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Synthesis and characterization of the *mer*-[$RuCl_3$(NO)(dppb)] isomer. X-ray structures of *fac*-[$RuCl_3$(NO)(dppm)], *cis*-[$RuCl_2(dppm)_2$] and *mer*-[$RuCl_3$(NO)(dppb)] [dppm=1,2-Bis(diphenylphosphino)methane and dppb=1,4-Bis(diphenylphosphino)butane]

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Abstract

The *fac*-[$RuCl_3$(NO)(dppm)] **(1)** and cis-[$RuCl_2(dppm)_2$] **(2)** complexes were obtained with co-crystallization in the solid state from the reaction of $RuCl_3$(NO) with the diphosphine in dichloromethane. *mer*-[$RuCl_3$(NO)(dppb)] **(3)** was obtained from [$RuCl_3$(dppb)(H_2O)] by bubbling NO for 30 min in the same solvent. The crystal and molecular structures of these three compounds have been determined from X-ray studies.

Keywords: Ruthenium; Nitrosyl; Complexes, Biphosphines; X-ray structure; Isomerism

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1. Introduction

The chemistry of nitrosyl transition metal complexes is of special interest because of the relevance of nitric oxide in biological systems [1–4]. Nitrosyl–ruthenium complexes have been studied due to their importance as potential catalysts in homogeneous processes, ambiental chemistry or with bioinorganic purpose.

Recently, we published a paper on nitrosyl ruthenium complexes with general formula [$RuCl_3$(NO)(P–P), where P–P=[$PPh_2(CH_2)_nPPh_2$] n=1–3 and [$PPh_2CH{=}CHPPh_2$] including the X-ray structure of the [$RuCl_3$(NO){$(PPh_2(CH_2)_3PPh_2$}] [5]. Now we are extending our studies to the *mer*-[$RuCl_3$(NO)(dppb)] complex including its X-ray structure and of the *fac*-[$RuCl_3$(NO)(dppm)] isomer.

2. Experimental

2.1. General considerations

All manipulations involving solutions of the complexes were performed under argon. Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. The $RuCl_3{\cdot}3H_2O$ was purchased from Degussa and the ligands dppm and dppb were purchased from Aldrich. The $RuCl_3$(NO) was prepared according to the literature [5]. Yields are based on the metal. Microanalyses were performed by Microanalytical Laboratory of Universidade Federal de São Carlos, São Carlos(SP) or of Universidade de São Paulo, São Paulo.

2.2. Measurements

The infrared spectra of the complexes were measured from powder samples diluted in CsI on an FTIR Bomem-Mechelson 102 spectrometer in the 4000–200 cm^{-1} region. The $^{31}P\{^1H\}$ spectra were recorded in CH_2Cl_2 on a

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Bruker 400 MHz spectrometer, with H_3PO_4 (85%) as internal reference.

2.3. Syntheses

The synthesis of the *fac*-[$RuCl_3NO$(dppm)] was described in our previous paper [5]. The *mer*-[$RuCl_3NO$(dppb)] was synthesized by bubbling NO [generated by reaction of dilute nitric acid (approx. 33%) over copper metal and dried passing it through a column containing anhydrous $CaCl_2$] in a dichloromethane solution of the [$RuCl_3$(dppb)(H_2O)] (0.1 g) for 30 min after what the volume of the solution was reduced and ether was added to precipitate a yellow-greenish solid which was washed with ether and dried under vacuum. The [$RuCl_3$(dppb)(H_2O)] was obtained and characterized in our laboratory from the reaction of the [Ru_2Cl_4($dppb)_3$] [6] with chlorine. Yield: 0.087 g, 85.3%. Found C, 50.9; H, 4.3; N, 1.9%. Calcd. for $C_{28}H_{28}Cl_3NORuP_2$.:. C, 50.7; H, 4.2; N 2.1%. ν_{NO} 1867 and $\nu_{(Ru-Cl)}$ 340 and 293 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 13.65(d) and δ 10.10(d), $J_{(P-P)}=37.0$ Hz.

2.4. X-ray diffraction data

Suitable crystals of complexes were grown by slow evaporation of dichloromethane/diethyl ether solutions. Single crystals were used for data collection and cell parameter determination on an Enraf-Nonius CAD-4 diffractometer, using Mo Kα radiation (graphite monochromator) in the ω-2θ scan mode, at room temperature.

The *fac*-[$RuCl_3$(NO)(dppm)] **(1)** complex co-crystallizes with *cis*-[$RuCl_2(dppm)_2$] **(2)** compound. The crystallographic parameters for the co-crystal compound **(1)** and **(2)** are: monoclinic system; s.g. $I2/a$; $a=20.632(5)$, $b=15.207(3)$, $c=36.096(7)$ Å; $\beta=91.71(1)$°C; $V=11\,320(5)$ Å^3; $Z=8$ [$RuCl_3$(NO)(dppm)] and 4 [$RuCl_2(dppm)_2$]; crystal size 0.10×0.08×0.12 mm. In the θ range from 2.13°C to 24.64°C, 9664 unique reflections were collected, with 3929 observed ($I\geq3\sigma(I)$), $R_{int}=0.026$. The structure was refined using F in two blocks of 340 parameters until $R=0.046$; $R_w=0.059$ and $R_{all}=0.21$; max. and min. residual density in the difference Fourier were 1.1 and −2.2 e/Å^3 respectively, with the hydrogen atoms located in their ideal positions (d CH=1.08Å, Biso=6.0Å^2). The co-crystal structure showed that the molecules **(1)** and **(2)** have C_2 symmetry with the Ru lying on the two-fold axis.

The crystallographic parameters for compound **(3)** are: monoclinic system; s.g. $P2_1/c$; $a=15.323(2)$, $b=9.690(1)$, $c=19.083(2)$ Å; $\beta=94.223(7)$°C; $V=2819.8(5)$ Å^3; $Z=4$, crystal size 0.10×0.10×0.05 mm. In the θ range from 2.13°C to 24.64°C 5723 unique reflections were collected, with 2168 observed ($I\geq2\sigma(I)$), $R_{int}=0.051$. The structure was refined using F in two blocks of 325 parameters until $R=0.0501$; $R_w=0.0481$ and $R_{all}=0.259$; max. and min. residual density in the difference Fourier were 0.51 and −0.21 e/Å^3 respectively, with the hydrogen atoms located in their ideal positions (d CH=0.98Å, Biso=1.3×B_{eq} of the attach atom).

3. Results and discussion

The IR spectra of the [$RuCl_3$(NO)(dppb)] complex shows ν(NO) at 1867 cm^{-1} indicating that it is indeed of the $\{Ru^{II} — NO^+\}$ [7,8]. The relevant interatomic bond lengths for complexes **(1)**, **(2)** and **(3)** are listed in Table 1 and bond angles in Table 2.

The molecular structure of the compounds **(1)** and **(2)** are showed in Fig. 1a and b, respectively, with labeled

Table 1
Selected bond distances (Å) for *fac*-[$RuCl_3NO$(dppm)], *mer*-[$RuCl_3NO$(dppb)] and *cis*-[$RuCl_2$(dppm)]

fac-[$RuCl_3NO$(dppm)]		*mer*-[$RuCl_3NO$(dppb)]		*cis*-[$RuCl_2$(dppm)]	
Ru(2)-Cl(1B)	2.439(3)	Ru-Cl(1)	2.383(2)	Ru(1)-Cl(1A)	2.437(3)
Ru(2)-Cl(2B)	2.430(3)	Ru-Cl(2)	2.374(3)		
Ru(2)-Cl(3B)	2.345(3)	Ru-Cl(3)	2.395(2)		
Ru(2)-N	1.716(8)	Ru-N	1.748(8)		
Ru(2)-P(1B)	2.338(3)	Ru-P(1)	2.412(2)	Ru(1)-P(1A)	2.342(3)
Ru(2)-P(2B)	2.336(3)	Ru-P(2)	2.498(3)	Ru(1)-P(2A)	2.312(3)
N-O	1.14(1)	N-O	1.18(2)		
		N-O′	1.15(2)		
		O-O′	0.86(2)		
P(1B)-C	1.84(1)	P(1)-C(1)	1.825(9)	P(1A)-C′	1.85(1)
P(2B)-C	1.84(1)	P(2)-C(4)	1.826(9)	P(2A)-C′	1.84(1)
P(1B)-C(1B)	1.78(1)	P(1)-C(1A)	1.82(1)	P(1A)-C(13A)	1.81(1)
P(1B)-C(7B)	1.80(1)	P(1)-C(7A)	1.814(9)	P(1A)-C(19A)	1.76(1)
P(2B)-C(13B)	1.800(9)	P(2)-C(1B)	1.825(9)	P(2A)-C(1A)	1.83(1)
P(2B)-C(19B)	1.808(9)	P(2)-C(7B)	1.831(9)	P(2A)-C(7A)	1.81(1)
		C(1)-C(2)	1.52(2)		
		C(3)-C(4)	1.55(1)		

Table 2
Selected bond angles (°) for *fac*-[$RuCl_3NO$(dppm)], *mer*-[$RuCl_3NO$(dppb)] and *cis*-[$RuCl_2$(dppm)]

fac-[$RuCl_3NO$(dppm)]		*mer*-[$RuCl_3NO$(dppb)]		*cis*-[$RuCl_2$(dppm)]	
Cl(1B)-Ru(2)-Cl(2B)	91.27(9)	Cl(1)-Ru-Cl(2)	177.8(1)	Cl(1A)-Ru(1)-Cl(1A)*	85.5(1)
Cl(1B)-Ru(2)-Cl(3B)	91.07(9)	Cl(1)-Ru-Cl(3)	90.25(9)		
Cl(2B)-Ru(2)-Cl(3B)	91.20(9)	Cl(2)-Ru-Cl(3)	88.14(9)		
Cl(1B)-Ru(2)-N	91.4(3)	Cl(1)-Ru-N	86.6(3)		
Cl(2B)-Ru(2)-N	92.2(3)	Cl(2)-Ru-N	92.0(4)		
Cl(3B)-Ru(2)-N	175.8(3)	Cl(3)-Ru-N	93.2(3)		
Cl(1B)-Ru(2)-P(1B)	169.5(1)	Cl(1)-Ru-P(1)	92.53(9)	Cl(1A)-Ru(1)-P(1A)	92.6(1)
Cl(1B)-Ru(2)-P(2B)	97.71(9)	Cl(1)-Ru-P(2)	89.92(9)	Cl(1A)-Ru(1)-P(2A)	163.1(1)
Cl(2B)-Ru(2)-P(1B)	98.39(9)	Cl(2)-Ru-P(1)	89.19(9)	Cl(1A)-Ru(1)-P(1A)*	92.4(1)
Cl(2B)-Ru(2)-P(2B)	169.8(1)	Cl(2)-Ru-P(2)	91.4(1)	Cl(1A)-Ru(1)-P(2A)*	88.4(1)
Cl(3B)-Ru(2)-P(1B)	84.70(9)	Cl(3)-Ru-P(1)	175.1(1)		
Cl(3B)-Ru(2)-P(2B)	83.73(9)	Cl(3)-Ru-P(2)	84.4(1)		
				P(1A)-Ru(1)-P(1A)*	173.2(1)
P(1B)-Ru(2)-P(2B)	72.34(9)	P(1)-Ru-P(2)	91.61(9)	P(1A)-Ru(1)-P(2A)	72.0(1)
				P(2A)-Ru(1)-P(2A)*	101.6(1)
				P(1A)-Ru(1)-P(2A)*	103.6(1)
P(1B)-Ru(2)-N	92.3(3)	P(1)-Ru-N	91.0(3)		
P(2B)-Ru(2)-N	92.5(3)	P(2)-Ru-N	175.7(3)		
Ru(2)-N-O	176.8(8)	Ru-N-O	157.(1)		
		Ru-N-O′	160.(1)		
		O-N-O′	43.(1)		
Ru(2)-P(1B)-C	94.7(3)	Ru-P(1)-C(1)	114.9(3)	Ru(1)-P(1A)-C′	95.4(3)
Ru(2)-P(1B)-C(1B)	111.2(3)	Ru-P(1)-C(1A)	122.8(3)	Ru(1)-P(1A)-C(13A)	122.9(4)
Ru(2)-P(1B)-C(7B)	122.1(3)	Ru-P(1)-C(7A)	107.8(3)	Ru(1)-P(1A)-C(19A)	122.7(4)
Ru(2)-P(2B)-C	94.6(3)	Ru-P(2)-C(4)	114.3(3)	Ru(1)-P(2A)-C′	96.5(4)
Ru(2)-P(2B)-C(13B)	113.5(3)	Ru-P(2)-C(1B)	111.4(3)	Ru(1)-P(2A)-C(1A)	122.3(4)
Ru(2)P(2B)C(19B)	121.6(3)	Ru-P(2)-C(7B)	120.7(3)	Ru(1)-P(2A)-C(7A)	127.0(4)

scheme and Fig. 2 is drawing of the *mer*-[$RuCl_3$(NO)(dppb)] complex.

In the [$RuCl_3$(NO)(dppb)] complex the NO is essentially linear with the ruthenium atom (∠ Ru–N–O=157(1)°) and the Ru–Cl, Ru–N and Ru–P bond lengths in this nitrosyl complex, close to 2.4, 1.7 and 2.5 Å, respectively, are comparable to those found for similar complexes as can be seen in Table 3 [5,9–13]. It is interesting to point out that in this complex the distance Ru–P(2) [2.498(3) Å] which has the NO group in *trans* position is shorter than the distance Ru–P(1) [2.412(2) Å] where the chlorine is in *trans* position. Here, like in our [$RuCl_3$(NO)(dppp)] complex the *trans* strengthening effect of the NO group was not observed [5]. This can be explained taking in consideration that probably the NO group does not present strong bonding when *trans* a bad donor atom like phosphorus [15,16]. The high thermal parameter of the oxygen atom of the NO group in the [$RuCl_3$(dppb)(NO)] molecule confirms the flexibility for the orientation of the nitrosyl with respect to the Ru–N bond in this class of complexes [5].

The NO bond lengths for complexes **(1)** and **(3)** are close to 1.14 Å, practically the same distance 1.06 Å of the free $N–O^+$ group [14] showing almost absence of backbonding in the bonding between the ruthenium and nitrogen atoms. In the *fac*-[$RuCl_3$(NO)(dppm)] complex the distance Ru–Cl(3) 2.345(3) Å is shorter than the bond lengths of the others two chlorine atoms present in the same molecule, Ru–Cl(1) and Ru–Cl(2), 2.439(3) Å and 2.430(3) Å, respectively. This is expected due to the *trans* strengthening effect of the NO group [10,12].

The observed Ru–N–O bond angle for the *mer*-[$RuCl_3$(NO)(dppb)] complex (approx. 160°) is smaller than the angle [172.0(6)°] found for same isomer with the 1,3-bis(diphenilphosphine)propane (dppp) ligand [8]. This effect can be attributed to the bigger repulsion between the extensive molecular orbital of the NO ligand and the phenyl rings bonded to the P(2) atom of the dppb ligand compared to the same repulsion with the P(2) atom of the dppp ligand. This is probably to due the larger carbon chain between the two phosphorus atoms P(1) and P(2) in the dppb ligand what makes the phosphorus orbital [P(2)] to move towards the NO orbital easily and consequently promotes a stronger repulsion with this orbital making the Ru–N–O angle smaller in this case The length of the chain between the two phosphorus atoms in the biphosphines also is reflected in the angles P(1)–Ru–N, which is 169.8(2)° for the complex with the dppp and 175.7(3)° for the P(2)–Ru–N dppb complex. The silent EPR of the *fac*-[$RuCl_3$(NO)(dppm)] and *mer*-[$RuCl_3$(NO)(dppb)] complexes confirm that the $\{Ru–NO^+\}$ species are diamagnetics, maintaining the linear structures of the Ru–NO bonds.

The crystallographic data found in this work for the *cis*-[$RuCl_2(dppm)_2$] co-crystallized with compound **(1)** are essentially the same found previously for this compound

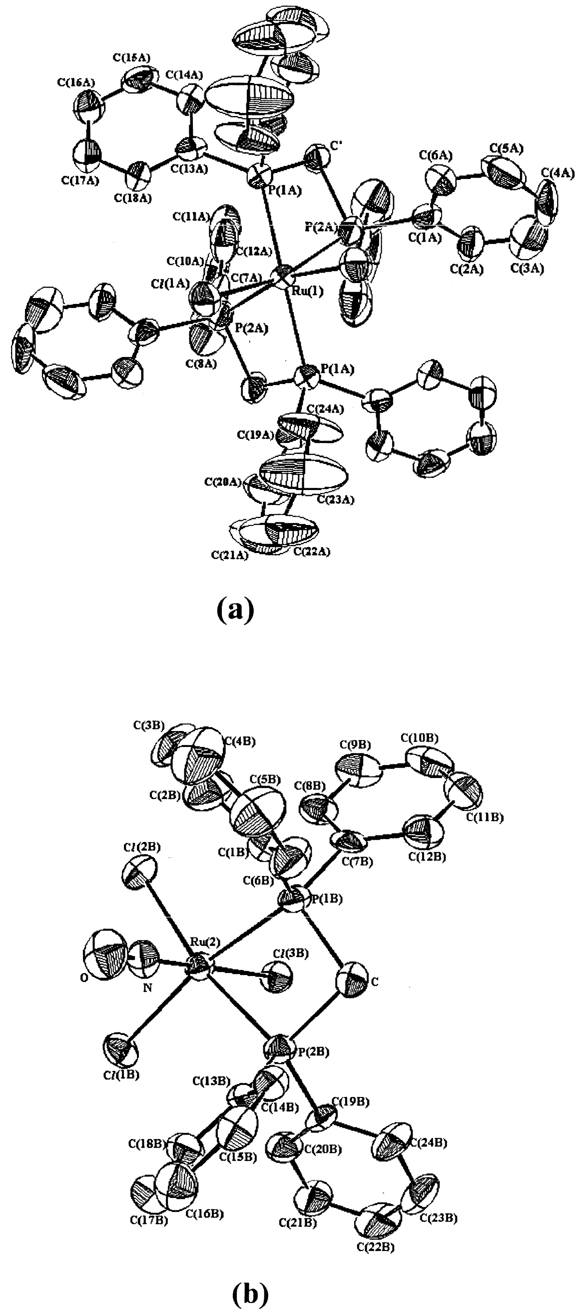

Fig. 1. ORTEP view of *fac*-[RuCl$_3$NO(dppm)] (a) and *cis*-[RuCl$_2$(dppm)] (b) with 50% probability thermal ellipsoids.

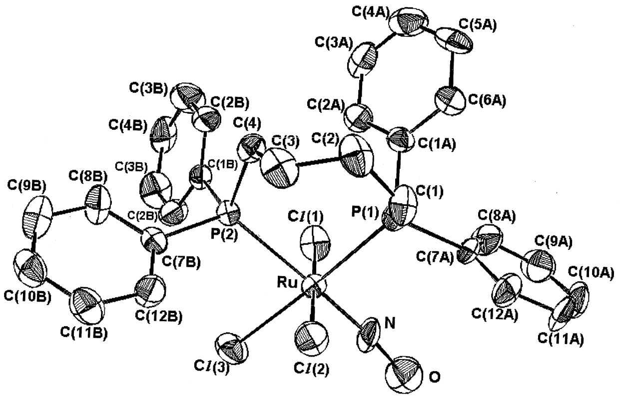

Fig. 2. ORTEP view of *mer*-[RuCl$_3$NO(dppb)] with 50% probability thermal ellipsoids.

Table 3
Comparison of Ru–Cl distances (Å) *trans* to NO in ruthenium compounds

Compound	Ru–Cl	Ru–NO	N–O	Ref.
[RuCl(py)$_4$(NO)]$^{2+}$	2,315(3)	1.766(8)	1.123(1)	[9]
[RuCl$_5$(NO)]$^{2-}$	2.357(1)	1.738(2)	1.131(3)	[10]
[RuCl$_3$(PMePh$_2$)$_2$(NO)	2.357(2)	1.744(6)	1.132(6)	[11]
[RuCl$_3$(PPh$_3$)$_2$(NO)]	2.353(2)	1.737(7)	1.142(8)	[12]
[RuCl$_3$(AsPh$_3$)$_2$(NO)]	2.346(2)	1.729(7)	1.151(9)	[13]
[RuCl$_3$(dppm)(NO)	2.345(3)	1.716(8)	1.14(1)	[a]
[RuCl$_3$(dppb)(NO)	2.384(2)	1.748(8)	1.15(2)	[a]

[a] This work

crystallized as *cis*-[RuCl$_2$(dppm)$_2$]·CHCl$_3$ in the space group P2$_1$/n [16]. In this complex **(2)** the Cl–Ru–Cl angle is 85.5(1)° which is less than the ideal value of 90°. In this work was also observed that angles between *cis* phosphorus atoms from different dppm ligands are considerably higher than 90°. The chelate ring is very much distorted as is shown by the P–Ru–P angles in the complexes. The steric strain is also imposed on the C′ and phosphorus atoms of the dppm ligand where the angle P(1A)–C′–P(2A) is 95.7(5)° and P(1A)–Ru–P(2A) is 72.0(1)° (Fig. 1b).

It is interesting also to mention that the isomerization process from the *mer* to the *fac*-[RuCl$_3$(NO)(dppb)] isomer was also observed through $^{31}P\{_1H\}$ experiments. In this case the doublets at δ 13.65(d) and δ 10.10(d) of a fresh CH$_2$Cl$_2$ solution do not totally disappear in an interval of time of 48 h and only 10 h after running the first spectra the intensity of these doublets is reasonably decreased and the singlet at δ 22.86 of the *fac* isomer is really observed. Thus the isomerization process of the *mer*-[RuCl$_3$(NO)(dppb)] is much slower than the observed for the *mer*-[RuCl$_3$(NO)(dppp)] [5]. This probably is due the stronger strain caused by the shorter carbon chain between the phosphorus atoms in the dppp ligand when compared with the dppb molecule.

Supplementary data

The supplementary material of *fac*-[RuCl$_3$(NO)(dppm)] **(1)** co-crystallized with *cis*-[RuCl$_2$(dppm)$_2$] **(2)** was deposited in the CCDC with the number 102519 and the number 102520 is for the *mer*-[RuCl$_3$(NO)(dppb)] **(3)**.

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