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Synthesis, characterization and molecular structure of the complex $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$

María Cristina Goite[1]*, *Rubén A. Machado*[1], *David Rivillo*[1], *Ysaura De Sanctis*[1], *Alejandro J. Arce*[1], *Antony J. Deeming*[2], *Reinaldo Atencio*[1], *Alexander Briceño*[1], *Lindora D'Ornelas*[3]

[1]*Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC).*
Apartado 21827. Caracas 1020-A, Venezuela.
[2]*Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK.*
[3]*Laboratorio de Síntesis Organometálica, Escuela de Química, Facultad de Ciencias,*
Universidad Central de Venezuela. Apartado 47102. Caracas, Venezuela.

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Abstract

Reaction of the labile compound $[Re_2(CO)_8(CH_3CN)]_2$ with 2,3-bis(2-pyridyl)pyrazine refluxing in a wet tetrahydrofuran solution (3% H_2O), gave the new compound $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ (**1**). The tetranuclear rhenium derivative **1** is a doubly zwitterion bearing 2,3-bis(2-pyridyl)-5--hydropyrazine anions. The X-ray crystal structure of **1** shows that the $C_{14}H_{11}N_4$ moieties are bonded in a chelating form to two rhenium centers through the N-atoms of pyridine and hydropirazine, where positive charges are supported by two metallic centers. The $(Re_2(CO)_6(C_{14}H_{11}N_4))$ moieties are linked together by two OH ligands bridging the rhenium atoms.

Keywords: Rhenium carbonyls, α-diimines, doubly zwitterion, 2,3-bis(2-pyridyl)pyrazine, crystal structures.

Síntesis, caracterización y estructura molecular del complejo $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$

Resumen

La reacción del compuesto lábil $[Re_2(CO)_8(CH_3CN)]_2$ con 2,3-bis(2-piridil)pirazina en una solución de tetrahidrofurano con 3% de H_2O a temperatura de reflujo, conduce a un nuevo compuesto $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ (**1**). El derivado tetranuclear de renio **1** es un doble zwitterion que contiene dos aniones 2,3-bis(2-piridil)-5-hidropirazina. La estructura cristalina de **1** demuestra que las unidades $C_{14}H_{11}N_4$ están enlazadas en forma quelato a dos centros de renio a través de los átomos de nitrógenos de la piridina y la hidropirazina, donde las cargas positivas son soportadas por dos centros metálicos. Las unidades de $(Re_2(CO)_6(C_{14}H_{11}N_4))$ están unidas por dos grupos OH en puente entre los átomos de renio.

Palabras clave: complejos de renio, α-diiminas, doble zwitterion, 2,3-bis(2-piridil)pirazina, estructuras cristalinas.

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* To whom correspondence should be addressed: mgoite@ivic.gob.ve

Introduction

The construction of self-assembled systems is an intensely active research area (1-7). In recent years, the use of corner based in metal center has increased because the directional properties of the coordinative bonds (8). Examples of transition-metal-based corner like building blocks are *cis*-$[Pt(en)]^{2+}$ (9-10), $[M_2(C_{12}H_{10}N_2)(C_2O_4)]$ (11) and *fac*-$Re(CO)_3$ (12). Structures like boxes, prisms or cage able to have molecular filling of their cavities, and their physical and chemical properties can be used as different kinds of sorters. Application as catalyst and template in shape-selective synthesis has been study also (1-7) Closed structures like $[Re(CO)_3(\mu\text{-}C_{18}H_{10}O_4)\ (\mu\text{-}C_{22}H_{16}N_4)\ Re(CO)_3]$ are rare example of metallocyclic-based molecular rotor, which can be obtained by supramolecular engineering (13).

The 2,3-bis(2-pyridyl)pyrazine (dpp) is a versatile ligand, widely used to build supramolecular transition-metal compounds (14). We have previously studied the interaction of dpp with labile metal complexes such as $[Os_3(CO)_{10}(CH_3CN)_2]$ (15) and $[Re_2(CO)_8(CH_3CN)_2]$ (16). With the osmium labile cluster, we found the formation of two structural isomers $[Os_3(\mu\text{-}H)(\mu,\eta^3\text{-}C_{14}H_9N_4)(CO)_9]$, which are the thermolysis products of $[Os_3(C_{14}H_{10}N_4)(CO)_{10}]$ (15). One isomer shows an ortho-metallated 2-pyridyl group and a N-coordinated 2-pyridyl, forming a seven-membered chelate ring, where the pyrazine unit remains uncoordinated. The other isomer contains a 2-pyridyl-1,4-pyrazine fragment metallated in the pyrazine ring to form a five-membered chelate ring, where the second pyridinic unit remains uncoordinated (15). For rhenium, structural isomers formulated as $[Re_2(CO)_8(C_{14}H_{10}N_4)]$ were obtained besides $[Re_2(CO)_8(C_{14}H_{10}N_4)Re_2(CO)_8]$ and $[Re_2(CO)_6(C_{14}H_{10}N_4)_2]$ (16). The latter contain the bis(2-pyridyl)pirazine ligand bonded to two binuclear rhenium fragments, coordinated in a chelate form to each rhenium core respectively.

Here we describe the isolation and characterization of a novel double-zwitterionic rhenium complex $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ (**1**), obtained from the hydrogenation of α-diimine ligand (dpp) under mild reaction conditions.

Experimental

General procedures

All reactions were carried out under dried and purified nitrogen. Solvents were purified by standard procedures and distilled prior to use (17). $[Re_2(CO)_8(CH_3CN)_2]$ was prepared by method previously described (18). 2,3-bis(2-pyridyl)pyrazine as purchased from Aldrich and used as supplied. Reactions were monitored by FT-IR in the range 2200-1750 cm^{-1} and the products were separated by TLC (SiO_2, Merck 60 HF_{254}). IR spectra were recorded on a Perkin Elmer Spectrum 100/100N spectrometer, using 0.5 mm calcium fluoride cells. ^1H NMR spectra were obtained on a Bruker AM300 (300 MHz) spectrometer.

Preparation of $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)_2$ (1)

A solution of 2,3-bis(2-pyridyl)pyrazine (0.034 g, 0.147 mmol) in 50 mL of wet THF (3% H_2O by volume) and $[Re_2(CO)_8(CH_3CN)_2]$ (0.100 g, 0.147 mmol) was refluxed for 2 h, under dried and purified nitrogen, during which time the colour of the solution changed from pale yellow to dark red. The solvent was removed under reduced pressure and TLC (SiO_2) of the residue (eluent: dichloromethane/n-hexane, 7/3 vol/vol) gave red-brown **(1)** (255), and a small number of other minor bands which were not characterized. ν_{CO} (cm^{-1}, CH_2Cl_2): 2018 vs, 1989 m, 1920m, 1907vs, 1897s. ^1H NMR [$CDCl_3$, 300 MHz, J(Hz)]: δ 9.01 (ddd, Ha, J= 5.5; 1.5; 0.5), 7.46 (ddd, Hb, J = 7.9; 5.5; 1.3), 7.81 (ddd, Hc, J = 7.9; 7.9; 1.5), 8.17 (ddd, Hd, J= 7.9; 1.3; 0.5), 8.74 (ddd, He, J= 5.7; 1.5; 1.0), 6.97 (ddd, Hf, J= 7.1; 5.7; 1.0), 7.61 (ddd, Hg, J = 8.4; 7.1; 1.5), 7.35 (bd, Hh, $J = 8.4; 5.7; 5.7$), 5.96 (t, Hi, $J = 3.0; 3.0$), 4.11 (dd, Hj, $J = 3.9; 3.0$), 2.84 (dd, Hk, $J = 3.9; 3.0$), –2.59 and –4.82 (s, 2 Re-OH-Re).

Crystal structure determination

Single crystals of $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ **(1)** were obtained by slow evaporation of a saturated dichloromethane/cyclohexane (1/3) solution. Data were collected at 150 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). Crystal data for $[\mathbf{1}\cdot CH_2Cl_2]$: $C_{41}H_{26}Cl_2N_8O_{14}Re_4$, M_r = 1670.4, crystal system: orthorhombic, space group: *Pbca*, a = 13.1292(8) Å, b = 20.3541(12) Å, c = 34.463(2) Å, V = 9209.7(9) Å^3, Z = 8, ρ_{calc} = 2.409 g cm^{-3}, 2θ range = 1.18 to 28.29 °, μ = 10672 mm^{-1}, F(000) = 6193, 77894 reflections collected, 11090 independent reflections (R_{int}=0.0871), 628 parameters,, $R1$ = 0.0724 ($I > 2\sigma(I)$), $wR2$ = 0.1719 (all data) S = 1.1163 for 8711 reflections with $F^2 > 2\sigma$, minimum/maximum residual electron density –2.094/5.450 eÅ^{-3}.

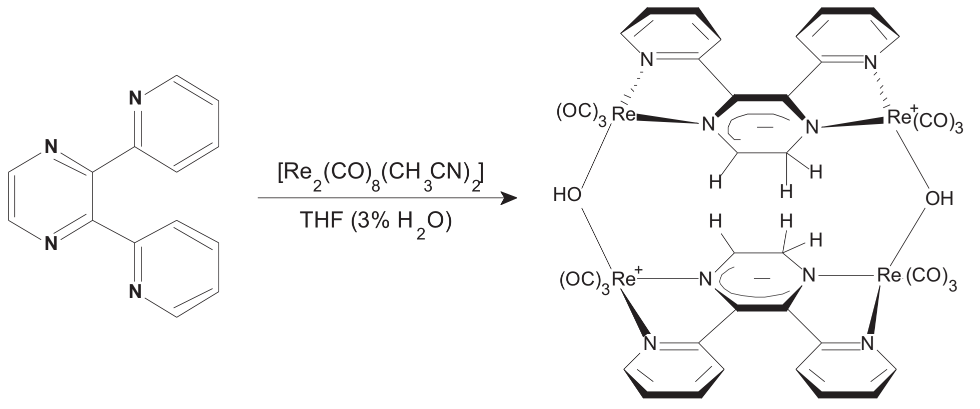
Results and discussion

Reaction of $[Re_2(CO)_8(CH_3CN)_2]$ with 2,3-bis(2-pyridil)pyrazine in a wet THF solution (3% H_2O) at refluxing temperature affords $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ (**1**) (scheme 1). Water concentrations affect the yield of **(1)**; the higher yield (25%) is obtained in 3% H_2O.

The IR pattern of **(1)** in the carbonyl stretching regions not resembles to examples reported in the literature. The ^{1}H NMR spectrum of complex **(1)** shows eight signals between δ = 9.01 and 7.35 ppm for the pyridinic protons. The presence of one triplet at δ = 5.96 ppm and two doublets at δ = 4.11 and 2.84 ppm, indicates partial hydrogenation of the pyrazine rings. In addition, two singlets at high field (δ = –2.59 and –4.82 ppm) corresponding to two protons are observed, which are quite similar to those found for $[Ru_3(\mu\text{-}OH)_2(CO)_8\{\mu\text{-}R\text{-}BINAP\}]$ (δ = –1.48) and $[Os_3(\mu\text{-}OH)(\mu\text{-}H)(CO)_9(PMe_2Ph)]$ (δ = –1.61) (19), $[Re_5(CO)_{17}(\mu\text{-}OH)(\mu\text{-}S)_2]\{C(NMe_2)_2\}_2$ (δ = –1.25) (20), $[Os_3(\mu\text{-}OH)(\mu\text{-}H)(CO)_{10}]$ (δ = 0.20) (21), and for various PPh_3-substituted derivatives of the latter (δ = –1.63, –1.48, and –1.30) (21), so compound **(1)** may contain two different OH ligands in a bridging mode.

Structural study

The ORTEP view of the molecular structure of **(1)** is shown in figure 1. The X-ray structure reveals that there are not available sites for hydrides. Each rhenium shows a distorted octahedral coordination, bonded to three facial carbonyls, two nitrogen atoms [Re1-N1= 2.167(11) Å, Re1-N2= 2.142(11) Å, Re2-N5= 2.155(11) Å, Re2-N6= 2.146(11) Å, Re3-N3= 2.136(11) Å, Re3-N4= 2.214(11) Å, Re4-N7= 2.117(10) Å, Re4-N8=



(1)

Scheme 1.

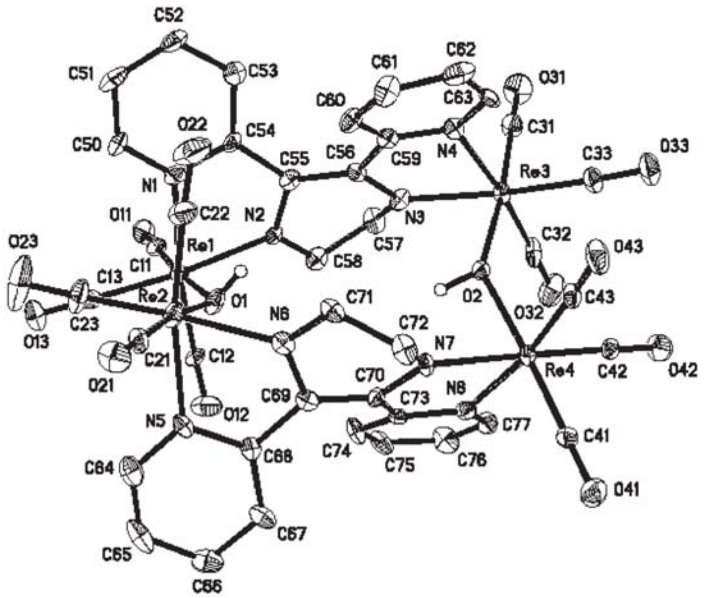


Figure 1. ORTEP view (30% probability ellipsoids) of the molecular structure of $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ **(1)**. Most H atoms omitted for clarity.

2.184(11) Å and to the oxygen atom of an hydroxy ligand [Re1-O1= 2.155(9) Å, Re2-O1= 2.137(9) Å, Re3-O2= 2.151(9) Å, Re4-O2= 2.117(8) Å, where the Re-O distances are comparable to those reported for other Re-OH species (22-25). The molecular structure reveals an almost two-fold symmetry axis containing both OH units. As a consequence the two '$Re(CO)_3C_{14}H_{11}N_4Re(CO)_3$' moieties are in chemically identical environments as suggested by the ^1H NMR data. The bond angles Re-OH-Re are 137.8(5)° and 142.5(4)°. Even though the O-H protons are oriented to the internal part of the molecule, they must be surrounded by different chemical environments, regarding the different δ values observed in the ^1H NMR spectrum for these protons. Hydrogenation of the pyrazine rings promotes reduction, leading to the single C-C bonds C57-C58 [1.49(2) Å and C71-C72 [1.49(2) Å so the resulting CH_2 groups (C57 and C71) are oriented towards Re3 and Re4 atoms. As the lengths C57-N3 [1.48(2) Å and C72-N7 [1.47(2) Å also correspond to a single bond character, the remaining bond lengths of the anionic hydropyrazine rings [C-N average = 1.34(2) Å and C-C average= 1.40(2) Å lie in the observed range for a conjugated system (26). Bond distances found for the hydropyrazine rings suggests that a negative charge is distributed among each group of atoms, N3-C56-C55-N2-C58 and N7-C70-C69-N6-C71. In order to compensate the negative charges, two rhenium atoms allocate the necessary positive charge. Therefore, compound $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ **(1)** can be described as an unprecedented double-zwitterion rhenium complex.

The formation of **(1)** can be explained by the reaction of the 2,3-bis(2-pyridyl)pyrazine ligand with $[Re_2(\mu\text{-}H)(\mu\text{-}OH)(CO)_8]$ specie. The latter complex has been postulated in an earlier work as reactive specie in photochemical or thermal reactions. The proposal mechanism pass through the formation of non observed $[Re_2(CO)_8(OH_2)]$, which likely could undergo by oxidative addition and loss of H_2O to yield $[Re_2(\mu\text{-}H)(\mu\text{-}OH)(CO)_8]$ (27).

Figure 2 shows the most plausible scheme for the formation of $[Re_2(CO)_6$

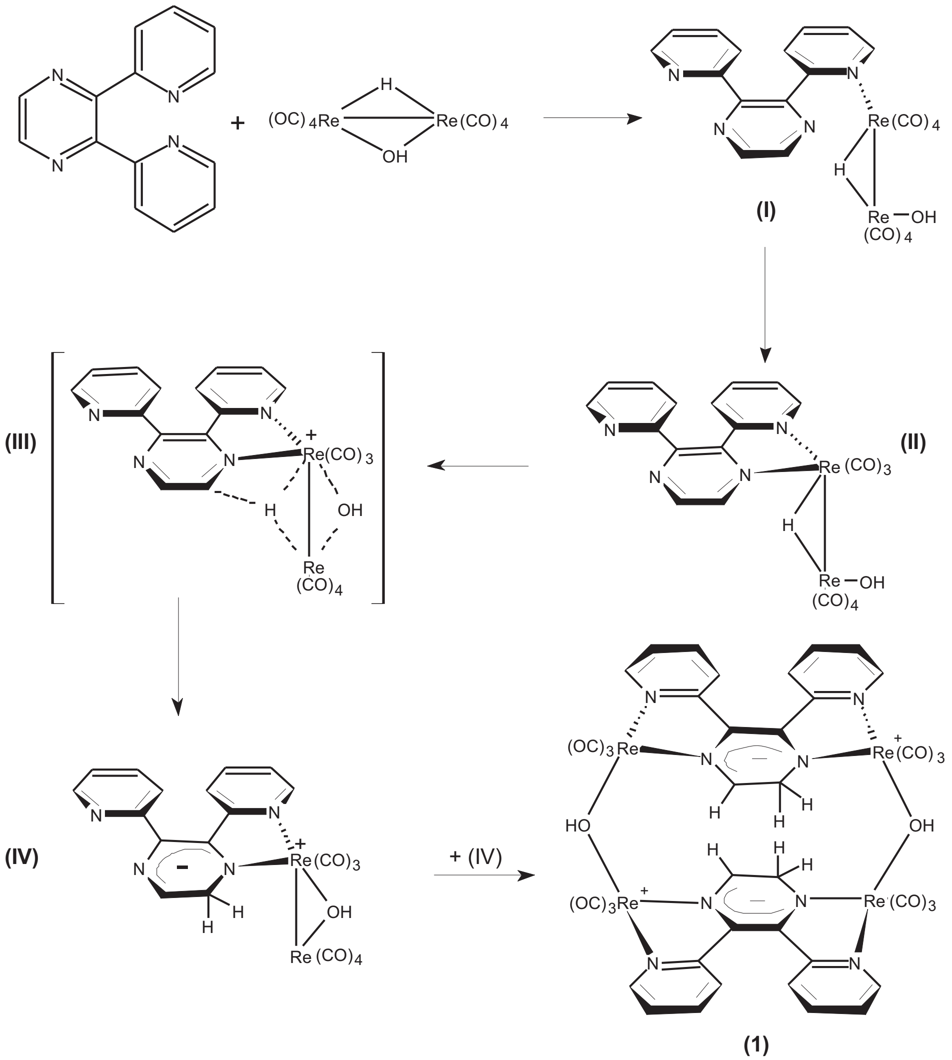


Figure 2. Proposed scheme for the formation of $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ **(1)**

$(C_{14}H_{11}N_4)(OH)]_2$ **(1)**. First, the organic ligand is coordinated through the nitrogen atom of a pyridyl unit to a rhenium atom **(I)**. Then, the second nitrogen atom is bonded to the same rhenium atom in a chelate fashion, to yield **(II)**. Insertion of a hydride in the pyrazine ring and simultaneously, the OH group ending in a bridging position thought an intermediate **(III)** yields specie **(IV)**. Self condensation of **(IV)** and rupture of metal-metal bond leads to doubly zwitterionic specie **1**. Studies on this type of reaction with other α-diimines currently underway in our lab.

Conclusion

Hydrogenation of pyrazinic rings in α-diimine (dpp) results in the formation of $[Re_2(CO)_6(C_{14}H_{11}N_4)(OH)]_2$ **(1)**, which allocate positive charges en the Re atoms and negative charges in the ligand. Complex **(1)** can be described as a new doubly zwitterionic compound, being the first example to the best of our knowledge.

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Supporting information available

CCDC 659584 contains the supplementary crystallographic data for (1). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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