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Short Communication

The trigonal-bipyramidal $[ReOI_2(PPh_3)_2]$ – The first monomeric oxorhenium(IV) complex with monodentate ligands only



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A R T I C L E I N F O

ABSTRACT

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Keywords: Oxorhenium(IV) Iodide Monomeric Trigonal-bipyramid The reaction of *cis*-[Re^VO₂I(PPh₃)₂] with 2-(3,5-dimethylpyrazol-1-yl)benzothiazole (dbt) in ethanol led to the isolation of the trigonal-bipyramidal oxorhenium(IV) complex *trans*-[ReOI₂(PPh₃)₂] (1). The complex is the first example of a monomeric oxo complex of rhenium(IV). Complex **1** was characterized by FTIR, ¹H NMR, microanalysis and single crystal X-ray diffraction.

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The oxo group and halides are most commonly found as ligands in the high oxidation state coordination chemistry of rhenium [1,2]. Normally the choice of halide has been either a chloride or bromide, and iodide has rarely been used as ligand. For example, the most common starting complexes for the synthesis of oxorhenium(V) complexes have been *trans*-[ReOX₃(PPh₃)₂] and [ReOX₄]⁻ (X = Cl, Br) [3]. Although [ReO(OEt)I₂(PPh₃)₂] and *cis*-[ReO₂I(PPh₃)₂] are easily synthesized [4], they are not commonly used as precursors. The chloro and bromo analogue of the latter complex do not exist, implying that the coordination chemistry of high oxidation state iodo-rhenium complexes may be different to that of chloride/bromide. Indeed, using *cis*-[ReO₂I(PPh₃)₂] as starting complex has led to some unusual and unexpected products, quite different to those formed by *trans*-[ReOX₃(PPh₃)₂] as precursors [5].

Oxorhenium(V) complexes acting as catalysts for various catalytic processes commonly contain iodo as a ligand. For example, *cis*-[ReO₂I(PPh₃)₂] is active as a catalyst in the enantioselective reduction of imines and hydrosilylation [6], and [(HBpz₃)ReO₂I] has been used to activate C—H bonds of alkyls/aryls [7].

To our knowledge, monomeric oxorhenium(IV) complexes containing only monodentate ligands have never been reported in the literature. Monomeric oxo complexes of rhenium(V) are well known, and they have even been reported for rhenium(III) [for example ReOI(MeC \equiv CMe)] [8] and rhenium(I) [ReO(MeC \equiv CMe)]⁻ [9].

As part of our program on benzothiazole complexes of rhenium in various oxidation states, we have reacted *cis*-[ReO₂I(PPh₃)₂] with the potentially bidentate *N*,*N*-donor 2-(3,5-dimethyl-pyrazol-1-yl)benzothiazole

* Corresponding author. E-mail address: Thomas.gerber@nmmu.ac.za (T.I.A. Gerber). (dbt) in ethanol [10]. The expectation was that coordination would occur via the nitrogen atoms on the benzothiazole and pyrazole moieties to form the *trans*-dioxorhenium(V) complex salt $[ReO_2(dbt)_2]I$, as was observed for other similar reactions with nitrogen-donor ligands [11]. Surprisingly, dbt did not coordinate to the metal, and the known oxorhenium(V) compound $[ReO(OEt)I_2(PPh_3)_2]$ [4] and oxorhenium(IV) complex $[ReOI_2(PPh_3)_2]$ (1) were isolated [12]. The product 1 is unusual since it is the first example of a monomeric monooxorhenium(IV) complex.

In the IR spectrum of **1** the ν (Re=O) appears as a very strong peak at 966 cm⁻¹. The ¹H NMR spectrum only contains the signals of the phenyl protons of the PPh3 ligands, with no other signals that can be ascribed to the protons of dbt. The complex is soluble, and gives orange solutions, in polar organic solvents.

Fig. 1 shows an ORTEP illustration of **1**, which is a five-coordinate rhenium(IV) complex containing only monodentate ligands, i.e. two triphenylphosphines, two iodos and an oxo group [13]. The complex adopts a trigonal-bipyramidal (tbp) geometry with the phosphines in the *trans* apical positions. The oxo oxygen and iodos form the trigonal plane. The distortion from the tbp geometry is the result of the *trans* P(1)—Re— $P(1^i)$ angle of 163.43(2)°, and the equatorial bond angles I(1)—Re— $I(1^i)$ [143.82(1)°] and O(1)—Re—(I) [108.09(1)°]. The two *trans* axial PPh₃ groups are bent away from the oxo group [O(1)—Re— $P(1) = 98.29(1)^\circ$; I(1)—Re— $P(1) = 87.58(2)^\circ$].

The Re=O bond length [1.688(3) Å] falls at the upper end of the range of 1.66 (2)–1.69(2) Å observed for this bond in other similar neutral monooxorhenium(V) complexes [14], and it shows considerable triple bond character. The Re—P bond lengths of 2.4547(7) Å are shorter than in the five-coordinate *cis*-[ReO₂I(PPh₃)₂] [2.488(3) Å], while the Re—I bonds [2.6951(3) Å] are longer [2.664(2) Å] [4].



Fig. 1. ORTEP representation of *trans*-[ReOI₂(PPh₃)₂] (1). Selected bond lengths [Å]: Re–I 2.6951(3), Re–O 1.688(3), Re–P 2.4547(7); bond angles[°]: P(1)–Re–P(1ⁱ) 163.43(2), O(1)–Re–I(1) 108.09(1), O(1)–Re–P(1) 98.29(1), I(1)–Re–I(1ⁱ) 143.82(1).

Compared to rhenium(III) or (V), complexes of rhenium(IV) are rare in the literature. It is an inter-mediate oxidation state which can easily be oxidized or reduced under mild conditions [15]. It was shown that perrhenate [ReO_4^-] is a common byproduct in the synthesis of rhenium(IV) complexes from rhenium(V) precursors [16], so it is likely that complex 1 originates from the disproportionation of [$\text{ReO}(\text{OEt})I_2(\text{PPh}_3)_2$] to 1 and ReO_4^- . Interestingly, the reaction of [$\text{ReO}(\text{OEt})CI_2(\text{PPh}_3)_2$] with acetylacetone (Hacac) gave [$\text{Re}^{IV}CI_2(\text{acac})_2$] as product [17].

Acknowledgements

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Appendix A. Supplementary data

Supplementary data for **1** (CCDC 1449984) 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.

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- [12] A mixture of *cis*-[ReO₂l(PPh₃)₂] (100 mg, 115 µmol) and 2-(3,5-dimethyl-pyrazol-1-yl)-benzothiazole (dbt) (53 mg, 231 µmol) was heated under reflux in 20 cm³ of ethanol for four hours. After cooling to room temperature, the solution was filtered to produce [ReO(OEt)₁₂(PPh₃)₂] as a green precipitate, which was washed with ethanol and dried under vacuum. Yield = 38 mg (32% based on Re), m.p. 173–175 °C. Anal. Calcd. for C₃₈H₃₅I₂O₂P₂Re: C, 44.5; H, 3.4. Found: C, 44.7; H, 3.3%. IR ($\nu_{max}/$ cm⁻¹): ν (Re=O) 943 m; δ (OCH₂) 906 s. ¹H NMR (295 K, ppm, CDCI₃): 7.32–7.82 (m, PPh₃); 3.64 (q, 2H, OCH₂CH₃); 1.17 (t, 3H, OCH₂CH₃). The mother liquor was left to evaporate at room temperature, and after 5 days orange-red crystals of 1 were harvested. These were washed with acetone and dried under vacuum. Yield = 14 mg (12% based on Re), m.p. 139–141 °C. Anal. Calcd. for C₃₆H₃₀L₂OP₂Re: C, 44.1; H, 3.1. Found: C, 44.6; H, 3.3%. IR ($\nu_{max}/$ cm⁻¹): ν (Re=O) 966 s. ¹H NMR (295 K, ppm, CDCI₃): 7.32–7.72 (m, PPh₃).
- [13] Crystallographic data for C₃₆H₃₀I₂OP₂Re (1): monoclinic; space group I2/a; a = 15.755(1), b = 9.8578(6), c = 22.536(2) Å; V = 3394.9(4) Å³; Z = 4; D_c = 1.918 g cm⁻³; μ = 5.519 mm⁻¹; data/parameters: 4248/191; S = 1.04; final R indices [I > 2 σ (I)]: R1 = 0.0164, wR2 = 0.0411.
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