



Novel rhenium(II) complex of 2,3,5,6-tetra(2-pyridyl)pyrazine – Synthesis, X-ray studies, spectroscopic characterization and DFT calculations

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ARTICLE INFO

Article history:

Received 8 March 2010

Accepted 23 April 2010

Available online 10 May 2010

Keywords:

Rhenium complexes

2,3,5,6-Tetra(2-pyridyl)pyrazine

X-ray structure

Electronic structure

DFT calculations

ABSTRACT

A novel rhenium complex of multi-dentate ligand 2,3,5,6-tetra(2-pyridyl)pyrazine – $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$ – has been synthesized and characterised spectroscopically and structurally. The electronic spectrum of $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$ has been investigated at the TDDFT level employing B3LYP functional in combination with LANL2DZ.

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The coordination chemistry of rhenium is a field of current growing interest from various viewpoints. The attention of scientists concentrates on synthetic aspects, structural, physicochemical properties and reactivity, as well as on topics with an applied character such as the development of radiotherapeutic cancer agents, nitrogen fixation and catalysis [1].

The ^{186}Re (1.07 MeV β -emitter, $t_{1/2}$ 90 h) and ^{188}Re (2.12 MeV β -emitter, $t_{1/2}$ 17 h) are among the most attractive isotopes for applications in targeted radionuclide therapy [2,3]. The diazenido and dinitrogen rhenium complexes are important in view of their significance in the field of nitrogen fixation [4–6]. Methyltrioxorhenium is one of the most versatile catalysts for olefin oxidation reactions, aldehyde olefination and olefin metathesis [7,8]. The *mer*, *trans*- $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and its derivatives catalyze the oxidation of sulfides to sulfoxides, thiols to disulfides and catalyze oxygen-transfer from sulfoxides to phosphines [8]. The $[\text{ReOCl}_2(\text{O}-\text{N})(\text{PPh}_3)]$ chelates with pyridinecarboxylate ligands exhibit a remarkable catalytic activity for the conversion of ethane to a mixture of propionic and acetic acids in a single-pot process [9]. The $[\text{CH}_3\text{ReO}(\text{pic})_2]$ complex is an active precursor in olefin oxidation and forms epoxides in a two-phase H_2O_2 – $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ system [10].

In this context, the design, synthesis and reactivity of novel rhenium complexes has become the aim of several laboratories, including ours.

Previously, we investigated the reactivity of oxorhenium(V) species – $[\text{ReOX}_3(\text{PPh}_3)_2]$ and $[\text{ReOX}_3(\text{AsPh}_3)(\text{OAsPh}_3)]$ ($X = \text{Cl}$ or Br) – towards

pyrazole, 3,5-dimethylpyrazole, benzotriazole, pyrazine, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 6-diphenyl-3-(2-pyridyl)-1,2,4-triazine, 2,2':2'6''-terpyridine [11–15].

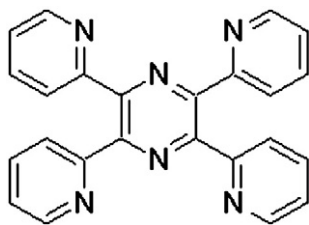
In this report we focus on the examinations of the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz; Scheme 1).

A variety of binding modes of tppz were reported so far. 2,3,5,6-tetra(2-pyridyl)pyrazine is able to act as a bidentate, tridentate, bis-bidentate, tris-bidentate and bis-tridentate forming both mono-, bi- and tri-nuclear complexes [16–19]. Recently, the synthesis and characterization of a series of mono-, di- and tri-nuclear rhenium(I) tricarbonyl complexes of tppz has been reported [20].

Here we present the synthesis, spectroscopic characterization and X-ray studies for $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$. Firstly, the complex was isolated with very small yield from the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_3]$ [21] with 2,3,5,6-tetra(2-pyridyl)pyrazine. Much higher yield of $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$ was achieved when the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_3]$ with 2,3,5,6-tetra(2-pyridyl)pyrazine was carried out in the presence of free PPh_3 [22]. The higher product yield in the presence of PPh_3 supports the mechanism of reduction via oxygen abstraction as OPPh_3 , proposed by Rouschias and Wilkinson for $[\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2]$ and confirmed recently for other systems [23,24]. Triphenylphosphine reacts with the starting oxocompound to produce phosphine oxide $\text{Re}(\text{III})$ complex. The good-leaving OPPh_3 ligand is easily replaced by initially monodentate tppz molecule, and releasing of chloride ions leads to formation of $[\text{Re}^{\text{III}}\text{Cl}(\text{tppz})(\text{PPh}_3)_2]\text{Cl}_2$. Such mechanism has been confirmed for the reaction of $[\text{ReOX}_3(\text{PPh}_3)_2]$ with biimidazole (biimH_2) in the presence of free PPh_3 , resulting in the formation of $[\text{Re}^{\text{III}}\text{X}_2(\text{biimH}_2)(\text{PPh}_3)_2]\text{X}$ [24]. In our case, the complex $[\text{Re}^{\text{III}}\text{Cl}(\text{tppz})(\text{PPh}_3)_2]\text{Cl}_2$ has not been isolated from the

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Scheme 1. Structure of tppz ligand.

reaction system, it disproportionates into Re(II) and Re(VII) forming the title complex $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$. Only few Re(II) complexes incorporating N-heterocycle ligands are known and 2,3,5,6-tetra(2-pyridyl)pyrazine is a structurally relevant multi-dentate ligand [25].

A strong absorption band at 909 cm^{-1} in the IR spectrum of $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$ [26] corresponds to $\nu(\text{Re}=\text{O})$ mode of the perrhenate anion and its location is in agreement with the literature value of $\nu_3(\text{Re}=\text{O})$ 918 cm^{-1} for ReO_4^- . The characteristic bands corresponding to the $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$ modes of the tppz ligand appear in the range of $1590\text{--}1530\text{ cm}^{-1}$ [27].

The complex $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$ crystallises in P-1 space group [28]. The classical hydrogen bonds are not found in the structure $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$, only some of no real significance C–H...X weak inter- and intramolecular hydrogen bonds exist [29].

The molecular structure and selected bond distance and angles of $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$ are presented in Fig. 1.

The pseudooctahedral environment of Re center in $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2]^+$ shows clear distortions induced by narrow bite angles of the tridentate coordinated 2,3,5,6-tetra(2-pyridyl)pyrazine. The chloride ion and tppz molecule hold the equatorial positions. The axial positions of the distorted octahedron of $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2]^+$ are occupied by triphenylphosphine molecules.

The Re–N bond lengths of $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2]^+$ are in good agreement with those found for the rhenium polypyridyl compounds

$([\text{ReCl}_2(\text{bipy})_2]\text{PF}_6 - 2.094(5)$ and $2.096(5)\text{ Å}$ [30] and in the $[\text{ReL}(\text{terpy})_2]^{2+}$ ($\text{L}=\text{Cl}, \text{OH}, \text{NCS}$) complexes – about 2.10 Å [31]), and significantly shorter than comparable distances for saturated amine complexes, where metal-to-ligand π -back bonding is not possible [32]. The electron rich central ion of $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2]^+$ shows larger affinity towards the pyrazine ring, and the $\text{Re}(1)\text{--N}(2)$ is slightly shorter than the $\text{Re}(1)\text{--N}(1)$ and $\text{Re}(1)\text{--N}(3)$ bonds (Fig. 1). The similar trend is observed in almost all terpy-metal complexes, in which the central M–N bond length is characteristically shorter than those terminals. Only in $[\text{ReO}(\text{SC}_6\text{H}_4\text{--Me-p})(\text{terpy})]^+$, in which terpy coordinates opposite the strong σ - and π -donor oxo ligand, the central nitrogen atom of the terpy ligand has a longer Re–N length than the distal nitrogen atoms [33].

The gas phase ground state geometries of the cation $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2]^+$ and ReO_4^- anion were optimised without any symmetry restrictions in a doublet and singlet state respectively with the DFT method using the hybrid B3LYP functional of GAUSSIAN-09 [34].

Currently density functional theory (DFT) is commonly used to examine the electronic structure of transition metal complexes. It meets with the requirements of being accurate, easy to use and fast enough to allow the study of relatively large molecules of transition metal complexes. Furthermore, understanding the electronic structure of coordination and organometallic compounds is an important goal of current spectroscopic, photophysical, photochemical and theoretical research. The calculations were performed using ECP basis set LANL2DZ [35] with an additional d and f function with the exponent $\alpha = 0.3811$ and $\alpha = 2.033$ [36] for rhenium and the standard 6-31G basis set for other atoms. For chloride, oxygen, nitrogen and phosphorous atoms, diffuse and polarization functions were added [37–42].

In general, the predicted bond lengths and angles are in agreement with the values based upon the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations [43].

A good agreement with the experimental values can be noticed for the Re–O and Re–N bond lengths. Larger differences between

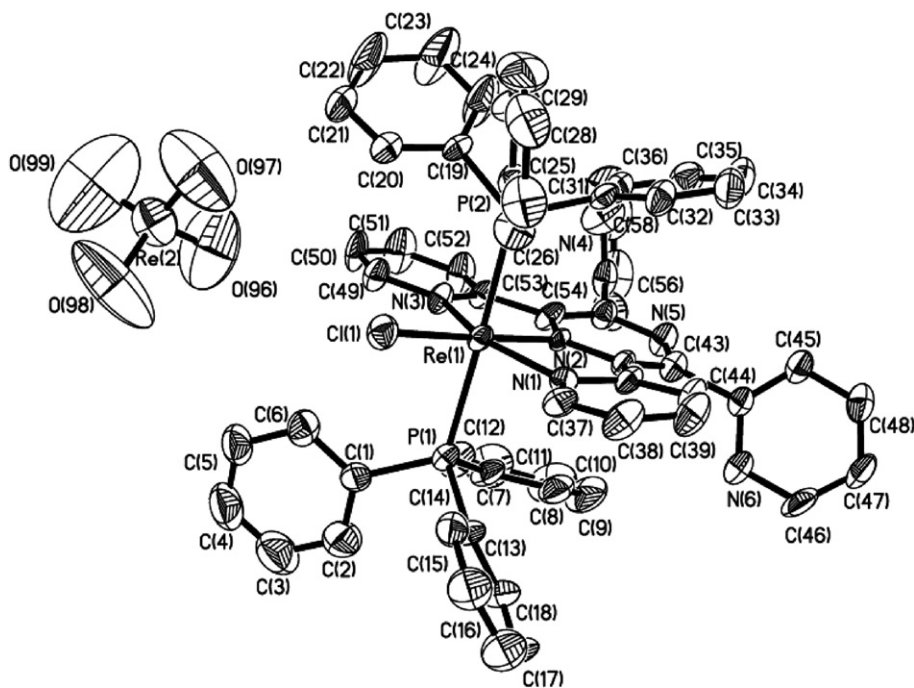


Fig. 1. Molecular structure of $[\text{ReCl}(\text{tppz})(\text{PPh}_3)_2][\text{ReO}_4]$. Selected bond lengths [Å]: $\text{Re}(1)\text{--N}(1)$ 2.093(6); $\text{Re}(1)\text{--N}(2)$ 1.975(6); $\text{Re}(1)\text{--N}(3)$ 2.078(6); $\text{Re}(1)\text{--Cl}(1)$ 2.390(2); $\text{Re}(1)\text{--P}(1)$ 2.459(2); $\text{Re}(1)\text{--P}(2)$ 2.4494(19). Bond angles [°]: $\text{N}(2)\text{--Re}(1)\text{--N}(1)$ 76.9(2); $\text{N}(3)\text{--Re}(1)\text{--N}(1)$ 153.9(2); $\text{N}(2)\text{--Re}(1)\text{--N}(3)$ 77.0(2); $\text{N}(2)\text{--Re}(1)\text{--Cl}(1)$ 176.54(17); $\text{N}(3)\text{--Re}(1)\text{--Cl}(1)$ 105.14(17); $\text{N}(1)\text{--Re}(1)\text{--Cl}(1)$ 100.90(16); $\text{N}(2)\text{--Re}(1)\text{--P}(2)$ 89.53(16); $\text{N}(3)\text{--Re}(1)\text{--P}(2)$ 88.48(17); $\text{N}(1)\text{--Re}(1)\text{--P}(2)$ 90.50(16); $\text{Cl}(1)\text{--Re}(1)\text{--P}(2)$ 87.84(7); $\text{N}(2)\text{--Re}(1)\text{--P}(1)$ 91.36(17); $\text{N}(3)\text{--Re}(1)\text{--P}(1)$ 90.15(17); $\text{N}(1)\text{--Re}(1)\text{--P}(1)$ 91.27(16); $\text{Cl}(1)\text{--Re}(1)\text{--P}(1)$ 91.34(7); $\text{P}(2)\text{--Re}(1)\text{--P}(1)$ 178.16(6).

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