

**SYNTHESIS AND STRUCTURE OF
DICARBONYLDICHLORO{2-(DIPHENYLPHOSPHINEOXIDE)PYRIDINE}RUTHENIUM(II)**

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ABSTRACT

Reaction of the dinuclear complex $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_2]$ with the ligand 2-(diphenylphosphineoxide)pyridine (PyPOPPh₂) in ethanol solution gave the neutral mononuclear complex $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$. The complex was characterized by elemental analysis, IR and RMN spectroscopy, and its molecular structure was determined by single-crystal X-ray diffraction.

Keywords: Ruthenium, 2-(diphenylphosphineoxide)pyridine complexes, Dicarbonyl complexes, Crystal structure.

INTRODUCTION

The unsymmetrical bidentate ligand 2-(diphenylphosphine)pyridine (PyPPh₂) shows a N,P-donor set, where the donor atoms can connect two identical or different metal centres. Due to the presence of the pyridyl ring this ligand presents a small flexibility (rigid short-bite ligand) and can be used to stabilize heterobinuclear complexes acting as bridging ligand.¹ Moreover, this compound can also act as a chelating ligand to give four-membered chelate complexes.² An example of this behaviour is the reaction of the trinuclear complex $[\text{Ru}(\text{CO})_3(\text{PyPPh}_2)_3]$ with Cl₂ in CH₂Cl₂, yielding the mononuclear complex $[\text{Ru}(\text{k}^2\text{-PyPPh}_2\text{-N,P})(\text{CO})_2\text{Cl}_2]$, which presents a *cis*(CO)-*cis*Cl arrangement.³

The formation of mononuclear dicarbonyldihalide ruthenium complexes containing bidentate ligands is complicated due to the various orientations of the carbonyl and halogen ligands, which allows the coexistence of both *cis* and *trans*-halogen isomers. In fact, the formation of mononuclear ruthenium bipyridine carbonyl complexes, such as $[\text{Ru}(\text{k}^2\text{-bpy-N,N})(\text{CO})_2\text{Cl}_2]$, gives a single isomer or a mixture depending of the choice of solvent and the starting ruthenium reagent.⁴ Recently, we found that the reaction of the binuclear complex $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]$ with an unsymmetrical quinolinquinone ligand affords mononuclear complexes of the type $[\text{Ru}(\text{k}^2\text{-N,O})(\text{CO})_2\text{Cl}_2]$ (N,O = 6-methoxybenzo[g]quinoline-5,10-dione), which shows a *cis*(CO)-*trans*Cl configuration.⁵

Following our interest in the reactions of the dimer complex $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]$ with bidentate unsymmetrical ligands, we report here the synthesis, spectroscopic and X-ray characterization of the neutral complex dicarbonyldichloro{2-(diphenylphosphineoxide)pyridine}ruthenium(II), $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$.

EXPERIMENTAL

General Remarks

The reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting compounds tricarbonyldichlororuthenium(II) dimer and 2-(diphenyl phosphine)pyridine were purchased from Aldrich. The ligand 2-(diphenyl phosphineoxide)pyridine was synthesized according to a literature procedure.⁶ Elemental analyses (C, H, N) were carried out by a Fisons EA 1108 CHNS-O microanalyzer. FTIR spectra were recorded throughout the 4000–250 cm⁻¹ region, with samples prepared as KBr discs on a Bruker Vector-22 spectrophotometer. The NMR spectra were recorded on a Bruker AC-200P and Avance-400 spectrometers and the chemical shifts are reported in ppm relative to SiMe₄ (H, ¹³C) and 85% H₃PO₄ (³¹P, positive shifts downfield) as internal and external standards, respectively.

Synthesis of $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$

To a solution of tricarbonyldichlororuthenium(II) dimer (236 mg; 0.46 mmol) in dry ethanol (2-diphenylphosphineoxide)pyridine (257 mg; 0.92 mmol) dissolved in ethanol was added. The reaction mixture was heated under reflux for 4 h, during which time the colour of the solution gradually changed from yellow to orange. Partial evaporation of the solution formed a pale yellow

solid, which was filtered, washed with cold ethanol and dried in vacuum. The complex was crystallized by diffusion of n-pentane into a chloroform solution. Yield 260 mg (56%). Anal. Found: C, 44.7; H, 2.4; N, 2.8%. C₁₉H₁₄Cl₂NO₃PRu required: C, 44.9; H, 2.9; N, 2.8%. IR (KBr, cm⁻¹): ν(CO), 2057, 1993. NMR (CDCl₃, 295 K): ¹H, δ: 7.52-8.04 (m, 13 H, Ph, Py), 9.23 (d, J = 5.3 Hz, 1H, H₃, Py). ³¹P{¹H}, δ: 58.8 (s). ¹³C{¹H}, δ 195.4 (CO), 194.3 (CO), 154.6-153.4 (CH, Py), 138.6-126.2 (CH, Ph).

Crystal structure determination of $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$

Suitable yellow crystals for X-ray diffraction were grown by slow diffusion of n-pentane into a chloroform solution of the complex. A summary of crystal data and refinement parameters is reported in Table 1. Data were obtained at 100(2) K from a Bruker SMART CCD area detector diffractometer equipped with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) using narrow frames. The SMART program package was used for data collection [7a]. The raw frame data were processed using SAINT [7b] and SADABS [7c]. Subsequent calculations were carried out using the SHELXTL program [7d]. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. All non-hydrogen atoms were refined with isotropic and subsequent anisotropic displacement parameters. Hydrogen atoms were included in observed positions and refined as free isotropic atoms.

Table 1. Crystallographic data and structure parameters for complex $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$.

Empirical formula	C ₁₉ H ₁₄ Cl ₂ NO ₃ PRu
Formula weight	507.25
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	9.945(5)
b (Å)	12.931(5)
c (Å)	15.744(5)
a (°)	77.052(5)
b (°)	89.658(5)
g (°)	82.970(5)
Volume (Å ³)	1957.9(14)
Z	4
Density (calc.)(Mg m ⁻³)	1.721
Absorption coefficient (mm ⁻¹)	1.175
Crystal size (mm)	0.13 x 0.10 x 0.03
θ range for data collection (°)	1.63 to 28.73
Index ranges	-13 ≤ h ≤ 12, -16 ≤ k ≤ 16, -21 ≤ l ≤ 20
Reflections collected	23771
Independent reflections	9172 (R _{int} = 0.0828)
Max. and min. transmission	0.9701 – 0.8585
Data/restraints/parameters	9172/0/488
Goodness-of-fit on F ²	0.974
Final R indices [I > 2σ(I)]	R1 = 0.0591, wR2 = 0.1131
R indices (all data)	R1 = 0.1287, wR2 = 0.1494
Largest diff. peak and hole (e Å ⁻³)	1.938 and -1.273

RESULTS AND DISCUSSION

The dinuclear complex $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_2]$ reacts in a 1:2 molar ratio with the 2-(diphenylphosphineoxide)pyridine ligand (PyPOPPh₂) in refluxing ethanol by cleavage of the chloride bridges to yield the neutral mononuclear complex $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$. The complex was isolated as stable solid and characterized by elemental analysis, FTIR and NMR spectroscopy. The solid-state infrared spectrum in KBr pellets shows two strong $\nu(\text{CO})$ vibrations at 1993 and 2057 cm^{-1} , which indicates that the carbonyl ligands are in a *cis* arrangement. However, the IR spectrum does not show the characteristic strong band in the 1200-1100 cm^{-1} region, where the P-O stretching absorption of the free ligand is found.⁶ The assignment of the P-O stretching in the complex is difficult, due to the presence of other absorptions of coordinated phosphine oxides in this range. Similar spectroscopic behaviour is found in related octahedral molybdenum complexes containing the 2-(diphenylphosphineoxide)pyridine ligand.⁸

The ¹H NMR spectrum of the complex shows a broad multiplet centred at δ : 7.8 ppm, assigned to the phenyl and 4,5,6-pyridine protons, and a doublet resonance at δ : 9.23 ppm ($J = 5.3$ Hz) assigned to H₃ proton of the pyridine moiety. These resonances were assigned of the basis of reported data.⁸ The ¹³C {¹H} NMR spectrum shows the carbon signals of the carbonyl group at δ : 195.4 and 194.3 ppm. The ³¹P {¹H} NMR spectrum exhibits a singlet resonance at δ : 58.8 ppm, indicating the presence of a single *cis*(CO) isomer in solution. Since the chloride ligands can be mutually *trans* or *cis* two isomers with a *cis*(CO)-*trans*Cl or *cis*(CO)-*cis*Cl arrangement are expected.

In order to determine the molecular structure in the solid state of the complex, an X-ray diffraction study was undertaken. Suitable crystals for structural determination were obtained from a slow diffusion of n-pentane into a chloroform solution of the complex. There are two independent molecules per asymmetric unit, which do not differ significantly in their geometry. In the complex, the ruthenium atom shows a distorted octahedral co-ordination sphere with the carbonyl groups bonded to the metal center in relative *cis* positions, and two chloride atoms linked in a *trans* disposition. The co-ordination sphere is completed with the chelating 2-(diphenylphosphineoxide)pyridine ligand bonded to the metal through nitrogen and oxygen atoms. Figure 1 displays the molecular diagram of the molecule, showing the atom-numbering scheme.

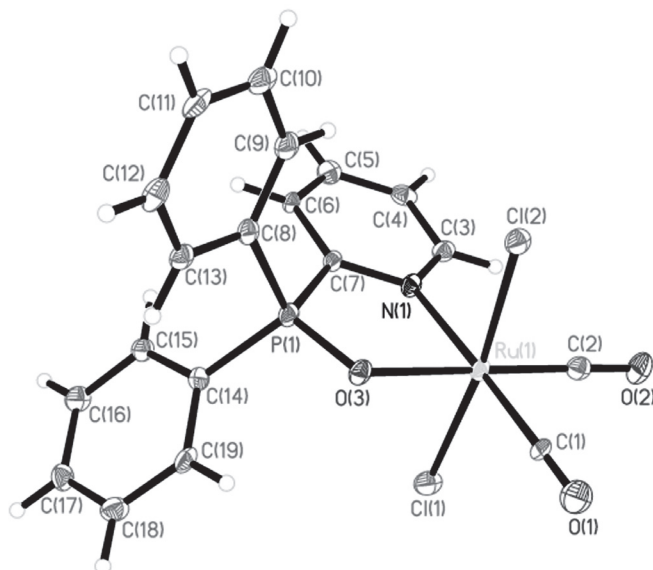


Figure 1. Molecular structure of the complex $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$, showing the atom labelling scheme.

The most relevant bond distances and bond angles are listed in Table 2. The bond distances from ruthenium to its neighboring atoms in the molecule (Ru-N, Ru-Cl, Ru-C and Ru-O. Table 2) compare well to those found in related *cis*(CO)/*trans*Cl ruthenium complexes, such as $[\text{Ru}(6\text{-methoxybenzo}[\text{g}]\text{quinoline-5,10-dione})(\text{CO})_2\text{Cl}_2]$ ⁵ [Ru-N, 2.123(4); Ru-Cl average 2.386(12); Ru-C average 1.8905(5); Ru-O, 2.123(3) Å] and $[\text{Ru}(4,4'\text{-dimethyl-2,2'-bipyridine})(\text{CO})_2\text{Cl}_2]$ ⁴ [Ru-N, average 2.1235(7); Ru-Cl average

2.3975(2); Ru-C average 1.8725(10) Å]. However, the Ru-Cl bond distances are smaller than the corresponding values observed in the *cis*(CO)/*cis*Cl type complexes, $[\text{Ru}(6,6'\text{-dimethoxycarbonyl-2,2'-bipyridine})(\text{CO})_2\text{Cl}_2]$ ⁹ [Ru-N, average 2.1367(14); Ru-Cl average 2.41515(7); Ru-C average 1.897(2) Å] and $[\text{Ru}\{2\text{-(diphenylphosphine)pyridine}\}(\text{CO})_2\text{Cl}_2]$ ³ [Ru-N, 2.119(6); Ru-Cl average 2.413(2); Ru-C average 1.876(8) Å]. The mean carbonyl distances [average 1.111(7) Å] are similar to those found in the above-mentioned ruthenium(II) complexes.

In the co-ordinated ligand, the P=O distance [1.512(4) Å] are similar to these found in the related complex $[\text{Mo}(\eta^3\text{-allyl})\text{Br}(\text{CO})_2\{2\text{-(diphenylphosphineoxide)pyridine}\}]$ ⁸ [P=O, 1.501(4) Å]. Angles involving the P atoms reflect a tetrahedral geometry: average 109.4(3)°.

Table 2. Selected bond lengths (Å) and angles (deg) for $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$

Ru(1)-C(2)	1.837(7)	Ru(1)-C(1)	1.913(7)
Ru(1)-O(3)	2.129(4)	Ru(1)-N(1)	2.160(5)
Ru(1)-Cl(2)	2.3749(19)	Ru(1)-Cl(1)	2.3858(19)
P(1)-O(3)	1.512(4)	O(1)-C(1)	1.069(7)
O(2)-C(2)	1.152(7)		
Cl(1)-Ru(1)-Cl(2)	172.82(6)	Cl(2)-Ru(1)-C(2)	93.47(19)
Cl(1)-Ru(1)-O(3)	87.97(11)	O(3)-Ru(1)-N(1)	82.69(17)
Cl(1)-Ru(1)-N(1)	90.16(13)	O(3)-Ru(1)-C(1)	93.3(2)
Cl(1)-Ru(1)-C(1)	91.46(18)	O(3)-Ru(1)-C(2)	179.2(2)
Cl(1)-Ru(1)-C(2)	91.08(15)	N(1)-Ru(1)-C(1)	175.6(2)
Cl(2)-Ru(1)-O(3)	88.69(9)	N(1)-Ru(1)-C(2)	97.9(2)
Cl(2)-Ru(1)-N(1)	85.09(13)	C(1)-Ru(1)-C(2)	86.1(3)
Cl(2)-Ru(1)-C(1)	92.91(18)	P(1)-O(3)-Ru(1)	117.7(2)
C(7)-N(1)-Ru(1)	118.1(4)	O(1)-C(1)-Ru(1)	179.3(6)
O(2)-C(2)-Ru(1)	177.8(5)		

All attempts to synthesize the related complex $[\text{Ru}(\text{k}^2\text{-PyPPh}_2\text{-N,P})(\text{CO})_2\text{Cl}_2]$, by reaction of the dinuclear complex $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_2]$ with the ligand 2-(diphenylphosphine)pyridine in ethanol were unsuccessful. In all cases we obtained an uncharacterized solid that presented several signals in the ³¹P NMR spectra. The expected formation of the strained four-membered chelate ring does not occur in ethanol, possibly due to the hemilabile properties of the coordinated ligand. In fact, the complex $[\text{Ru}(\text{k}^2\text{-PyPPh}_2\text{-N,P})(\text{CO})_2\text{Cl}_2]$ easily reacts with PyPPh₂ to lead to the complex $[\text{Ru}(\text{k}^1\text{-PyPPh}_2\text{-P}_2)(\text{CO})_2\text{Cl}_2]$ with the ligand acting in its monodentate form.³ As expected, the complex $[\text{Ru}(\text{k}^2\text{-PyPOPPh}_2\text{-N,O})(\text{CO})_2\text{Cl}_2]$ does not react with an excess of the ligand PyPOPPh₂, showing the higher stability of the five-membered chelate ring.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC- 671766 . Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: /44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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