Polyhedron 28 (2009) 3473–3478

Contents lists available at ScienceDirect

Polyhedron

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

Driving forces in substitution reactions of octahedral complexes: The influence of the competitive effect

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ARTICLE INFO

Article history:
Received 25 January 2009
Accepted 16 July 2009
Available online 19 July 2009

Keywords:
Octahedral complexes
trans Effect
Steric effect
X-ray structures
Ruthenium complexes

ABSTRACT

The reaction of *cis*-[$RuCl_2$(P–P)(N–N)] type complexes (P–P = 1,4-bis(diphenylphosphino)butane or (1,1′-diphenylphosphino)ferrocene; N–N = 2,2′-bipyridine or 1,10-phenantroline) with monodentate ligands (L), such as 4-methylpyridine, 4-phenylpyridine and benzonitrile forms [RuCl(L)(P–P)(N–N)]$^+$ species. Upon characterization of the isolated compounds by elemental analysis, $^{31}P\{^1H\}$ NMR and X-ray crystallography it was found out that the type of the L ligand determines its position in relation to the phosphorus atom. While pyridine derivatives like 4-methylpyridine and 4-phenylpyridine coordinate *trans* to the phosphorus atom, the benzonitrile ligand (bzCN), a good π acceptor, coordinates *trans* to the nitrogen atom. A $^{31}P\{^1H\}$ NMR experiment following the reaction of the precursor *cis*-[$RuCl_2$(dppb)(phen)] with the benzonitrile ligand shows that the final position of the entering ligand in the complex is better defined as a consequence of the competitive effect between the phosphorus atom and the cyano-group from the benzonitrile moiety and not by the *trans* effect. In this case, the benzonitrile group is stabilized *trans* to one of the nitrogen atoms of the N–N ligand. A differential pulse voltammetry experiment confirms this statement. In both experiments the [RuCl(bzCN)(dppb)(phen)]PF_6 species with the bzCN ligand positioned *trans* to a phosphorus atom of the dppb ligand was detected as an intermediate complex.

1. Introduction

Simple rules have been devised in chemistry to predict the existence and stability of coordination compounds of transition metals. It is well-established that outer orbitals can accommodate up to 18 electrons furnishing a high stability to these complexes. Attack on a metal atom by a nucleophile agent by means of a substitution reaction can add electrons to the highest unoccupied atomic orbital or to an antibonding molecular orbital of the ligands. This kind of reaction usually proceeds by a dissociative mechanism in which the electronic and steric effects of the substituent ligand play a crucial role [1,2]. Over the past years, several research groups have been studying the coordination chemistry of ruthenium mainly because of the wide range of applications and reactivity of ruthenium complexes [3–8].

Ruthenium complexes containing tertiary phosphine and/or imine ligands constitute a special chapter in the coordination chemistry of ruthenium. Thus, in this work we present some results that are helpful to understand the formation of products as a consequence of chloride substitution reactions in hexacoordinated ruthenium complexes that contain phosphine ligands. The key point is the dissociation of one chloride ligand in *cis*-[$RuCl_2$-(P–P)(N–N)] type complexes, where P–P and N–N are, respectively, diphenylphosphine and bidentate nitrogen donor ligands, but the final structure of the products of the reactions are better defined by the competitive effect between the entering ligand and the other coordinated atoms present in the precursors.

2. Experimental

2.1. Chemicals

All manipulations were carried out under purified argon using standard Schlenk technique. Reagent grade solvents were appropriately distilled and dried before use. All chemicals used in this work were purchased from Aldrich. The *cis*-[$RuCl_2$(dppb)(bipy)], *cis*-[$RuCl_2$(dppf)(bipy)], and *cis*-[$RuCl_2$(dppb)(phen)] starting complexes, where dppb = 1,4-bis(diphenylphosphine)butane, dppf = 1,1′-bis(diphenylphosphine)ferrocene, bipy = 2,2′-bipyridine, and

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doi:10.1016/j.poly.2009.07.029

phen = 1,10-phenantroline, were prepared according to literature methods [9].

2.2. Apparatus

$^{31}P\{^{1}H\}$ NMR experiments were recorded on a BRUKER equipment 9.4 T (400 MHz for hydrogen frequency) in CH_2Cl_2, using a capillary containing D_2O. The microanalyses were performed in the Microanalytical Laboratory, Department of Chemistry at Universidade Federal de São Carlos, São Carlos (SP), using a FISIONS CHNS, mod. EA 1108 micro analyser.

2.3. X-ray crystallography

Crystals of the isolated complexes were grown by slow evaporation of dichloromethane/diethyl ether solution. These 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 [10]. Integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [11]. Gaussian absorption corrections were carried out [12]. The structures were solved by direct methods with SHELXS-97 [13]. All hydrogen atoms were stereochemically positioned and refined with the riding model. The ORTEPs shown in Fig. 1 were prepared using ORTEP-3 for windows [14]. Hydrogen atoms of 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 collections and some experimental details are summarized in Table 1.

2.4. Synthesis

cis-[RuCl(L)(P–P)(N–N)](PF_6) type complexes, where N–N = 2,2′-bipyridine (bipy) or 1,10-phenantroline (phen), P–P = 1,4-bis-(diphenylphosphino)butane (dppb) or 1,1′-bis(diphenylphosphino)-ferrocene (dppf), and L = 4-methylpyridine (4-Mepy), benzonitrile (bzCN), and 4-phenylpyridine (4-Phpy), were prepared by reacting the *cis*-[$RuCl_2$(P–P)(N–N)] complex (0.128 mmol) dissolved in CH_2Cl_2 with three times of excess of the L ligands and 0.256 mmol of NH_4PF_6 in methanol (ca. 5 mL) under argon atmosphere for 3 h.

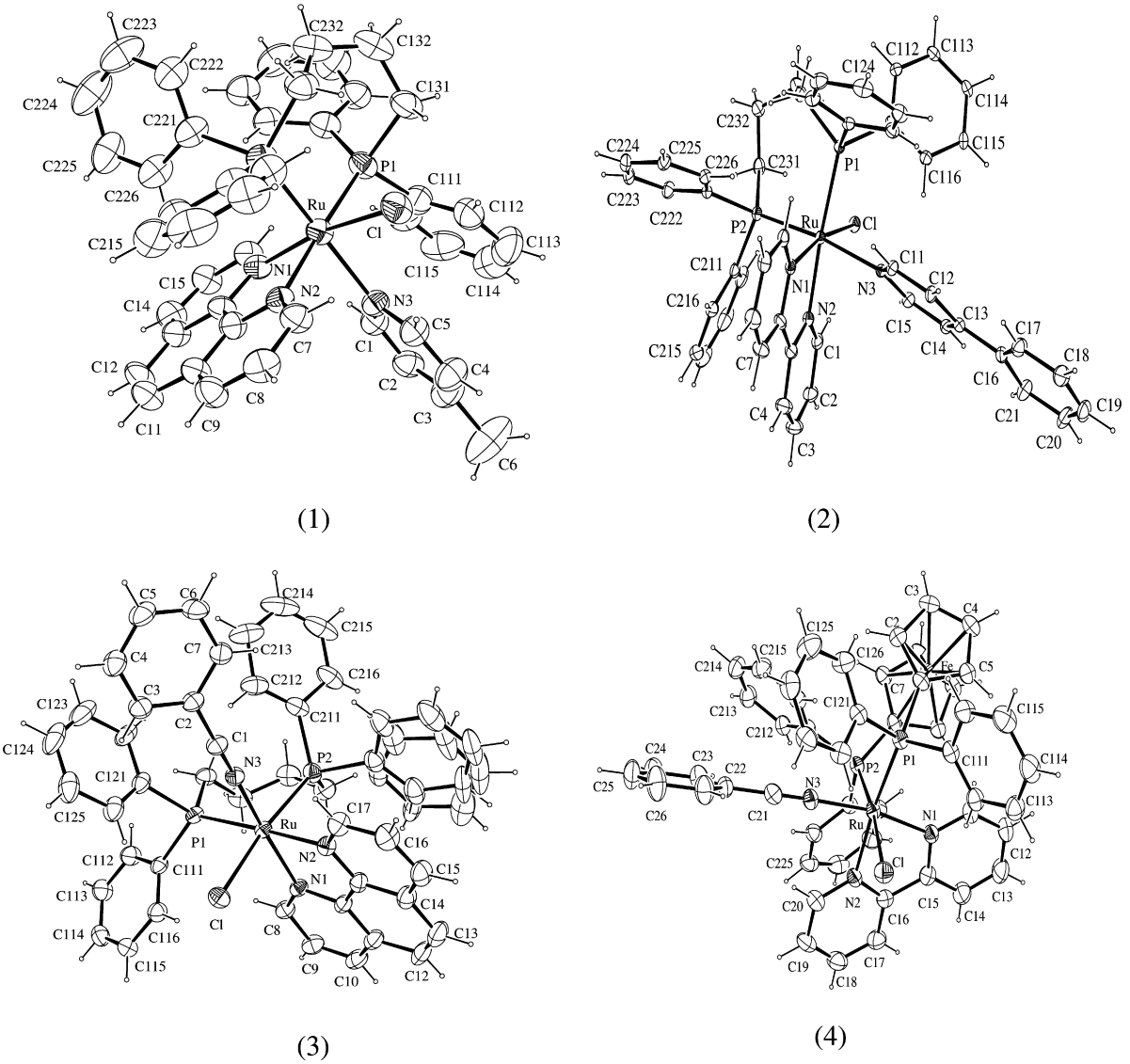

Fig. 1. *ORTEP* [15] view of the [RuCl(4-Mepy)(dppb)(phen)](PF_6)·0.5H_2O **(1)**, [RuCl(4-Phpy)(dppb)(bipy)](PF_6)·CH_2Cl_2 **(2),** [RuCl(bzCN)(dppb)(phen)](PF_6)·0.5H_2O **(3)** and [RuCl(bzCN)(dppf)(bipy)]Cl·H_2O·3/2(C_7H_5N) **(4)** complexes, showing the atoms labeling and the 30% probability ellipsoids.

Table 1
Crystallographic data for the [RuCl(4-Mepy)(dppb)(phen)](PF_6)·0.5H_2O **(1)**, [RuCl(4-Phpy)(dppb)(bipy)](PF_6)·CH_2Cl_2 (**2**), [RuCl(bzCN)(dppb)(phen)](PF_6)·0.5H_2O **(3)** and [RuCl(bzCN)(dppf)(bipy)]Cl·H_2O·3/2(C_7H_5N) **(4)** complexes.

	$C_{46}H_{43}N_3P_3ClF_6Ru·1/2(H_2O)$	$C_{49}H_{45}N_3P_3ClF_6Ru\cdots CH_2Cl_2$	$C_{47}H_{41}N_3P_3ClF_6Ru·1/2(H_2O)$	$C_{51}H_{41}N_3P_2ClFeRu·H_2O·3/2(C_7H_5N)$
Formula weight	990.27	1104.24	1000.27	1158.32
T (K)	293(2)	120(2)	293(2)	293(2)
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	$P2_1/n$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.6530(8)	11.7052(3)	10.9870(2)	10.5579(3)
b (Å)	30.366(3)	37.922(1)	12.6320(3)	13.9123(5)
c (Å)	16.513(1)	10.6068(3)	17.2550(3)	19.2628(6)
α (°)	90	90.000	74.673(1)	79.203(2)
β (°)	94.032(3)	90.000	73.093(1)	89.644(2)
γ (°)	90.000	90.000	81.746(1)	73.281(2)
V (Å^3)	5328.6(7)	4708.2(2)	2204.00(8)	2658.41(15)
Z	4	4	2	2
ρ_{calcd} (Mg m^{-3})	1.234	1.558	1.507	1.147
Absorption coefficient (mm^{-1})	0.487	0.669	0.590	0.765
F(0 0 0)	2020	2248	1018	1186
Crystal size (mm^3)	0.34 × 0.09 × 0.08	0.23 × 0.18 × 0.16	0.34 × 0.14 × 0.09	0.22 × 0.06 × 0.02
Method/θ range for data collection (°)	2.47–25.00	3.48–27.50	3.00–27.51	3.124–27.52
Index ranges	$-12 \leqslant h \leqslant 12$, $-36 \leqslant k \leqslant 36$, $-19 \leqslant l \leqslant 19$	$-12 \leqslant h \leqslant 15$, $-49 \leqslant k \leqslant 49$, $-13 \leqslant l \leqslant 13$	$-14 \leqslant h \leqslant 14$, $-16 \leqslant k \leqslant 16$, $-22 \leqslant l \leqslant 22$	$-12 \leqslant h \leqslant 13$, $-18 \leqslant k \leqslant 17$, $-25 \leqslant l \leqslant 25$
Reflections collected	25 701	25 549	19 449	58 072
Reflections unique/R_{int}	9078 [R_{int} = 0.1258]	10 320 [R_{int} = 0.0420]	10 026 [R_{int} = 0.0373]	12 113 [R_{int} = 0.0947]
Completeness to θ	25.00° (96.6%)	27.50° (98.7%)	27.51° (98.8%)	27.52° (99.0%)
Data/restraints/parameters	9078/0/545	10 320/1/595	10 026/0/644	12 113/0/667
Absorption correction	gaussian	semi-empirical from equivalents	gaussian	multi-scan
Maximum/minimum transmission	0.981 and 0.887	0.869 and 0.746	0.950 and 0.841	0.998 and 0.824
Final R indices [$I > 2\sigma(I)$][a,b]	R_1 = 0.0897, wR_2 = 0.2412	R_1 = 0.0348, wR_2 = 0.0911	R_1 = 0.0372, wR_2 = 0.0903	R_1 = 0.0526, wR_2 = 0.1107
R indices (all data)	R_1 = 0.1180, wR_2 = 0.2577	R_1 = 0.0443, wR_2 = 0.1124	R_1 = 0.0569, wR_2 = 0.1062	R_1 = 0.1166, wR_2 = 0.1331
Goodness-of-fit (GOF) on F^2, S	1.027	1.151	1.059	1.024
Largest difference in peak and hole (e Å^{-3})	0.885 and −0.724	0.766 and −0.985	0.459 and −0.917	0.736 and −0.655

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w(|F_o|^2-|F_c|^2)^2/\sum w|F_o^2|^2]^{1/2}$.

The solution was then filtered, concentrated to ca. 2 mL and hexane was added to precipitate the products. The solids were filtered off, rinsed with water (3 × 5 mL) and diethyl ether (3 × 5 mL) and dried under vacuum. The complex **(4)** was also synthesized in the same way, but without adding the NH_4PF_6.

*2.4.1. [RuCl(4-Mepy)(dppb)(phen)](PF_6) **(1)**Anal. Calc. for [$C_{46}H_{43}ClF_6N_3P_3Ru$]: C, 55.30; H, 4.42; N, 4.28. Found: C, 55.45; H, 4.30; N, 4.32%. Yield: 90%. $^{31}P\{^1H\}$ NMR: δ 37.9 and δ 37.3 (J_{P-P} = 38.8 Hz).*

*2.4.2. [RuCl(4-Phpy)(dppb)(bipy)](PF_6) **(2)***

Anal. Calc. for [$C_{49}H_{45}ClF_6N_3P_3Ru$]: C, 57.74; H, 4.45; N, 4.12. Found: C, 57.42; H, 4.46; N, 4.28%. Yield: 87%. $^{31}P\{^1H\}$ NMR: δ 38.0. The presence of just one singlet instead of doublets in this type of complex is assigned to solvent and temperature effects as already discussed in our previous works [15,16].

*2.4.3. [RuCl(bzCN)(dppb)(phen)](PF_6) **(3)***

Anal. Calc. for [$C_{47}H_{41}ClF_6N_3P_3Ru$]: C, 56.95; H, 4.17; N, 4.24. Found: C, 56.45; H, 3.97; N, 4.27%. Yield: 91%. $^{31}P\{^1H\}$ NMR: δ 40.9 and δ 32.4 (J_{P-P} = 30.8 Hz).

*2.4.4. [RuCl(bzCN)(dppf)(bipy)]Cl **(4)***

Anal. Calc. for [$C_{51}H_{41}Cl_2N_3P_2FeRu$] **(4)**. C, 63.83; H, 4.27; N, 5.45. Found: C, 53.75; H, 4.33; N, 5.20%. $^{31}P\{^1H\}$ NMR: δ 43.7 and δ 35.6 (J_{P-P} = 27.5 Hz).

*2.4.5. [RuCl(bzCN)(dppf)(bipy)](PF_6) **(5)***

Anal. Calc. for [$C_{51}H_{41}ClF_6N_3P_3FeRu$]: C, 55.93; H, 3.77; N, 3.84. Found: C, 56.12; H, 3.97; N, 4.20%. Yield: 93%. $^{31}P\{^1H\}$ NMR: δ 43.5 and δ 35.3 (J_{P-P} = 27.5 Hz).

3. Results and discussion

The X-ray structures of the complexes **(1–4)** are shown in Fig. 1.

In all cases, the isolated complexes were formed by the displacement of one chloride atom from the respective precursor *cis*-[$RuCl_2$(dppb)(bipy)], *cis*-[$RuCl_2$(dppb)(phen)] or *cis*-[$RuCl_2$-(dppf)(bipy)]. As depicted in Fig. 1, the 4-Mepy and 4-Phpy ligands are coordinated *trans* to phosphorus atoms in complexes **(1)** and **(2)**, respectively, while in complexes **(3)** and **(4)** the benzonitrile ligand occupy the position *trans* to nitrogen atoms of the N–N ligands. Recently the [RuCl(dppb)(bipy)(4-Mepy)]PF_6 complex was synthesized by us showing the same structure of **(1)** and **(2)** [17].

Some selected bond lengths of complexes **(1–4)** are in Table 2.

The bond lengths in Table 2 are in the range found for similar ruthenium phosphine complexes, but the distances Ru–N of the bzCN ligand in complexes **(3)** and **(4)** [Ru–N(3)] are shorter than the other Ru–N bond lengths (involving the nitrogen atoms of the 2,2′-bipyridine or of the 1,10-phenantroline) since the cyano-group is a stronger π acceptor than the nitrogen atoms in the rings of the aromatic amino ligands [9,18–23]. The distances Ru–N(2), which are *trans* to phosphorus atoms in the four complexes, are longer than the distances of Ru–N(1), as a consequence of the strong *trans* influence of the phosphorus atoms of the diphosphine

Table 2
Selected bond lengths (Å) for complexes **(1–4)**, with estimated standard deviations in parentheses.

Complex	Ru–N(1)	Ru–N(2)[a]	Ru–N(3)[b]	Ru–P(1)	Ru–P(2)	Ru–Cl
(**1**) $0.5H_2O$	2.074(5)	2.130(5)	2.190(5)	2.3428(18)	2.3259(19)	2.4352(16)
(**2**) CH_2Cl_2	2.099(3)	2.122(3)	2.170(3)	2.3582(9)	2.3317(9)	2.4168(9)
(**3**) $0.5H_2O$	2.0919(19)	2.111(2)	2.011(2)	2.3434(7)	2.3166(7)	2.4555(7)
(**4**) $H_2O{\cdot}3/2$ (C_7H_5N)	2.089(3)	2.106(3)	2.002(3)	2.3749(10)	2.3163(10)	2.4687(10)

[a] Nitrogen *trans* P(1).
[b] Nitrogen from the entering ligand (L).

ligands. The Ru–P(1) bond lengths of complexes (**1–4)** are longer than the distances Ru–P(2). This observation suggests that the *trans* influence of the bidentate N–N ligands is stronger than the same effect of the monodentates ligands (4-Mepy, 4-Phpy and chloride).

In order to elucidate the mechanism of formation of the $[RuCl(bzCN)(dppb)(phen)]PF_6$ complex with the bzCN ligand coordinated *trans* to the nitrogen atom of the 1,10-phenantroline, the reaction of the benzonitrile ligand with the precursor *cis*-$[RuCl_2(dppb)(phen)]$ was followed by the NMR technique [$^{31}P(^1H)$]. Thus, as can be seen in Fig. 2 initially three complexes are present in the solution: the precursor (δ 42.8 and 31.3); the final product $[RuCl(bzCN)(dppb)(phen)]PF_6$ with the bzCN *trans* to a nitrogen (δ 40.9 and 32.4) and an intermediate complex (δ 40.4 and 37.6). Since in the end of the reaction only the complex $[RuCl(bzCN)(dppb)(phen)]PF_6$ (δ 40.9 and 32.4) with the entering ligand positioned *trans* to the nitrogen atom of the 2,2′-bipyridine molecule is present in solution, according to its X-ray structure (Fig. 1), the intermediate very probably consists of a complex with the same composition as the final product but with the bzCN ligand coordinated *trans* to a phosphorus atom of the diphosphine. The fact that the two doublets for this intermediate are very close from each other reinforce our suggestion that in this case both phosphorus atoms are *trans* to nitrogen atoms (one of the 1,10-phenantroline and the other one of the bzCN ligand).

An interesting point that must be addressed to explain the position of the bzCN ligand in the $[RuCl(bzCN)(dppb)(phen)](PF_6)$ **(3)** and in the [RuCl(bzCN)(dppf)(bipy)]Cl **(4)** complexes is the fact that the phosphorus atom is a strong π acceptor as well as is the cyano-group of the benzonitrile ligand. Thus, when two good π acceptor ligands are mutually *trans*, they compete for electron density residing in the same metal d orbital and the amount of M → C back-bonding is reduced by trying to labilize each other. Consequently, by the competition for the metal center electrons between the diphosphine phosphorus atom and the cyano-group of the bzCN, the bond Ru–NCbz results thermodynamically less stable. Therefore, this ligand is easily dissociated and then located in the position *trans* to one of the nitrogen atoms of the N–N ligands where the competitive effect is less accentuated, since the pyridine rings from the 1,10-phenantroline or from the 2,2′-bipyridine ligand are not strong π electron acceptors. The differential pulse voltammetry experiment supports this suggestion. As shown in Fig. 3, the intermediate complex with the bzCN ligand positioned *trans* to the phosphorus atom (δ 40.4 and 37.6 in the $^{31}P\{^1H\}$ spectra)

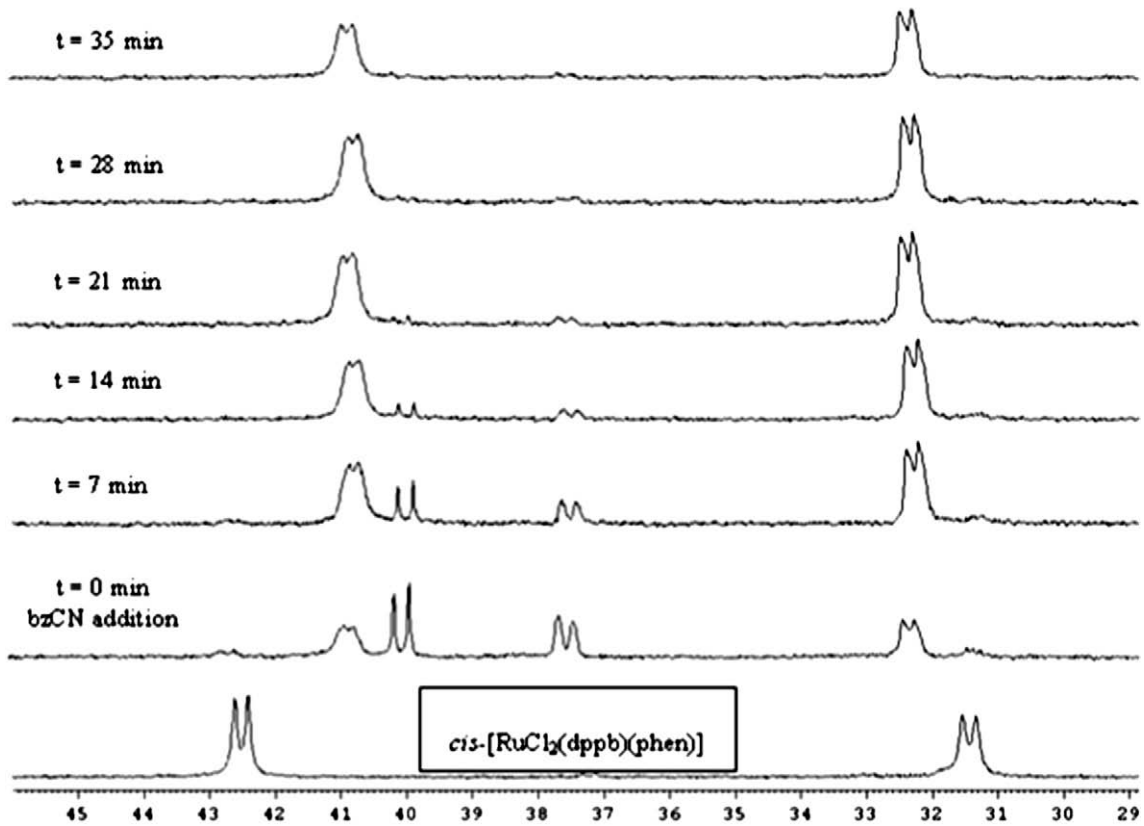

Fig. 2. The $^{31}P\{^1H\}$ NMR spectra, in CH_2Cl_2, following the reaction of the precursor *cis*-$[RuCl_2(dppb)(phen)]$ (bottom) with the bzCN ligand (20 times excess).

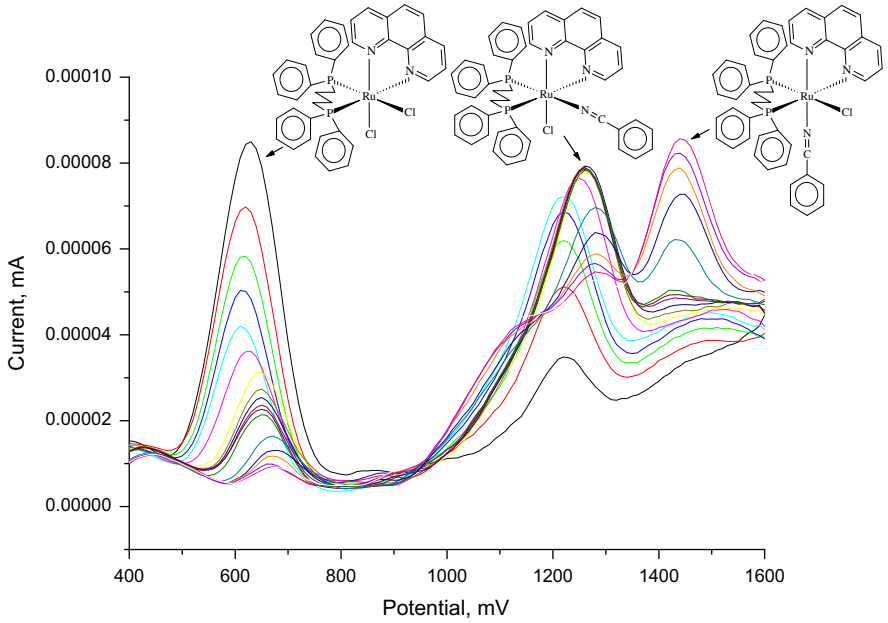

Fig. 3. The differential pulse voltammograms, in CH_2Cl_2, following the reaction of the precursor *cis*-[$RuCl_2$(dppb)(phen)] with the bzCN ligand (20 times excess) (Pt vs. AgCl, 0.1 M PTBA; [Ru] = 1.0×10^{-3} mol L^{-1}; [bzCN] = 20×10^{-3} mol L^{-1}; T = 293 K). Interval of each measurement 7 min.

shows a lower oxidation potential than the other isomer, the final product of the reaction (δ 40.9 and 32.4), with the bzCN ligand sited *trans* to the nitrogen atom. This behavior, provoked by competitive effect, has previously observed by us and by others [24–26].

The same phenomenon observed for the benzonitrile ligand in its reaction with the *cis*-[$RuCl_2$(dppb)(bipy)], *cis*-[$RuCl_2$(dppf)(bipy)] complexes was also observed when acetonitrile (δ 42 e 34 ppm, when acetonitrile is coordinated *trans* to P atom, and δ 43 e 34.5 ppm, when acetonitrile is coordinated *trans* to N atom), a small molecule, was used as entering ligand, suggesting that in these reactions the steric effect does not play a decisive role for the stereochemistry of the final products. Here we would like to point out that in this work "*trans* effect" is used to define the competition for the electron density of the metal that occurs between one strong and one weak π acceptor ligand, while "competitive effect" is used in the case when this competition occurs between two good π acceptor ligands mutually *trans*. These two phenomena are indeed the driving forces in the octahedral complexes studied in this work, leading to thermodynamically stable products, depending of the characteristics of the entering ligand.

The kinetic study of the dissociation of a coordinated chloride, using differential pulse voltammetry for the benzonitrile complex, yielded a rate saturation which is typical of a dissociative mechanism. The limiting first order specific rate of dissociation of the chloride was found to be about $1.0 \pm 0.1 \times 10^{-2}$ s^{-1} and the isomerization rate for the [RuCl(bzCN)(dppb)(phen)]PF_6 (bzCN *trans* to phosphorus to the species *trans* to the nitrogen) was found to be $5.0 \pm 0.1 \times 10^{-4}$ mol L^{-1} s^{-1}. These values are consistent with the data observed in the $^{31}P\{^1H\}$ spectra, in Fig. 2, where the dissociation of the chloride is much faster than the isomerization process. This observed isomerization rate is in the same order as those found for the isomerization of the *trans*-[$RuCl_2$(dppb)(X-bipy)] to the correspondents *cis*-[$RuCl_2$(dppb)(X-bipy)] complexes (X-bipy = 2,2′-bipyridine derivatives) [27].

4. Conclusions

In complexes with general formula *cis*-[$RuCl_2$(P–P)(N–N)] (P–P – diphosphine and N–N = 2,2′-bipyridine or 1,10-phenantroline) the chloride *trans* to the phosphorus atoms is more labile than that one *trans* to the nitrogen atoms, but the final position of an entering good π acceptor ligand is better defined by the competitive effect, which plays a crucial role in the process. The dissociation of the chloride from the *cis*-[$RuCl_2$(dppb)(phen)], *trans* to a phosphorus atoms, follows a dissociative mechanism and its constant rate is $1.0 \pm 0.1 \times 10^{-2}$ s^{-1} while the isomerization rate for the [RuCl(bzCN)(dppb)(phen)]PF_6 (bzCN *trans* to phosphorus to the species *trans* to the nitrogen) is $5.0 \pm 0.1 \times 10^{-4}$ mol L^{-1} s^{-1}.

5. Supplementary data

CCDC 707431, 707432, 707433 and 707434 contain the supplementary crystallographic data for (**1**), (**2**), (**3**) and (**4**), 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

Financial support from CAPES, CNPq, FAPESP.

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