



## *fac-/mer*-[RuCl<sub>3</sub>(NO)(P–N)] (P–N = [*o*-(*N,N*-dimethylamino)phenyl]diphenylphosphine): Synthesis, characterization and DFT calculations

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### ABSTRACT

Complex *fac*-[RuCl<sub>3</sub>(NO)(P–N)] (**1**) was synthesized from the reaction of [RuCl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>(NO)] and the P–N ligand, *o*-[*N,N*-dimethylamino]phenyl]diphenylphosphine in refluxing methanol solution, while complex *mer,trans*-[RuCl<sub>3</sub>(NO)(P–N)] (**2**) was obtained by photochemical isomerization of (**1**) in dichloromethane solution. The third possible isomer *mer,cis*-[RuCl<sub>3</sub>(NO)(P–N)] (**3**) was never observed in direct synthesis as well as in photo- or thermal-isomerization reactions. When refluxing a methanol solution of complex (**2**) a thermally induced isomerization occurs and complex (**1**) is regenerated.

The complexes were characterized by NMR (<sup>31</sup>P{<sup>1</sup>H}, <sup>15</sup>N{<sup>1</sup>H} and <sup>1</sup>H), cyclic voltammetry, FTIR, UV–Vis, elemental analysis and X-ray diffraction structure determination. The <sup>31</sup>P{<sup>1</sup>H} NMR revealed the presence of singlet at 35.6 for (**1**) and 28.3 ppm for (**2**). The <sup>1</sup>H NMR spectrum for (**1**) presented two singlets for the methyl hydrogens at 3.81 and 3.13 ppm, while for (**2**) was observed only one singlet at 3.29 ppm. FTIR Ru–NO stretching in KBr pellets or CH<sub>2</sub>Cl<sub>2</sub> solution presented 1866 and 1872 cm<sup>−1</sup> for (**1**) and 1841 and 1860 cm<sup>−1</sup> for (**2**). Electrochemical analysis revealed a irreversible reduction attributed to Ru<sup>II</sup>–NO<sup>+</sup> → Ru<sup>II</sup>–NO<sup>0</sup> at −0.81 V and −0.62 V, for (**1**) and (**2**), respectively; the process Ru<sup>II</sup> → Ru<sup>III</sup>, as expected, is only observed around 2.0 V, for both complexes.

Studies were conducted using <sup>15</sup>NO and both complexes were isolated with <sup>15</sup>N-enriched NO. Upon irradiation, the complex *fac*-[RuCl<sub>3</sub>(NO)(P–N)] (**1**) does not exchange <sup>14</sup>NO by <sup>15</sup>NO, while complex *mer,trans*-[RuCl<sub>3</sub>(NO)(P–N)] (**2**) does. Complex *mer,trans*-[RuCl<sub>3</sub>(<sup>15</sup>NO)(P–N)] (**2'**) was obtained by direct reaction of *mer,trans*-[RuCl<sub>3</sub>(NO)(P–N)] (**2**) with <sup>15</sup>NO and the complex *fac*-[RuCl<sub>3</sub>(<sup>15</sup>NO)(P–N)] (**1'**) was obtained by thermal-isomerization of *mer,trans*-[RuCl<sub>3</sub>(<sup>15</sup>NO)(P–N)] (**2'**).

DFT calculation on isomer energies, electronic spectra and electronic configuration were done. For complex (**1**) the HOMO orbital is essentially Ru (46.6%) and Cl (42.5%), for (**2**) Ru (57.4%) and Cl (39.0%) while LUMO orbital for (**1**) is based on NO (52.9%) and is less extent on Ru (38.4%), for (**2**) NO (58.2%) and Ru (31.5%).

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### 1. Introduction

Two events have made nitric oxide (NO) one of the most studied small molecules. In 1992, NO was considered the molecule of the year by Science and the 1998s Nobel Prize in physiology or medicine awarded to Robert Furchgott, Ferid Murad and Louis Ignarro for the discovery of NO as a signaling molecule in biological systems. After these events, an impressive number of works have been published dealing with properties and applications of NO containing transition metal complexes [1–17]. Therefore ruthenium is of crucial importance in the NO chemistry and probably

is one of the most studied transition metal with NO in coordination compounds [1–28]. The chemistry of this successful association has been explored by chemists focusing on different aspects. The most explored aspect is the use of such complexes as NO controlled releasing or scavenger compounds [1,2]. Many other insights have been explored, ranging from electronic and molecular structure [3–6,29–33] to catalysis [7–9]. Recently, application of ruthenium-nitrosyl complexes as anticancer agent has emerged [10–13].

In general, ruthenium/nitrosyl complexes are associated with co-ligands such as pyridines [3], salen [2,14], amines [15–18], porphyrins [15,34–39] and diphosphines [12,19–26]. The chemistry of ruthenium/nitrosyl complexes with chelated P–N ligands is rare, and only two works can be found in the literature so far [27,28].

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In this work, we present the synthesis, characterization of *fac/mer*-[RuCl<sub>3</sub>(NO)(P–N)] (P–N = *o*-[(*N,N*-dimethylamino)phenyl]-diphenylphosphine). These complexes were characterized by FTIR, NMR (<sup>31</sup>P{<sup>1</sup>H}, <sup>15</sup>N{<sup>1</sup>H}, <sup>1</sup>H), cyclic voltammetry, UV–Vis, X-ray diffraction studies and elemental analysis. X-ray structure for (1) has been published previously [28], although will be presented to enlighten the discussion. <sup>15</sup>N-enriched nitrosyl complexes were also isolated. Density functional theory was also applied in an attempt to understand the electronic structure of these compounds.

## 2. Experimental methods

### 2.1. Measurements

The IR spectra were recorded on a FTIR Bomem-Michelson 102 spectrometer in the 4000–400 cm<sup>−1</sup> region using solid samples pressed in KBr pellets or dichloromethane solution in a CaF<sub>2</sub> crystal with path length of 1 mm. NMR spectra (<sup>31</sup>P{<sup>1</sup>H}, <sup>15</sup>N{<sup>1</sup>H} and <sup>1</sup>H)

were acquired at room temperature on a Bruker AVANCE 400 NMR spectrometer, operating at 9.4 T, equipped with a 5 mm multinuclear direct detection probe. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra were obtained in CH<sub>2</sub>Cl<sub>2</sub> (D<sub>2</sub>O capillary was inserted in the solution), while <sup>1</sup>H and <sup>15</sup>N{<sup>1</sup>H} NMR spectra were obtained in CDCl<sub>3</sub>. The <sup>31</sup>P, <sup>15</sup>N and <sup>1</sup>H NMR chemical shifts are given in parts per million related to H<sub>3</sub>PO<sub>4</sub> (85%, capillary), CH<sub>3</sub>NO<sub>2</sub> (neat, capillary) and TMS (tetramethylsilane, internal), respectively. The coupling constants are given in Hertz, and the splitting of hydrogen, phosphorus and nitrogen signals are defined as s, singlet; d, doublet; m, multiplet. EPR spectra were measured at 77 K on a Bruker EMX-micro EPR spectrometer, operating at X band, equipped with a rectangular TE<sub>102</sub> resonator cavity. Cyclic voltammetry (CV) experiments were carried out at room temperature in CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>CN containing 0.1 M [Bu<sub>4</sub>N]ClO<sub>4</sub> (TBAP) (Fluka Purum) (in these conditions, Half-wave potential for ferrocene is 0.423 V) using a PARC 273 (Princeton Applied Research). The working and auxiliary electrodes were stationary Pt foils; the reference electrode was Ag/AgCl in a Luggin capillary probe filled with the electrolyte solution (TBAP in CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>CN). The electronic spectra were obtained from dichloromethane solution of the complexes in quartz cuvettes with path length of 1 cm, with concentrations ranging from 10<sup>−6</sup> to 10<sup>−2</sup> on a Hewlett–Packard diode array 8452A spectrophotometer. The elemental analyses were performed on a Fisons CHNS-O, EA 1108 Element analyser.

**Table 1**  
Crystal data and structures refinement.

	<i>fac</i> -[RuCl <sub>3</sub> (NO)(P–N)] [28]	<i>mer,trans</i> - [RuCl <sub>3</sub> (NO)(P–N)]
Empirical formula	C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> OCl <sub>3</sub> Ru	C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> OCl <sub>3</sub> Ru
Formula weight	542.77	542.77
Temperature (K)	150(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	9.3629(1)	8.7986 (1)
<i>b</i> (Å)	14.6378(2)	15.2385(3)
<i>c</i> (Å)	15.3757(3)	16.2248(2)
Volume (Å <sup>3</sup> )	2107.27(6)	2175.38(6)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (mg/m <sup>3</sup> )	1.711	1.657
Absorption coefficient (mm <sup>−1</sup> )	1.214	1.176
<i>F</i> (0 0 0)	1088	1088
Crystal size (mm <sup>3</sup> )	0.315 × 0.309 × 0.296	0.47 × 0.23 × 0.15
Theta range for data collection (°)	3.43–27.5	3.42–27.48
Index ranges	−12 ≤ <i>h</i> ≤ 11 −19 ≤ <i>k</i> ≤ 18 −19 ≤ <i>l</i> ≤ 19	−11 ≤ <i>h</i> ≤ 11 −19 ≤ <i>k</i> ≤ 19 −21 ≤ <i>l</i> ≤ 18
Reflections collected	15 860	16 965
Independent reflections	4828 [R(int) = 0.0258]	4942 [R(int) = 0.0230]
Completeness to theta = 27.5°	99.7%	99.4%
Absorption correction	Gaussian	Gaussian
Maximum and minimum transmission	0.754 and 0.655	0.830 and 0.622
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Computing <sup>a</sup>	COLLECT, HKL Denzo and Scalepack SHELXS-97, SHELXL-97	COLLECT, HKL Denzo and Scalepack SHELXS-97, SHELXL-97
Data/restraints/parameters	4828/0/256	4942/0/256
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.104	1.147
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0231, <i>wR</i> <sub>2</sub> = 0.0565	<i>R</i> <sub>1</sub> = 0.0316, <i>wR</i> <sub>2</sub> = 0.0818
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0238, <i>wR</i> <sub>2</sub> = 0.0569	<i>R</i> <sub>1</sub> = 0.0321, <i>wR</i> <sub>2</sub> = 0.0821
Absolute structure parameter	0.04(2)	−0.03(3)
Extinction coefficient	0.0071(6)	0.0143(10)
Largest difference peak and hole	0.589 and −0.659 e Å <sup>−3</sup>	2.044 and −0.445 e Å <sup>−3</sup>

<sup>a</sup> Data collection, data processing, structure solution and structure refinement, respectively.

### 2.2. X-ray diffraction data

Crystal data for complexes (1) and (2) (Table 1): formula weight = 542.77, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. For (1) *a* = 9.3629(1) Å, *b* = 14.6378(2) Å, *c* = 15.3757(3) Å, *V* = 2107.27 Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.711 g cm<sup>−3</sup>, *R*(*wR*) = 0.0231(0.0565) for 15 860 reflections [*I* > 2σ(*I*)], and for (2) *a* = 8.7986(1) Å, *b* = 15.2385(3) Å, *c* = 16.2248(2) Å, *V* = 2175.38 Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.657 g cm<sup>−3</sup>, *R*(*wR*) = 0.0316(0.0818) for 16 965 reflections [*I* > 2σ(*I*)]. X-ray diffraction data collection using the COLLECT program [40] was performed on an Enraf-Nonius Kappa-CCD diffractometer utilizing graphite-monochromated Mo *K*α radiation (0.71073 Å). Final unit cell parameters were based on all reflections. Integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [41]. A Gaussian absorption correction was applied [42]. The structure was solved by direct methods using SHELXS-97 [43]. The model was refined by full-matrix least-squares on *F*<sup>2</sup> with SHELXL-97 [44]. All hydrogen atoms were stereochemically positioned and refined with the riding model.

### 2.3. Method of calculation

Calculations were performed with GAUSSIAN 03 program [45]. The DFT and TDDFT methods were used with the B3LYP functional [46–48]. In the calculations the PCM solvent model was used [49], with dichloromethane (DCM) as the solvent. The PCM calculations were performed on the optimized geometries without solvent. The DGauss DZVP [50] basis sets were employed for ruthenium with two additional polarization *f* functions with the exponents 1.9472 and 0.7489. These basis sets are of the form (18s12p9d2f)/[6s5p3d2f]. For C, N, O, P, Cl and H the standard 6–31G\* basis set was employed. The specified basis set has already been successfully applied to the calculations for other ruthenium complexes [51]. Natural orbital bond (NBO) population analysis [52] was used for calculating the atomic charges, bond orders and for characterization of the Ru–NO bonding. The molecular structures were depicted by the program MOLDEN [53]. Molecular orbitals were drawn with the use of program GOPENMOL [54].

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