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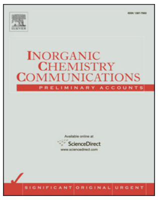

Short Communication

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

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ABSTRACT

The reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with 1-(1,3-benzothiazol-2-yl)-3-benzoylthiourea (Hbbt) in methanol led to the isolation of the complex [$ReOCl_2$(cbt)(PPh_3)] (**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 Hbbt by a triphenylphosphine of the starting complex, with S = PPh_3 also been formed as by-product. Compound **1** was characterized by elemental analysis, FTIR, proton NMR and single crystal X-ray diffraction.

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 [$ReOCl_3(PPh_3)_2$] as precursor, the complex [$ReOCl_2$(hbt)(PPh_3)] 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 Aβ plaques *via* intercalation and π–π interactions [8].

We considered Hbbt (Scheme 1) as an interesting ligand for the oxorhenium(V) moiety. Hbbt 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 [$ReOCl_3(PPh_3)_2$] 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 sp^2-hybridized carbon atom (see Scheme 1) in the complex [$ReOCl_2$(cbt)(PPh_3)] (**1**). Crystals of S = PPh_3 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 π → π* 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 ^{1}H NMR spectrum is complicated by the signals of the phenyl protons of PPh_3, 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 *N*H proton occurs as a singlet at

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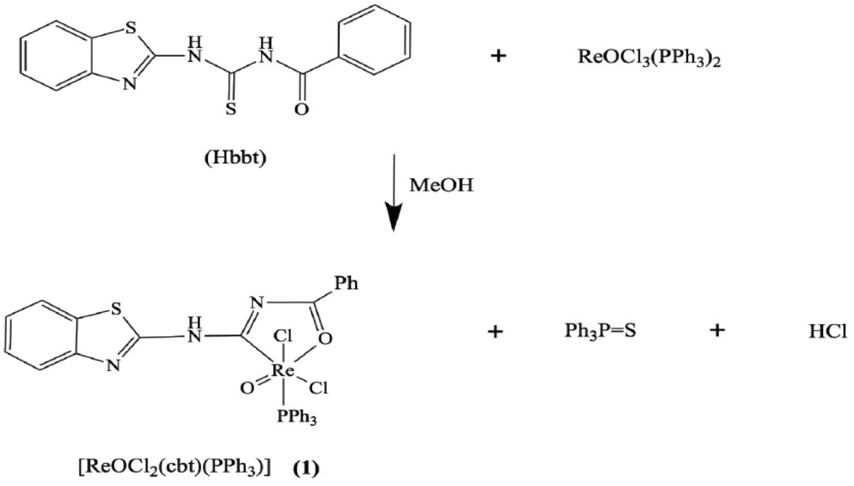

Scheme 1. Summary of the formation reaction of complex **1**.

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 metallocycle [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 sp^2-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–

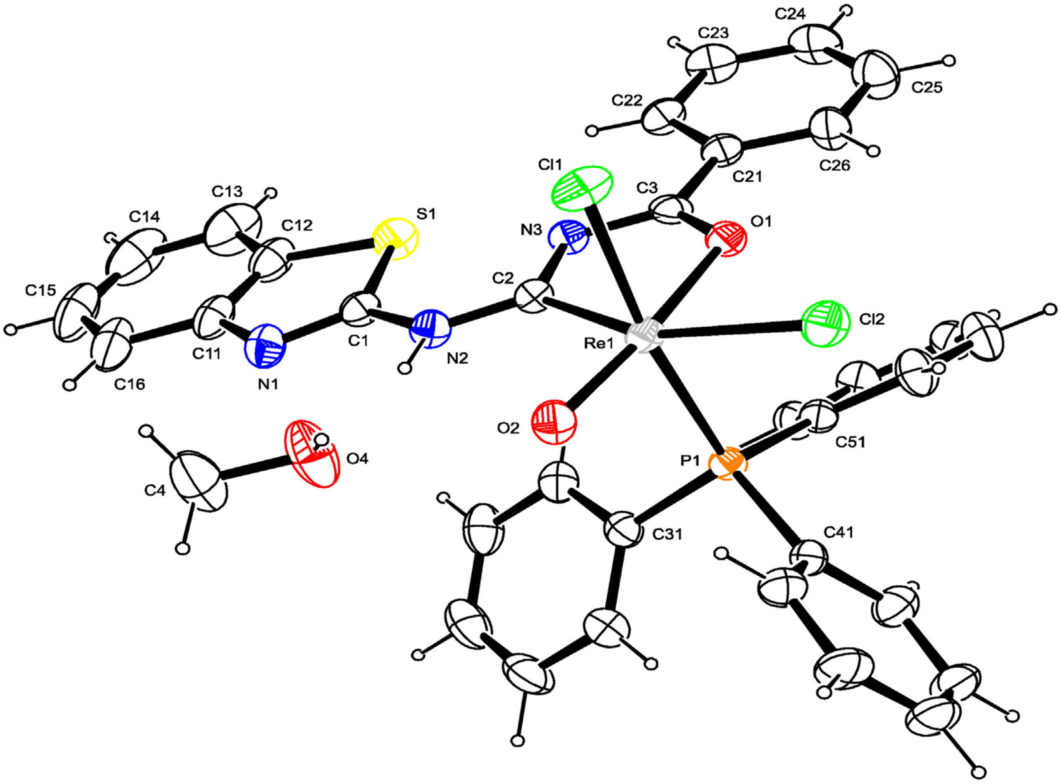

Fig. 1. ORTEP view of complex **1** showing 50% probability displacement ellipsoids and atom labelling. Selected bond lengths [Å]: Re(1)–O(2) 1.673(3), Re(1)–O(1) 2.074(3), Re(1)–C(2) 2.080(5), Re(1)–P(1) 2.472(1), Re(1)–Cl(1) 2.393(1), Re(1)–Cl(2) 2.366(1), C(1)–N(1) 1.286(6), C(3)–O(1) 1.290(6), C(2)–N(3)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

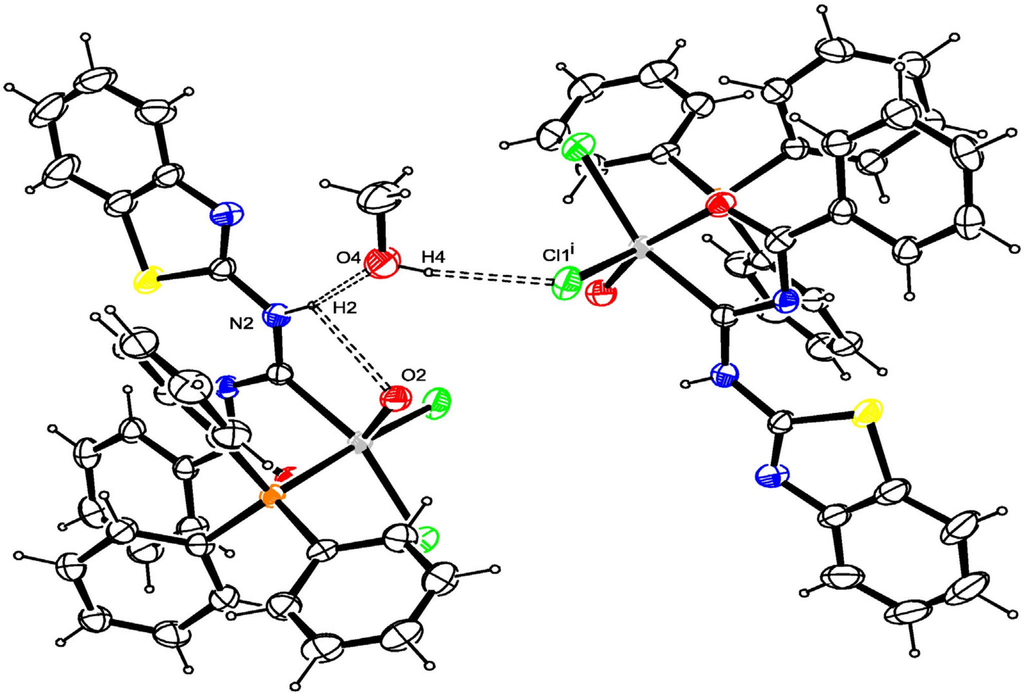

Fig. 2. Intra- and inter-molecular hydrogen-bonds in **1**.EtOH. Thermal ellipsoids are drawn at 50% probability. Symmetry elements: (i) x, −1 + y, z.

Cl(2) [113.6(1)°] and O(2)–Re–C(2) [92.1(2)°]. The O(2)–Re–P(1) angles equals 88.4(1)°.

The Re = O(2) bond length of 1.673(3) Å falls at the lower end of the range observed [1.66(1)–1.69(2) Å] for neutral octahedral monooxorhenium(V) complexes, which is probably due to the coordination of the neutral O(1) *trans* to it [18–20]. The Re–Cl(1) bond [2.393(1) Å] is longer that the Re–Cl(2) one [2.366(1) Å], due to the larger *trans* effect of the phosphorus atom of PPh_3 [Re–P(1) = 2.472(1) Å].

The bonding in the molecule is complemented by the intramolecular hydrogen-bond N(2)–H(2)···O(2) [2.49 Å], and the methanol solvent of crystallization is involved in two hydrogen-bonds, to N(2)H [O(4)···H(2)–N(2) = 1.93 Å] and to Cl(1) [O(4)–H(4)···Cl(1) = 2.41 Å] (Fig. 2).

We believe that the electronegativity of the nitrogen atoms adjacent to the C═S group in Hbbt, and the formation of a stable five-membered chelate ring in complex **1**, are critical factors in the driving force of the unusual reaction described here. The abstraction of the sulfur will only occur after the initial coordination of Hbbt and substitution of a triphenylphosphine group. The removal of sulfur by triphenylphosphine has been observed in the complex (*p*-perthiocumato)(*p*-dithiocumato) nickel(II), and it was found that the rate of abstraction depends on the concentrations of both the complex and phosphine [21]. The abstraction of sulfur by PPh_3 has also occurred in the rhenium(III) complex $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$ to form the seven-coordinate $[Re(S_2CC_6H_5)_3(PPh_3)]$ [22].

The activation of hydrocarbon C—H bonds is well known in organometallic chemistry, and examples are mainly electron-rich complexes of the later transition metals [23]. Also, the C—H bond cleavage of a methine carbon of a Schiff base by a ruthenium(II) complex has recently been reported [24].

Acknowledgments

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Appendix A. Supplementary data

Supplementary data for **1** (CCDC 1448650) are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2016.03.020

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[11] Synthesis of $[ReOCl_2(cbt)(PPh_3)]$ (**1**). A mixture of 1-(1,3-benzothiazol-2-yl)-3-benzoylthiourea (Hbbt) (40 mg, 120 μmol) and *trans*-$[ReOCl_3(PPh_3)_2]$ (100 mg, 120 μmol) in 20 cm^3 of methanol was stirred at reflux for 2 hours. The reaction mixture was cooled to room temperature and filtered, leaving a green precipitate. The mother liquor was left to slowly evaporate at room temperature, resulting in green crystals after 3 days. Yield: 63 mg (62%). M.p. 146–147 °C. Anal. Calcd. for $C_{33}H_{25}Cl_2N_3O_2PReS\cdot CH_4O$: C, 48.2; H, 3.4; N, 5.0. Found: C, 48.6; H, 3.6; N, 4.7%. Conductivity (nitromethane, 10^{-3} M) 29 ohm^{-1} cm mol^{-1}. IR (KBr, ν_{max}/cm^{-1}): ν(N—H) 3055; ν(Re═O) 947; ν(C═N) 1588; ν(C═O) 1694; ν(Re–C) 508. ^1H NMR ($CDCl_3$, 295 K, ppm): 7.64–7.78 (m, 9H), 7.46–7.59 (m, 15H, P*Ph*$_3$), 3.51 (s, H, N*H*). Electronic spectrum (DMF, λ (ε, M^{-1} cm^{-1})): 300 (21050), 387 (5200), 663 (305) nm.
[12] Crystallographic data for S = PPh_3: monoclinic; space group $P2_1/c$; a = 18.1858(8), b = 9.5533(4), c = 17.8970 (8) Å; β = 106.040(2)°; V = 2988.3(2) $Å^3$; Z = 8; D_c = 1.309 g cm^{-3}; μ = 0.310 mm^{-1}; data/parameters: 7429/361; S = 1.04; final R indices [I > 2σ(I)]: R1 = 0.0317, wR2 = 0.0941.

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[15] Crystallographic data for **1**.MeOH: monoclinic; space group $P2_1/n$; a = 11.2178(5), b = 11.1662(5), c = 25.982 (1) Å; β = 90.183(2)°; V = 3254.5(3) $Å^3$; Z = 4; D_c = 1.730 g cm^{-3}; μ = 4.051 mm^{-1}; data/restraints/parameters: 8085/0/408; S = 1.26; final R indices [$I > 2\sigma(I)$]: R1 = 0.0399, wR2 = 0.0858.
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