Polyhedron 29 (2010) 2297–2303

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

On the synthesis and structures of the complexes [RuCl(L)(dppb)(N–N)]PF_6 (L = CO, py or 4-NH_2py; dppb = 1,4-bis(diphenylphosphino)butane; N–N = 2,2′-bipyridine or 1,10-phenanthroline) and [(dppb)(CO)Cl_2-Ru-pz-$RuCl_2$(CO)(dppb)] (pz = pyrazine)

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ARTICLE INFO

Article history:
Received 29 December 2009
Accepted 30 April 2010
Available online 7 May 2010

Keywords:
Ruthenium complexes
Diphenylphosphine
Structure
Carbonyl

ABSTRACT

The "Ru(P–P)" unit (P–P = diphosphine) is recognized to be an important core in catalytic species for hydrogenation of unsaturated organic substrates. Thus, in this study we synthesized six new complexes containing this core, including the binuclear complex [(dppb)(CO)Cl_2Ru-pz-$RuCl_2$(CO)(dppb)] (pz = pyrazine) which can be used as a precursor for the synthesis of cationic carbonyl species of general formula [RuCl(CO)(dppb)(N–N)]PF_6 (N–N = diimine). Complexes with the formula [RuCl(py)(dppb)(N–N)]PF_6 were synthesized by exhaustive electrolysis of these carbonyl compounds or from the precursors [$RuCl_2$(dppb)(N–N)]. The new complexes were characterized by microanalysis, conductivity measurements, IR and $^{31}P\{^1H\}$ NMR spectroscopy, cyclic voltammetry and X-ray crystallography.

1. Introduction

The "Ru(P–P)" core is recognized as an active catalytic species for the hydrogenation of unsaturated organics [1–14]. In view of this, several synthetic routes based on different precursors have been developed to obtain complexes containing this type of unit. In the past, our laboratory has prepared and isolated the complexes [$RuCl_2$(dppb)(N–N)], where N–N = a diimine ligand [15,16]. Some of these complexes, synthesized from [$RuCl_2$(dppb)PPh_3], [Ru_2Cl_4(dppb)$_3$] or [$RuCl_3$(dppb)H_2O], have been used by us to catalyze hydrogenation and hydrogen transfer [5,16,17]. More recently, we have promoted reactions of some of these [$RuCl_2$(dppb)(N–N)] complexes with mono-anionic bidentate ligands such as 4,6-dimethyl-2-mercaptopyrimidine to obtain cationic complexes that showed antitumor activity, with low IC_{50} values (i.e. strong inhibition) against MDA-MB-231 human breast tumor cells, and also acted as potential antimycobacterial drugs against *Mycobacterium tuberculosis* H37Rv ATCC 27264 [18]. Encouraged by these results, we are now investigating new routes to synthesize cationic complexes with the general formula [RuCl(L)(dppb)(N–N)]PF_6, where L is CO or N-heterocyclic ligands, which contain the "Ru(P–P)" core, where P–P = 1,4-bis(diphenylphosphino)butane, to study their antimycobacterial and antitumoral activities. It is worth mentioning that phosphine complexes of various transition metals have been evaluated as potential antitumor agents in various human tumor lines [19–21]. This paper describes the synthesis, spectroscopic and electrochemical characterization and X-ray structures of new complexes containing the 1,4-bis(diphenylphosphino)butane ligand.

2. Experimental

2.1. Materials for synthesis

All manipulations were carried out under purified argon with standard Schlenk techniques. Reagent grade solvents were appropriately distilled and dried before use. All chemicals used were of reagent grade or comparable purity. All chemicals were purchased from Aldrich and were used as received. The precursors

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doi:10.1016/j.poly.2010.04.028

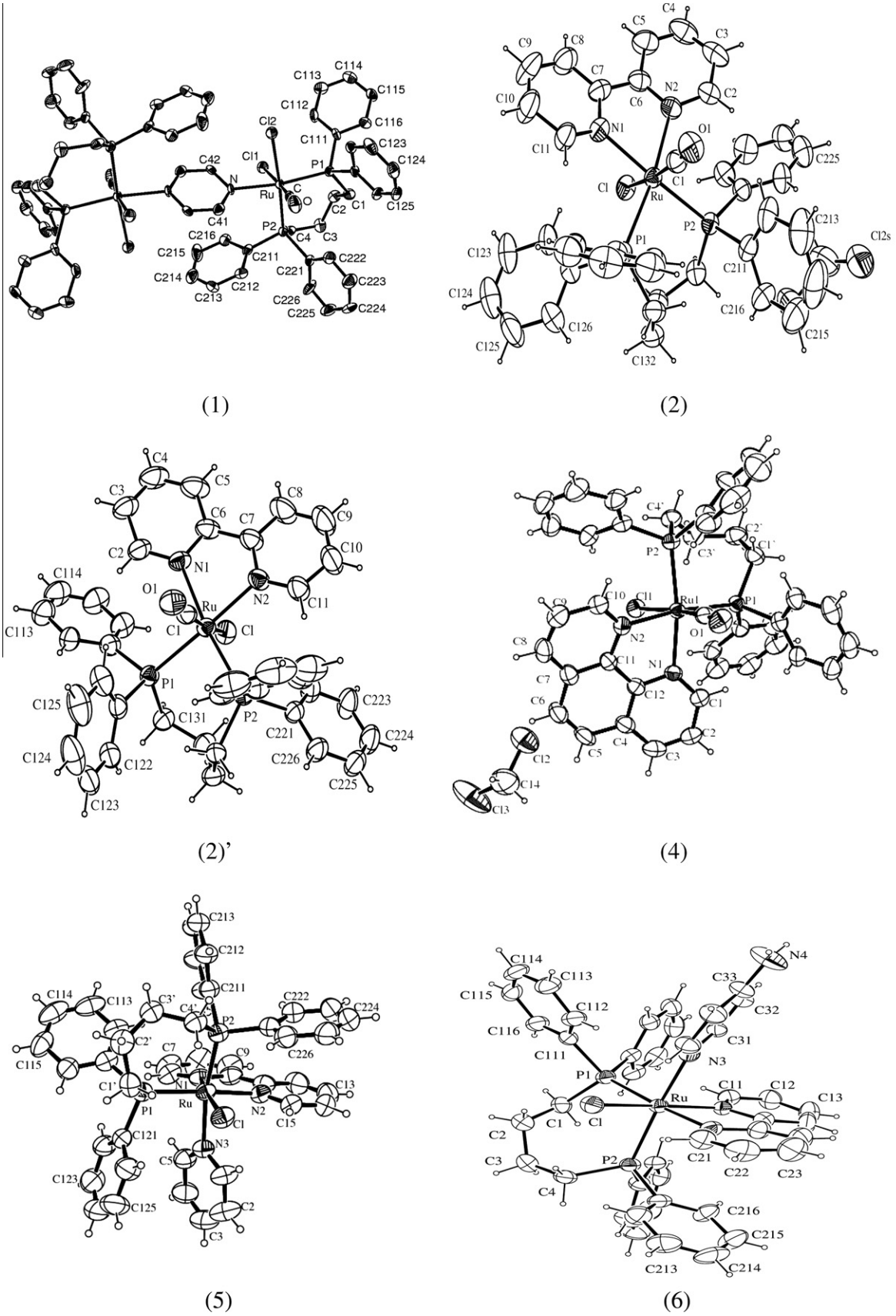


Fig. 1. ORTEP[28] view of: (A) $[Ru_2Cl_4(CO)_2(pz)(dppb)_2]$ (**1**), (B) *tc*-$[RuCl(CO)(dppb)(bipy)]PF_6{\cdot}CH_2Cl_2$ (**2**), *tc*-$[RuCl(CO)(dppb)(bipy)]PF_6{\cdot}0.3CH_3OH$ (**2**)′, (C), *tc*-$[RuCl(CO)(dppb)(phen)]PF_6{\cdot}CH_2Cl_2$ (**4**), *ct*-$[RuCl(py)(dppb)(bipy)]PF_6$ (**5**), *ct*-$[RuCl(4\text{-}NH2py)(dppb)(bipy)]\ PF_6$ (**6**), showing the atom labeling and the 50% probability ellipsoids [for (**6**), 30%].

cis-[$RuCl_2$(P–P)(N–N)] (2,2′-bipyridine or 1,10-phenanthroline) and [$Ru_2Cl_4(CO)_2(dppb)_3$] were prepared according to the literature methods [15,22].

2.2. Instrumentation

The IR spectra of the complexes were collected on a FTIR Bomem-Michelson 102 spectrometer in the 200–4000 cm^{-1} region using solid samples pressed into CsI pellets. All the NMR spectra were recorded on a Bruker 9.4 T instrument (400 MHz for hydrogen frequency) for samples in CH_2Cl_2, using a capillary containing D_2O. Cyclic voltammetry (CV) experiments were carried out at room temperature in CH_2Cl_2 containing 0.10 M $Bu_4N^+ClO_4$ (TBAP) (Fluka Purum), using a BAS-100B/W Bioanalytical Systems Instrument; the working and auxiliary electrodes were stationary Pt foils, a Lugging capillary probe was used and the reference electrode was Ag/AgCl. Under these conditions, ferrocene is oxidized at 0.43 V (Fc^+/Fc). Microanalysis was performed by Microanalytical Laboratory of Universidade Federal de São Carlos, São Carlos (SP), using a Fisons CHNS, mod. EA 1108 elemental analyzer.

2.3. X-ray crystallography

Crystals of the complexes were grown by slow evaporation of the solutions in dichloromethane/diethyl ether. The crystals were mounted on an Enraf-Nonius Kappa-CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The final unit cell parameters were based on all reflections. Data collections were made using the COLLECT program [23]; integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [24]. Absorption correction was carried out by the Gaussian method [25]. The structure was solved by direct methods with SHELXS-97 [26]. The model was refined by full-matrix least squares on F^2, by means of SHELXL-97 [27]. All hydrogen atoms were stereochemically positioned and refined with the riding model. The ORTEPs shown in Fig. 1 were prepared with ORTEP-3 for Windows [28]. Hydrogen atoms on the aromatic rings were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the atom to which each one is bonded. The data collected and some experimental details are summarized in Table 1.

2.4. Synthesis

Throughout the text the first letter in the prefix to a complex formula refers to the position of the CO relative to the chlorine atom and the second letter refers to the same ligand relative to the phosphorus atom.

2.4.1. [$Ru_2Cl_4(CO)_2(pz)(dppb)_2$] (**1**)

Complex (**1**), [$Ru_2Cl_4(CO)_2(pz)(dppb)_2$], was prepared from 100 mg (0.0595 mmol) of [$Ru_2Cl_4(CO)_2(dppb)_3$] dissolved in CH_2Cl_2 (10 mL) and 5.6 mg (0.0700 mmol) pyrazine. The mixture was stirred for 48 h after that the volume of the solution was reduced to 1 mL and ether was added to precipitate the product, which was washed with hexane and ether and dried under vacuum. Yield

Table 1
Crystallographic data for [$Ru_2Cl_4(CO)_2(pz)(dppb)_2$] (**1**), tc-[RuCl(CO)(dppb)(bipy)]PF_6·CH_2Cl_2 (**2**), tc-[RuCl(CO)(dppb)(bipy)]PF_6·0.3CH_3OH (**2**)′ tc-[RuCl(CO)(dppb)(phen)]PF_6·CH_2Cl_2 (**4**), ct-[RuCl(py)(dppb)(bipy)]PF_6 (**5**) and ct-[RuCl(4-NH_2py)(dppb)(bipy)]PF_6·CH_2Cl_2 (**6**).

	(**1**)	(**2**)	(**2**)′	(**4**)	(**5**)	(**6**)
Formula	$C_{62}H_{60}Cl_4N_2O_2P_4{\cdot}Ru_2$	$C_{40}H_{38}Cl_3F_6N_2OP_3Ru$	$C_{39.3}H_{37.2}ClF_6N_2O_{1.3}P_3Ru$	$C_{42}H_{38}Cl_3F_6N_2OP_3Ru$	$C_{43}H_{41}ClF_6N_3P_3Ru$	$C_{44}H_{44}Cl_3F_6N_4P_3Ru$
Formula weight	1333.02	977.10	901.77	1001,12	943.26	1043.20
T (K)	296(2)	293(2)	293(2)	293(2)	293(2)	120(2)
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P\ 2_12_12_1$	$P2_1/c$	$P2_1/n$
a (Å)	9.889(7)	18.907(1)	15.3418(2)	11.80400(10)	10.27740(10)	19.227(1)
b (Å)	14.217(2)	18.910(3)	18.6634(2)	18.7680(2)	27.2866(5)	9.987(1)
c (Å)	20.978(5)	11.604(1)	14.1058(2)	19.0790(2)	15.0142(2)	25.161(1)
β (°)	90.63(2)		96.5300(10)		102.3520(10)°.	111.47(1)
V (Å^3)	2949(2)	4148.8(9)	4012.71(9)	4226.71(7)	4113.05(8)	4496.2(5)
Z	2	4	4	4	4	4
ρ_{calcd} (Mg m^{-3})	1.501	1.564	1.493	1.573	1.523	1.541
Absorption coefficient (mm^{-1})	0.847	0.749	0.639	0.737	0.630	0.696
F(0 0 0)	1356	1976	1830	2024	1920	2120
Crystal size (mm^3)	0.30 × 0.30 × 0.12	0.24 × 0.2 × 0.06	0.3 × 0.24 × 0.22	0.24 × 0.26 × 0.28	0.081 × 0.210 × 0.320	0.20 × 0.08 × 0.04
θ Range for data collection (°)	1.73–24.98	2.98–26.35	3.02–27.48	2.95–27.48	3.15–27.5	2.94–24.43
Index ranges	$-11 \leqslant h \leqslant 11$ $0 \leqslant k \leqslant 16$ $0 \leqslant l \leqslant 24$	$-23 \leqslant h \leqslant 22$ $-13 \leqslant k \leqslant 23$ $-14 \leqslant l \leqslant 13$	$-19 \leqslant h \leqslant 19$ $-24 \leqslant k \leqslant 23$ $-18 \leqslant l \leqslant 18$	$-15 \leqslant h \leqslant 15$ $-24 \leqslant k \leqslant 22$ $-24 \leqslant l \leqslant 23$	$-13 \leqslant h \leqslant 13$ $-34 \leqslant k \leqslant 35$ $-18 \leqslant l \leqslant 19$	$-22 \leqslant h \leqslant 22$ $-11 \leqslant k \leqslant 9$ $-29 \leqslant l \leqslant 29$
Reflections collected	5313	18 908	32 724		32 220	22 088
Reflections unique (R_{int})	5168 (0.0964)	8356 (0.0601)	9191 (0.0303)	9589 (0.0307)	9393 (0.0811)	7408 (0.076)
Completeness to θ	24.98°(100%)	26.35°(98.6%)	27.48°(99.7%)	27.48°(99.2%)	27.5°(99.3%)	24.43°(99.6%)
Data/restraints/parameter	5168/0/344	8356/0/505	9191/1/496	9589/0/523	9393/0/514	7408/0/595
Maximum/minimum transmission	0.9052 and 0.7852	0.940 and 0.856	0.841 and 0.769	0.843 and 0.800	1.165 and 0.856	0.973 and 0.873
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0521, wR_2 = 0.1037	R_1 = 0.0431, wR_2 = 0.1068	R_1 = 0.0540, wR_2 = 0.1354	R_1 = 0.0357, wR_2 = 0.0860	R_1 = 0.0490, wR_2 = 0.1195	R_1=0.073, wR_2 = 0.210
R indices (all data)	R_1 = 0.2371, wR_2 = 0.1565	R_1 = 0.0589, wR_2 = 0.1192	R_1 = 0.0665, wR_2 = 0.1407	R_1 = 0.0463, wR_2 = 0.0918	R_1 = 0.0927, wR_2 = 0.1376	R_1=0.097, wR_2 = 0.223
GOF on F^2	0.972	1.018	1.186	1.028	1.043	1.149
Largest difference in peak and hole (e Å^{-3})	0.571 and −0.838	0.500 and −0.672	0.739 and −0.737	0.531 and −0.465	0.425 and −0.949	1.016, −0.769

60% (47.6 mg). *Anal.* Calc. for $C_{62}H_{60}Cl_4N_2O_2P_4Ru_2$: C, 57.01; N, 2.32; H, 4.65. Found: C, 55.86; N, 2.21; H, 4.54%. X-ray suitable single crystals were obtained from dichloromethane/ether solution, by slow evaporation.

2.4.2. tc-[RuCl(CO)(dppb)(bipy)]PF_6 (**2**)

Complex (**2**), *tc*-[RuCl(CO)(dppb)(bipy)]PF_6 was prepared from 50.0 mg (0.0298 mmol) of $[Ru_2Cl_4(CO)_2(dppb)_3]$ dissolved in CH_2Cl_2 (10 mL), 14.0 mg (0.0896 mmol) 2,2́-bipyridine and 28.0 mg (0.172 mmol) NH_4PF_6. The mixture was refluxed for 6 h, after that it was concentrated to approximately 2 mL and a solid was precipitated with ether, washed well with water and ether and dried under vacuum. Yield 53% (28.2 mg). *Anal.* Calc. for $C_{39}H_{36}ClF_6N_2OP_3Ru$: C, 52.17; N, 3.41; H, 4.22. Found: C, 52.50; N, 3.14; H, 4.07%. X-ray suitable single crystals were obtained from dichloromethane/ether solution, by slow evaporation.

Besides the complex $[Ru_2Cl_4(CO)_2(dppb)_3]$, [(dppb)(CO)Cl_2-Ru-pz-$RuCl_2$(CO)(dppb)] can also be used as a precursor to obtain species with the general formula [RuCl(CO)(dppb)(N–N)]PF_6.

2.4.3. cc-[RuCl(CO)(dppb)(bipy)]PF_6 (**3**)

The complex (**3**), *cc*-[RuCl(CO)(dppb)(bipy)]PF_6 was prepared by refluxing 100 mg (0.112 mmol) of tc-[RuCl(CO)(dppb)(bipy)]PF_6 (**2**), dissolved in a mixture of CH_2Cl_2 and CH_3OH (10 mL/10 mL), for 24 h. The volume of the solution was reduced to ca. 2 mL and ether was added to precipitate a yellow solid, which was filtered off and washed with ether and dried under vacuum. Yield: 86% (85.9 mg). *Anal.* Calc. for $C_{39}H_{36}ClF_6N_2OP_3Ru$: C, 52.91; N, 3.49; H, 3.95. Found: C, 52.50; N, 3.14; H, 4.07%. X-ray suitable single crystals were obtained from methanol/ether solution, by slow evaporation.

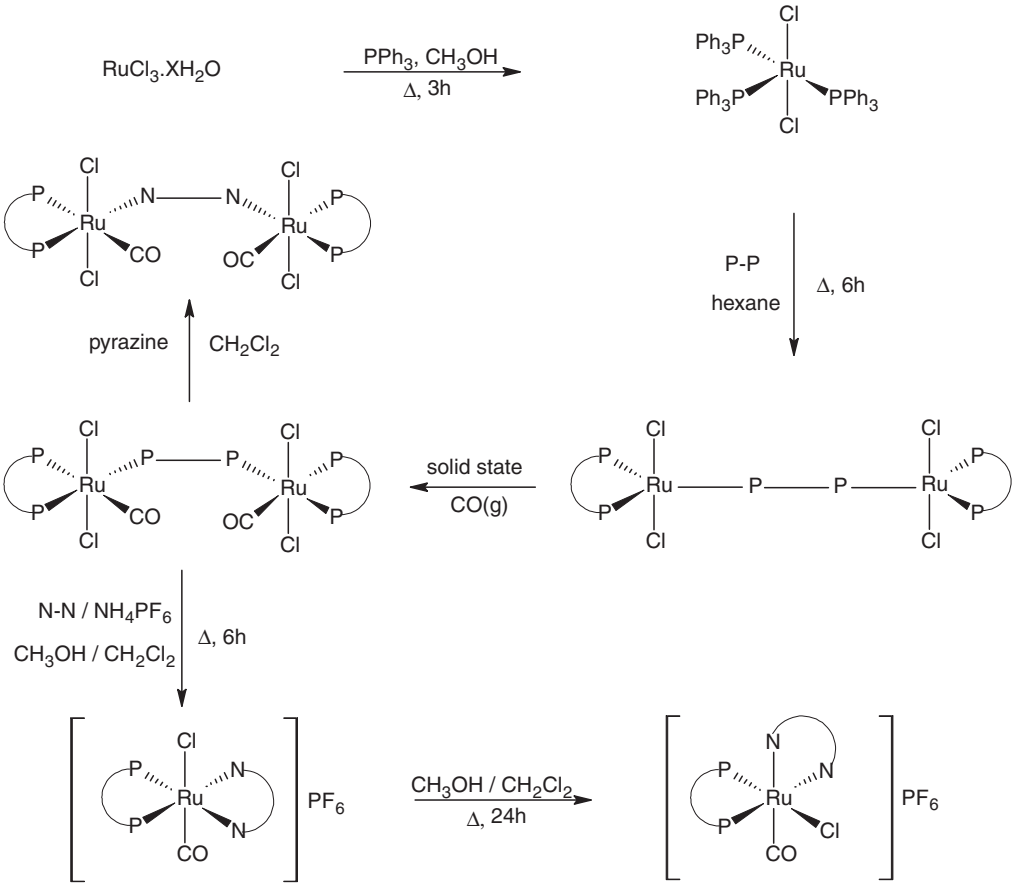
2.4.4. tc-[RuCl(CO)(dppb)(phen)]PF_6 (**4**)

The complex (**4**), *tc*-[RuCl(CO)(dppb)(phen)]PF_6 was prepared analogously to (**2**), from 100.0 mg (0.0595 mmol) of $[Ru_2Cl_4(CO)_2(dppb)_3]$ dissolved in CH_3OH (10 mL), 35 mg (0.194 mmol) of 1,10-phenanthroline and 35 mg (0.215 mmol) NH_4PF_6. The mixture was refluxed for 24 h, after that it was concentrated to approximately 2 mL and a solid was precipitated with ether, filtered off, and washed well with water and ether and dried under vacuum. Yield: 60% (65.4 mg). *Anal.* Calc. for $C_{41}H_{36}ClF_6N_2OP_3Ru.CH_2Cl_2$: C, 50.39; N, 2.80; H, 3.83. Found: C, 50.29; N, 2.79; H, 3.93%. X-ray suitable single crystals were obtained by recrystallization in dichloromethane, after leaving the solution undisturbed over the bench top for 24 h.

2.4.5. tc-[RuCl(py)(dppb)(bipy))]PF_6 (**5**)

The complex (**5**), *tc*-[RuCl(py)(dppb)(bipy))]PF_6 was prepared by electrolyzing 50 mg (0.0560 mmol) of *tc*-[RuCl(CO)(dppb)(bipy)]PF_6 in acetonitrile at about 2.1 V in the presence of excess pyridine (10 times), using NH_4PF_6 as the electrolyte, and then the product was electrolyzed at 0.7 V. The solution containing the reduced product was concentrated to approximately 2 mL and a solid was precipitated with ether, rinsed well with water and ether and dried under vacuum. Yield: 65% (34.3 mg). *Anal.* Calc. for $C_{43}H_{41}ClF_6N_3P_3Ru$: C, 54.68; N, 4.46; H, 4.40. Found: C, 54.75; N, 4.45; H, 4.38%. X-ray suitable single crystals were obtained from dichloromethane/ether solution, by slow evaporation.

[RuCl(py)(dppb)(bipy)]PF_6 was also obtained from the precursor *cis*-[$RuCl_2$(dppb)(bipy)] 50 mg (0.0662 mmol) dissolved in CH_2Cl_2 (20 mL) and 16.2 μL (0.201 mmol) of pyridine. The mixture was stirred for 3 h, after that NH_4PF_6 (17.5 mg, 0.107 mmol), dissolved in a minimum volume of CH_3OH, was added. After 30 min



Scheme 1. Synthetic route for the complexes (**1**–**4**).

of stirring, the solution was concentrated to about 1 mL and hexane was added to precipitate the product which was washed with water and ether and dried under vacuum. Yield: 54% (33.7 mg).

*2.4.6. tc-[RuCl(4-NH$_2$py)(dppb)(bipy)]PF$_6$ (**6**)*

The complex (**6**), *tc*-[RuCl(4-NH$_2$py)(dppb)(bipy)]PF$_6$ was first obtained by electrolyzing 37 mg (0.0415 mmol) of tc-[RuCl(-CO)(dppb)(bipy)]PF$_6$ at about 2.1 V in the presence of excess of 4-aminopyridine (three times), using NH_4PF_6 as electrolyte, in acetonitrile, and then the product was electrolyzed at 0.7 V. The solution containing the reduced product was concentrated to approximately 2 mL and a solid was precipitated with ether, rinsed well with water and ether and dried under vacuum. Yield: 60% (23.9 mg). *Anal.* Calc. for $C_{43}H_{42}ClF_6N_4P_3Ru.C_5H_6N_2$: C, 54.19; N, 7.24; H, 4.48. Found: C, 54.78; N, 7.99; H, 4.60%.

[RuCl(4-NH$_2$py)(dppb)(bipy)]PF$_6$ was also obtained from a mixture of 100 mg (0.132 mmol) of the precursor cis-[RuCl$_2$(dppb)(bipy)] dissolved in CH_2Cl_2 (20 mL) and 37 mg (0.393 mmol) 4-aminopyridine This solution was stirred for 20 h, after which NH_4PF_6 44.0 mg (0.270 mmol), dissolved in a minimum volume of CH_3OH, was added. After 30 min of stirring the solution was concentrated to about 1 mL and hexane was added to precipitate the product which was washed with water and ether and dried under vacuum. Yield: 69% (87.3 mg). X-ray suitable single crystals were obtained from dichloromethane/ether solution, by slow evaporation.

3. Results and discussion

The synthesis of complexes (**1**–**4**) followed the Scheme 1 and the complexes (**5**–**6**) followed the Scheme 2.

The $^{31}P\{^1H\}$ NMR spectra of complexes (**3**) and (**6**) exhibit two doublets suggesting that their phosphorus atoms are not magnetically equivalent, while for compounds (**2**), (**4**) and (**5**), only one singlet is present in their spectra showing the equivalence of their phosphorus atoms, *trans* to the nitrogen atoms in the 2,2′-bipyridine or 1,10-phenanthroline ligands (Table 2).

The IR spectra of the carbonyl complexes show typical ν_{CO} bands around 1970 cm^{-1}. The complexes (**2**–**6**), in acetone, are 1:1 electrolyte as suggested by their observed molar conductivity measurements (see Table 2).

The cyclic voltammograms of complexes (**2**–**4**) showed irreversible oxidation of Ru^{II} to Ru^{III} at higher potentials than the reversible process observed for complexes (**5**–**6**). This is a consequence of the presence of the carbonyl ligand in the complexes (**2**–**4**). These data are in Table 3.

The bond lengths (Å) and angles (°) for the complexes [Ru$_2$Cl$_4$(-CO)$_2$(pz)(dppb)$_2$] (**1**), *tc*-[RuCl(CO)(dppb)(bipy)]PF$_6$·CH$_2$Cl$_2$ (**2**) and *tc*-[RuCl(CO)(dppb)(bipy)]PF$_6$·0.3CH$_3$OH (**2**)′ are in Table 5; those for the complexes *tc*-[RuCl(CO)(dppb)(phen)]PF$_6$·CH$_2$Cl$_2$ (**4**), *ct*-[RuCl(py)(dppb)(bipy)]PF$_6$ (**5**) and *ct*-[RuCl(4-NH2py)(dppb)(bipy)]PF$_6$ (**6**) are in Table 5 and their ORTEP structures are shown in Fig. 1.

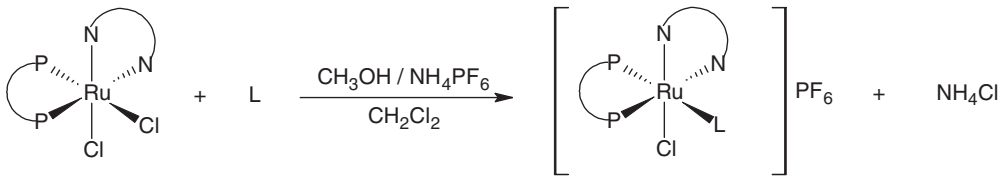
Regarding complex (**2**), *tc*-[RuCl(CO)(dppb)(bipy)]PF$_6$, seen in Table 4, two structures were refined, one containing CH_3OH (monoclinic) and the other containing CH_2Cl_2 (orthorhombic). Both unit cells for the complexes are shown in Fig. 2, and as can be seen, while the monoclinic species, is centro-symmetric, the orthorhombic, is not.

The distances for the Ru–Cl, Ru–P, Ru–N and C–O bonds and bond angles found for the compounds are within the normal range found for similar Ru^{II} complexes [29–36].

Table 3
Electrochemical data for complexes (**1**–**6**).

Complex	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)
[Ru$_2$Cl$_4$(CO)$_2$(pz)(dppb)$_2$] (**1**)	0.87		
tc-[RuCl(CO)(dppb)(bipy)]PF$_6$ (**2**)	2.11		
cc-[RuCl(CO)(dppb)(bipy)]PF$_6$ (**3**)	2.10		
tc-[RuCl(CO)(dppb)(phen)]PF$_6$ (**4**)	2.10		
ct-[RuCl(py)(dppb)(bipy)]PF$_6$ (**5**)	1.17	1.09	1.13
ct-[RuCl(4-NH$_2$py)(dppb)(bipy)]PF$_6$ (**6**)	1.08	0.98	1.03

E_{pa} = anodic peak potential; E_{pc} = cathodic peak potential. The $E_{1/2}$ values were obtained by (E_{pa} + E_{pc}/2).



Scheme 2. General reaction for the synthesis of the *ct*-[RuCl(L)(dppb)(bipy)]PF$_6$ complexes (**5** and **6**).

Table 2
$^{31}P\{^1H\}$ NMR chemical shifts for the complexes (**1**–**6**), in CH_2Cl_2; infrared ν_{CO} (cm^{-1}), in CsI pellets and molar conductivity in acetone.

Complex	$^{31}P\{^1H\}$; ($^2J_{p-p}$/Hz)	ν_{CO} (cm^{-1})	μS/cm (RT)
[Ru$_2$Cl$_4$(CO)$_2$(pz)(dppb)$_2$] (**1**)	−117.42 (s) −112.62/−111.60 (d) −110.90(d)/−97.10 (d) −95.66(m) $^2J_{p-p}$ = 30 Hz	1958	1.2
tc-[RuCl(CO)(dppb)(bipy)]PF$_6$ (**2**)	27.8 (s)	1970	163.0
cc-[RuCl(CO)(dppb)(bipy)]PF$_6$ (**3**)	35.0 (d); 27.0 (d) $^2J_{p-p}$ = 29.60 Hz	1976	148.0
tc-[RuCl(CO)(dppb)(phen)]PF$_6$ (**4**)	28.4 (s)	1965	155.0
ct-[RuCl(py)(dppb)(bipy)]PF$_6$ (**5**)	38.01 (s)		150.0
ct-[RuCl(4-NH$_2$py)(dppb)(bipy)]PF$_6$ (**6**)	37.8 (d); 37.1 (d) $^2J_{p-p}$ = 34.00 Hz		161.0

(s) = singlet; (d) doublet and (m) multiplet.

Table 4
Selected bond lengths (Å) and angles (°) for (**1**) $[Ru_2Cl_4(CO)_2(pz)(dppb)_2]$, (**2**) $[RuCl(CO)(dppb)(bipy)]PF_6{\cdot}CH_2Cl_2$ and (**2**)′ $RuCl(CO)(dppb)(bipy)]PF_6{\cdot}0.3CH_3OH$.

1		2		2′	
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ru–Cl(1)	2.445(3)	Ru–Cl	2.4458(13)	Ru–Cl	2.4416(11)
Ru–Cl(2)	2.432(3)	Ru–N(1)	2.155(4)	Ru–N(1)	2.155(3)
Ru–N	2.208(7)	Ru–N(2)	2.147(4)	Ru–N(2)	2.158(3)
Ru–C	1.839(14)	Ru–C(1)	1.847(5)	Ru–C(1)	1.846(5)
Ru–P(1)	2.321(3)	Ru–P(1)	2.3820(13)	Ru–P(1)	2.3737(10)
Ru–P(2)	2.337(3)	Ru–P(2)	2.3749(2)	Ru–P(2)	2.3902(10)
C–O	1.086(3)	C(1)–O(1)	1.150(6)	C(1)–O(1)	1.142(5)
N–C(41)	1.320(13)	N(1)–C(11)	1.335(7)	N(1)–C(2)	1.337(6)
N–C(42)	1.325(12)	N(2)–C(2)	1.345(6)	N(2)–C(11)	1.338(6)
Bond	Angle(°)	Bond	Angle(°)	Bond	Angles(°)
C–Ru–N	89.2(4)	C(1)–Ru–N(1)	92.47(19)	C(1)–Ru–N(1)	85.76(15)
C–Ru–Cl(1)	175.1(4)	C(1)–Ru–N(2)	90.62(18)	C(1)–Ru–N(2)	96.01(16)
N–Ru–P(1)	171.4(2)	N(2)–Ru–P(1)	74.90(16)	N(1)–Ru–N(2)	75.72(13)
C–Ru–P(1)	91.1(4)	C(1)–Ru–P(1)	89.52(15)	C(1)–Ru–P(1)	95.42(12)
C–Ru–P(2)	96.0(4)	C(1)–Ru–P(2)	96.05(15)	C(1)–Ru–P(2)	89.49(12)
P(2)–Ru–Cl(2)	175.14(11)	N(1)–Ru–P(1)	97.14(12)	N(1)–Ru–P(1)	98.71(10)

Table 5
Selected bond lengths (Å) and angles (°) for the (**4**) *tc*-$[RuCl(CO)(dppb)(phen)]PF_6{\cdot}CH_2Cl_2$, (**5**) *ct*-$[RuCl(py)(dppb)(bipy)]PF_6$ and (**6**) *ct*-$[RuCl(4\text{-}NH_2py)(dppb)(bipy)]PF_6$ complexes.

4		5		6	
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ru–N(1)	2.161(3)	Ru–$N_{(L)}$ trans P	2.215(3)	Ru–$N_{(L)}$ trans P	2.175(7)
Ru–N(2)	2.157(3)	Ru–$N_{(bipy)}$ trans P	2.117(3)	Ru–$N_{(bipy)}$ trans P	2.130(7)
C(13)–O(1)	1.133(4)	Ru–$N_{(bipy)}$ trans Cl	2.073(3)	Ru–$N_{(bipy)}$ trans Cl	2.105(7)
Ru–P(1)	2.372(9)	Ru–P trans $N_{(L)}$	2.3242(9)	Ru–P trans $N_{(L)}$	2.335(2)
Ru–P(2)	2.370(8)	Ru–P trans $N_{(bipy)}$	2.3483(9)	Ru–P trans $N_{(bipy)}$	2.343(2)
Ru–Cl	2.451(8)	Ru–Cl	2.4252(8)	Ru–Cl	2.425(2)
Bond	Angles(°)	Bond	Angles(°)	Bond	Angles(°)
C(13)–Ru(1)–N(2)	89.93(13)	Cl–Ru–$N_{3(L\ trans\ P2)}$	88.3(9)	Cl–Ru–$N_{3(L\ trans\ P2)}$	90.7(2)
C(13)–Ru(1)–N(1)	91.90(12)	Cl–Ru–$P_{2(trans\ L)}$	84.4(3)	Cl–Ru–$P_{2(trans\ L)}$	85.3(8)
C(13)–Ru(1)–P(2)	95.95(10)	Cl–Ru–$N_{2(bipy\ trans\ P1)}$	92.9(9)	Cl–Ru–$N_{2(bipy\ trans\ P1)}$	91.3(2)
P(1)–Ru(1)–Cl(1)	97.30(3)	Cl–Ru–$P_{1(trans\ bipy)}$	87.4(3)	Cl–Ru–$P_{1(trans\ bipy)}$	88.1(8)
N(2)–Ru(1)–P(2)	98.15(7)	P_2–Ru–$N_{1(bipy\ trans\ Cl)}$	101.6(8)	P_2–Ru–$N_{1(bipy\ trans\ Cl)}$	97.8(2)
N(1)–Ru(1)–P(2)	170.41(8)	P_2–Ru–N_2	89.5(9)	P_2–Ru–N_2	90.6(2)
C(13)–Ru(1)–P(1)	90.22(11)	P_2–Ru–P_1	93.5(3)	P_2–Ru–P_1	94.0(8)
N(2)–Ru(1)–P(1)	171.92(8)	N_2–Ru–N_3	83.2(12)	N_2–Ru–N_3	81.0(3)
N(1)–Ru(1)–P(1)	95.63(8)	N_2–Ru–N_1	77.9(12)	N_2–Ru–N_1	77.6(3)
N(1)–Ru(1)–Cl(1)	84.91(8)	N_3–Ru–N_1	84.6(11)	N_3–Ru–N_1	84.5(3)
C(13)–Ru(1)–Cl(1)	172.09(11)	P_1–Ru–N_3	93.8(9)	P_1–Ru–N_3	94.4(2)
N(2)–Ru(1)–Cl(1)	82.28(7)	P_1–Ru–N_1	101.3(10)	P_1–Ru–N_1	102.7(2)

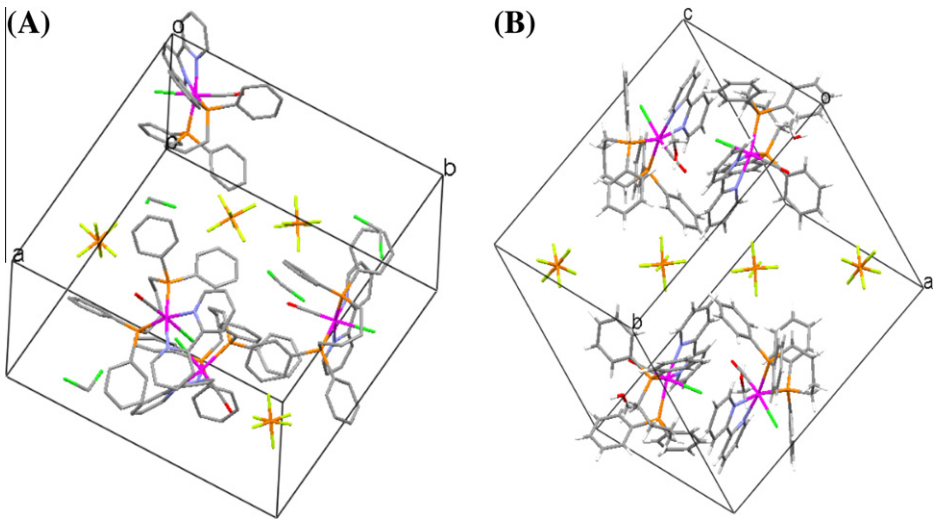


Fig. 2. Unit cells of the complex (**A**) tc-$[RuCl(CO)(dppb)(bipy)]PF_6{\cdot}CH_2Cl_2$ (**2**) and (B) *tc*-$[RuCl(CO)(dppb)(bipy)]PF_6{\cdot}0.3CH_3OH$ (**2**)′.

4. Concluding remarks

The binuclear complex $[Ru_2Cl_4(CO)_2(pz)(dppb)_2]$ was derived from the compound $[Ru_2Cl_4(CO)_2(dppb)_3]$, showing that it is possible to change the bridge ligand in this complex. Thus, both complexes can be used to obtain carbonyl complexes with the general formula $[RuCl(CO)(dppb)(N–N)]PF_6$, where N–N is a diimine. Concomitant with electrolytic oxidation of the metal center in the *tc*-$[RuCl(CO)(dppb)(bipy)]PF_6$ complex, the CO ligand is dissociated, generating new species with general formula *ct*-$[RuCl(L)(dppb)(bipy)]PF_6$, when L is dissolved in the medium. These complexes can also be obtained from the respective precursors *cis*-$[RuCl_2(dppb)(N–N)]$, by the replacement of one chlorine by the monodentate ligand L, such as pyridine and its derivatives. In both cases, the ligand L is trans positioned to the phosphorus atoms and cis to the chloride.

5. Supplementary data

CCDC 712141, 712142, 712143, 712144, 712145 and 746016 contain the supplementary crystallographic data for (**1**), (**2**), (**2**)′, (**4**), (**5**) and (**6**), respectively. 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 CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

We thank CAPES, CNPq and FAPESP for financial support, and M.P.A. thanks Johnson Matthey plc for the loan of $RuCl_3 \cdot nH_2O$.

References

[1] A.M. Joshi, K.S. MacFarlane, B.R. James, J. Organomet. Chem. 488 (1995) 161.
[2] A.M. Joshi, B.R. James, Chem. Commun. (1989) 1785.
[3] D.E. Fogg, B.R. James, Inorg. Chim. Acta 222 (1994) 85.
[4] B.R. James, A. Pacheco, S.J. Rettig, I.S. Thorburn, R.G. Ball, J.A. Ibers, J. Mol. Catal. 41 (1987) 147.
[5] A.A. Batista, A.L. Bogado, R.F. Souza, U. Schuchardt, J. Mol. Catal. A – Chem. 203 (2003) 129.
[6] K. Abdur-Rashid, S.E. Clapham, A. Hadzovic, J.N. Harvey, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 124 (2002) 15104.
[7] S.E. Clapham, A. Hadzovic, R.H. Morris, Coord. Chem. Rev. 248 (2004) 2201.
[8] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A.F. England, T. Ikariya, R. Noyori, Angew. Chem., Int. Ed. 37 (1998) 1703.
[9] K. Murata, K. Okano, M. Miyagi, H. Iwane, R. Noyori, T. Ikariya, Org. Lett. 1 (1999) 1119.
[10] R. Noyori, T. Ohkuma, Pure Appl. Chem. 71 (1999) 1493.
[11] R. Noyori, T. Ohkuma, Angew. Chem., Int. Ed. 40 (2001) 40.
[12] R. Noyori, C.A. Sandoval, K. Muniz, T. Ohkuma, Philos. Trans. R Soc. A Math. Phys. Eng. Sci. 363 (2005) 901.
[13] R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345.
[14] T. Ohkuma, H. Doucet, T. Pham, K. Mikami, T. Korenaga, M. Terada, R. Noyori, J. Am. Chem. Soc. 120 (1998) 1086.
[15] A.A. Batista, S.L. Queiroz, G. Oliva, M.T.P. Gambardela, R.H.A. Santos, B.R. James, Inorg. Chim. Acta 267 (1998) 209.
[16] M.P. de Araujo, E.M.A. Valle, J. Ellena, E.E. Castellano, E.N. Dos Santos, A.A. Batista, Polyhedron 23 (2004) 3163.
[17] M.P. de Araujo, A.F. Teixeira, A.L. Bogado, G. Von Poelhsitz, A.A. Batista, J. Ellena, E.E. Castellano, Organometallics 24 (2005) 6159.
[18] F.B. do Nascimento, G. Von Poelhsitz, F.R. Pavan, D.N. Sato, C.Q.F. Leite, H.S. Selistre-de-Araújo, J. Ellena, E.D. Castellano, V.M. Deflon, A.A. Batista, J. Inorg. Biochem. 102 (2008) 1783.
[19] S.J. Berners-Price, R.J. Bowen, P. Galettis, P.C. Healy, M.J. McKeage, Coord. Chem. Rev. 185–6 (1999) 823.
[20] A.A. Batista, S.L. Queiroz, Química Nova 19 (1996) 651.
[21] G. Von Poelhsitz, A.L. Bogado, M.P. de Araujo, H.S. Selistre-de-Araujo, J. Ellena, E.E. Castellano, A.A. Batista, Polyhedron 26 (2007) 4707.
[22] M. Bressan, P. Rigo, Inorg. Chem. 14 (1975) 2286.
[23] Enraf-Nonius (1997–2000) COLLECT. Nonius BV, Delft, The Netherlands.
[24] Z. Otwinowski, W. Minor, HKL Denzo and Scalepack, in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, vol. 276, Academic Press, New York, 1997, p. 307.
[25] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.
[26] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Resolution, University of Göttingen, Göttingen, Germany, 1997.
[27] G.M. Sheldrick, SHELXL-97, Program for Crystal Structures Analysis, University of Göttingen, Göttingen, Germany, 1997.
[28] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[29] L.R. Dinelli, A.A. Batista, K. Wohnrath, M.P. de Araujo, S.L. Queiroz, M.R. Bonfadini, G. Oliva, O.R. Nascimento, W.P. Cyr, K.S. MacFarlane, B.R. James, Inorg. Chem. 38 (1999) 5341.
[30] K. Wohnrath, M.P. de Araujo, L.R. Dinelli, A.A. Batista, I.S. Moreira, E.E. Castellano, J. Ellena, J. Chem. Soc., Dalton Trans. 19 (2000) 3383.
[31] A.L.R. Silva, M.O. Santiago, I.C.N. Diogenes, S.O. Pinheiro, E.E. Castellano, J. Ellena, A.A. Batista, F.B. do Nascimento, I.S. Moreira, Inorg. Chem. Commun. 8 (2005) 1154.
[32] M.O. Santiago, C.L. Donicci, I.S. Moreira, R.M. Carlos, S.L. Queiroz, A.A. Batista, Polyhedron 22 (2003) 3205.
[33] A.A. Batista, K. Wohnrath, A.G. Ferreira, J. Zuckerman-Schpector, E.E. Castellano, Polyhedron 17 (1998) 2013.
[34] A.A. Batista, M.O. Porcu, O.R. Nascimento, O. Oliva, J. Coord. Chem. 30 (1993) 345.
[35] M.P. de Araujo, A.A. Batista, M.O. Porcu, G. Oliva, M.P.D.H.F. Souza, M. Bonfadini, O.R. Nascimento, J. Coord. Chem. 54 (2001) 81.
[36] S.L. Queiroz, A.A. Batista, M.P. de Araujo, R.C. Bianchini, G. Oliva, B.R. James, Can. J. Chem. – Revue Canadienne de Chimie 81 (2003) 1263.