *trans*-[ReOCl₃(PPh₃)₂] with 1-(1,3-benzothiazol-2-yl)-3-benzoylthiourea (Hbht) in methanol led to the isolation of the complex [ReOCl₂(cbt)(PPh₃)] (**1**). It contains the monoanionic bidentate chelate *N*-((benzothiazol-2-ylamino)methylene)benzamide (cbt). The new ligand cbt is coordinated *via* a neutral ketonic oxygen and an anionic imino-acyl carbon atom, and was formed by the abstraction of the thionyl sulfur of Hbht by a triphenylphosphine of the starting complex, with S = PPh₃ also been formed as by-product. Compound **1** was characterized by elemental analysis, FTIR, proton NMR and single crystal X-ray diffraction.

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Due to its central position in the Periodic Table, the metal rhenium is probably the most versatile of all transition metals, since it occurs in all oxidation states from $-I$ to $+VII$ [1]. The considerable current interest in the coordination chemistry of the metal is not only due to the possible application of its ^{186/188}Re isotopes in nuclear medicine, but also due to the large variety of the structural, photophysical, redox and photochemical properties of its complexes [2]. These properties are mainly determined by the coordination sphere of the metal ion [2,3].

Benzothiazole compounds have exhibited a large variety of biological activities [4]. Previous studies on rhenium complexes of benzothiazoles have concentrated on the oxidation states $+I$ and $+V$. With benzothiazole (bt) the complex [Re^I(CO)₃(bt)₂Cl] was isolated, in which each bt ligand is coordinated in a monodentate manner *via* the thiazole nitrogen atom [5]. With [ReOCl₃(PPh₃)₂] as precursor, the complex [ReOCl₂(hbt)(PPh₃)] was characterized from the reaction with 2-(2'-hydroxyphenyl)-2-benzothiazole (Hhbt) [6]. A benzothiazole derivative conjugated as a monoamine-monoamide was used to synthesize an oxorhenium(V) complex, which showed selective binding to amyloid aggregates in the brains of patients with Alzheimer's disease [7]. Our aim is to synthesize complexes in which the benzothiazole moiety is uncoordinated, leaving it free to bind to A β plaques *via* intercalation and π - π interactions [8].

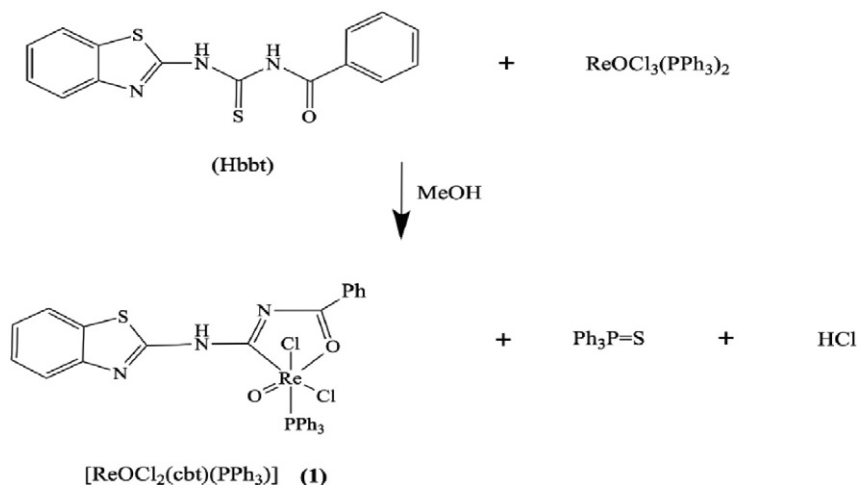
We considered Hbht (Scheme 1) as an interesting ligand for the oxorhenium(V) moiety. Hbht has a few coordination possibilities, from dianionic tridentate (NSO), to bidentate (NS or SO) and even

monodentate [9]. It is important to note that these chelation modes will all lead to the formation of six-membered metallocycles [10]. However, in its reaction with [ReOCl₃(PPh₃)₂] in methanol [11], the thione sulfur atom was abstracted by a triphenylphosphine group, to form the chelate cbt, which is coordinated to the metal *via* a neutral ketonic oxygen atom and monoanionic imino-acyl sp²-hybridized carbon atom (see Scheme 1) in the complex [ReOCl₂(cbt)(PPh₃)] (**1**). Crystals of S = PPh₃ were found in the residue obtained from the evaporation of the mother liquor, and its identity was established by an X-ray crystal structure determination [12]. As far as could be established, complex **1** is the first example of an oxorhenium(V) complex containing a methine carbon-to-rhenium(V) σ bond in its coordination sphere. It is also a rare occurrence in high oxidation state coordination chemistry.

The Re=O stretching frequency appears at 947 cm⁻¹ in the IR spectrum of **1**. A medium intensity and a strong intensity peak at 1694 and 1588 cm⁻¹ are assigned to ν (C=O) and ν (C=N) respectively. The N-H stretch occurs at 3055 cm⁻¹, and a strong peak at 508 cm⁻¹ is tentatively assigned to ν (Re-C). The UV-vis spectrum in DMF shows an absorption band at 300 nm, ascribed to the $\pi \rightarrow \pi^*$ transition in the coordinated ligand cbt, and another at 387 nm, which is ascribed to a combination of the ligand-to-metal charge transfer transitions LMCT [$p_{\pi}(O^{2-}) \rightarrow d_{\pi}^*(Re)$, $p_{\pi}(C^-) \rightarrow d_{\pi}^*(Re)$ and $p_{\pi}(Cl^-) \rightarrow d_{\pi}^*(Re)$] respectively [13]. A weak absorption at 663 nm is assigned to a d-d transition [$(d_{xy})^2 \rightarrow (d_{xy})^1(d_{xz})^1$]. The position of these bands and their assignment are in accordance with other Schiff base complexes of oxorhenium(V) complexes [14]. The ¹H NMR spectrum is complicated by the signals of the phenyl protons of PPh₃, in addition to the multiplets of the aromatic protons of cbt, which give rise to nine-proton multiplets in the region 7.64–7.78 ppm. The NH proton occurs as a singlet at

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Scheme 1. Summary of the formation reaction of complex **1**.

3.51 ppm. Conductivity measurements show that complex **1** is a non-electrolyte in nitromethane.

Single-crystal X-ray crystallography [15] of complex **1** intimates that the cbt ligand is monoanionic and coordinates to the rhenium(V) centre as a bidentate chelate through the anionic methine carbon C(2) and neutral ketonic oxygen atom O(1) to form a five-membered metalocycle [see Fig. 1]. The O(1)–C(3) bond is double [1.290(6) Å], and the Re–O(1) bond length of 2.074(3) Å is longer than previously found for anionic oxygen atoms coordinated *trans* to the oxo group, and that normally occur in the range 1.94–2.01 Å [16]. The O(1)–C(3)–C(21) bond angle [120.0(4)°] shows the sp²-hybridization of C(3). Although bonding parameters for Re–C(methine) bonds are not

available in the literature, the Re–C(2) distance of 2.080(5) Å corresponds to the lengths of Re–C(aryl) σ bonds, which occur in the narrow range 2.06(2)–2.10(3) Å [17]. The N(2)–C(2)–N(3)–C(3) backbone of the chelate shows considerable delocalization of π-electron density, with the interatomic bond lengths very similar to each other [N(2)–C(2) = 1.341(6), N(3)–C(2) = 1.345(6), N(3)–C(3) = 1.335(6) Å].

The bite angle [O(1)–Re–C(2) = 72.4(2)°] of cbt contributes considerably to the distortion of the octahedron around the metal centre, as shown by the *trans* angles C(2)–Re–Cl(2) [154.2(1)°] and O(2)–Re–O(1) [163.0(2)°], in contrast to the angle P(1)–Re–Cl(1) [172.29(5)°]. The steric influence and *trans* effect of the oxo ligand are reflected in the large *cis* angles O(2)–Re–Cl(1) [99.1(1)°], O(2)–Re–

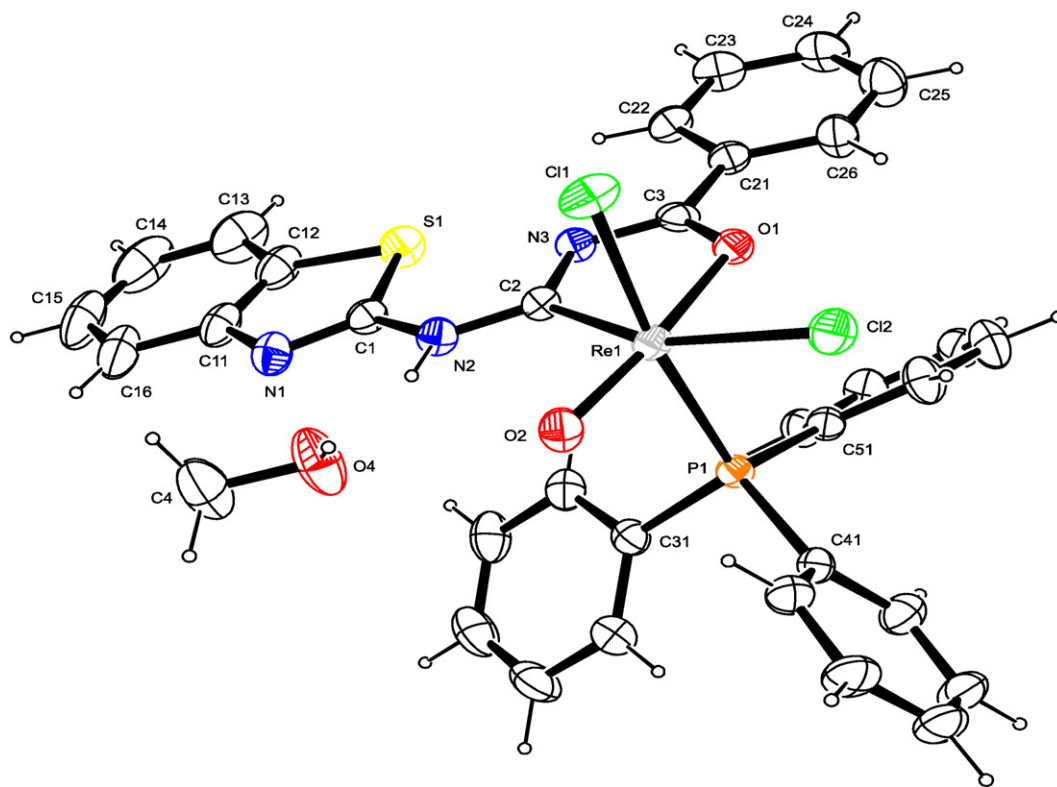


Fig. 1. ORTEP view of complex **1** showing 50% probability displacement ellipsoids and atom labelling. Selected bond lengths [Å]: Re(1)–O(2) 1.673(3), Re(1)–O(1) 2.074(3), Re(1)–C(2) 2.080(5), Re(1)–P(1) 2.472(1), Re(1)–Cl(1) 2.393(1), Re(1)–Cl(2) 2.366(1), C(1)–N(1) 1.286(6), C(3)–O(1) 1.290(6), C(2)–N(3) 1.345(6). Bond angles [°]: O(2)–Re(1)–O(1) 163.0(2), O(2)–Re(1)–Cl(1) 99.1(1), O(2)–Re(1)–Cl(2) 113.6(1), O(1)–Re(1)–C(2) 72.4(2), O(1)–C(3)–C(21) 120.0(4).

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