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A study of the reactivity of *trans*-[$RuCl_2(dppm)_2$] toward isocyanides

Javier Ruiz, Marta E.G. Mosquera, Victor Riera *

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo, Spain

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Abstract

The treatment of *trans*-[$RuCl_2(dppm)_2$] with isocyanides in different reaction conditions affords *trans*-[RuCl(CNR)$(dppm)_2$]Cl (**3a**: R = ^{t}Bu, **3b**: R = Ph), *trans*-[RuCl(CNR)$(dppm)_2$]PF_6 (**4a** and **4b**), *trans*-[RuCl$(CNR)_2$(dppm)(dppm-*P*)]PF_6 (**6a** and **6b**), and *trans*-[$Ru(CNR)_2(dppm)_2$]$(PF_6)_2$ (**7a** and **7b**). During the course of these reactions several intermediates resulting from ring-opening and -closing processes of the dppm ligands were spectroscopically characterized. Finally, **6a** was selectively oxidized with H_2O_2 to give *trans*-[RuCl$(CNR)_2$(dppm)(dppmO-*P*)]PF_6 (**8**), which was transformed to *trans*-[$Ru(CNR)_2$(dppm)(dppmO)]$(PF_6)_2$ (**9**) by treatment with $TlPF_6$.

Keywords: Ruthenium; Diphosphine; Isocyanides

1. Introduction

The coordination chemistry of ruthenium(II) with tertiary phosphine ligands has received considerable attention in the literature [1], and continuous efforts in the isolation and structural characterization of new phosphine and diphosphine ruthenium(II) complexes are justified by their potential application to the field of homogeneous catalysis [2].

A number of diphosphine (L–L) halide complexes of ruthenium(II) are known, including those of the type [$RuX_2(L–L)_2$] (X = halide) [3,4]. Mixed-ligand isocyanide phosphine complexes of general formula [$RuX_2(CNR)_2(PR'_3)_2$] (various isomers; R, R' = alkyl or aryl) have also been reported in the literature [5]. However, to our knowledge, the only mononuclear mixed-ligand isocyanide diphosphine ruthenium(II) complexes so far described are: [$RuCl_2(CNPh)_2$(dppm-*P*)$_2$], [RuCl$(CNR)_3$(dppm)]Cl (R = Ph, ^{t}Bu) and [RuCl$(CNPh)_2$(dppm)(dppm-*P*)]PF_6, recently published by our group [6]. As an extension of this chemistry, the present work reports the synthesis of new mixed-ligand isocyanide dppm ruthenium(II) complexes, notably those containing two chelating diphosphine ligands.

2. Results and discussion

The course of the substitution reactions of *trans*-[$RuCl_2(dppm)_2$] with isocyanides strongly depends on the following factors: (i) the type of isocyanide (alkyl or aryl isocyanide); (ii) the amount of isocyanide added; (iii) the nature of the solvent; (iv) the presence of a halogen abstractor. Our synthesis approach, which summarizes all these points, is shown in Scheme 1. For all the complexes described throughout this paper the analytical and IR data are given in Table 1, and the NMR data in Table 2.

2.1. Reaction of *trans*-[$RuCl_2(dppm)_2$] with one equivalent of isocyanide. Synthesis of *trans*-[RuCl(CNR)$(dppm)_2$]PF_6

The treatment of dichloromethane solutions of *trans*-[$RuCl_2(dppm)_2$] with equivalent amounts of isocyanide afforded, after 2 days of stirring at room temperature, the cationic species *trans*-[RuCl(CNR)$(dppm)_2$]Cl (**3a**: R = ^{t}Bu; **3b**: R = Ph) which were isolated as pale yellow solids in good yield. The interchange of the anion by using $NaPF_6$ gave, finally, *trans*-[RuCl(CNR)$(dppm)_2$]PF_6 (**4a**, **4b**). A closely related carbonyl derivative, *trans*-[RuCl(CO)$(dppm)_2$]BF_4, has already been described in the literature, and its crystalline struc-

* Corresponding author.

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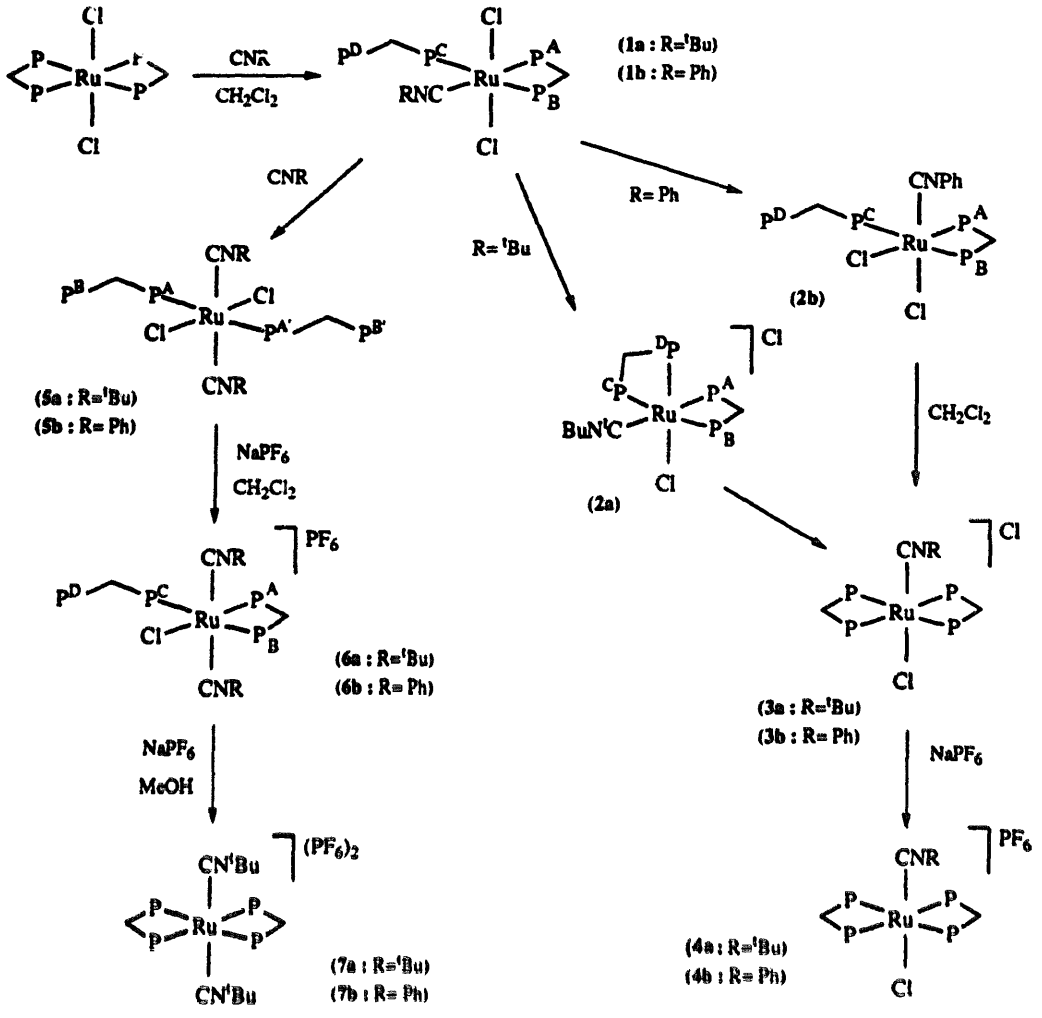


Scheme 1.

ture recently elucidated by X-ray analysis [7]. Apart from the microanalytical data, complexes of type **4** are clearly characterized by the presence of one νCN band of the isocyanide ligand in the IR spectrum, and by the appearance of only one peak in the $^{31}P\{^1H\}$ NMR spectrum, showing the equivalence of the four phosphorus atoms.

During the course of this reaction, several intermediates were detected spectroscopically, but always mixed with either the starting material or the final product **3**, thus precluding isolation of these intermediates as pure samples. The first intermediate (**1a** or **1b** in Scheme 1) arises from a ring-opening of a chelated dppm with coordination of an isocyanide molecule. The proposed arrangement of the two dppm ligands in **1a** and **1b** is supported by the pattern of their $^{31}P\{^1H\}$ NMR spectra and by the high value of $^2J_{P-P(trans)} = 328$ (**1a**) and 324 Hz (**1b**). The trans arrangement of the two chlorine atoms, and hence the disposition of the isocyanide ligand trans to a phosphorus atom, is mainly supported by the $^{13}C\{^1H\}$ NMR spectrum, which shows a resonance for the CNR carbon atom consisting of a slightly broad doublet, with a high value of $^2J_{P-C(trans)} = 107$ Hz, which is in agreement with the literature data for this type of coupling constant [6].

After more reaction time, a second intermediate was detected whose structure depended on the type of isocyanide. Thus, for CN^{t}Bu, a complex appearing to be the ionic intermediate *cis*-[RuCl(CNR)(dppm)$_2$]Cl (**2a**) was present, in a low percentage, when the reaction mixture was left at room temperature for approximately 24 h. The structure of this complex is proposed on the basis of its $^{31}P\{^1H\}$ NMR spectrum, which is typical for a cis arrangement of two chelated dppm ligands, with coupling constants being observed between all types of phosphorus atoms. **2a** is not stable in solution and evolves to its trans isomer **3a**.

On the contrary, in the case of phenyl isocyanide, a second intermediate **2b** is also observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. Very probably **2b** corresponds to a stereoisomer of **1b** having the two chlorine atoms located in cis position. In fact, its phos-

Table 1
IR and analytical data for compounds 1–9

Compound	$\nu_{C\equiv N}$ [a] (cm^{-1})	Analysis (%) [b]		
		C	H	N
1a	2128			
1b	2099			
3a	2133	64.66 (64.52)	5.41 (5.22)	1.39 (1.37)
3b	2111	65.21 (65.58)	4.97 (4.78)	1.38 (1.34)
4a	2133	58.22 (58.28)	4.86 (4.71)	1.26 (1.24)
4b	2111	59.29 (59.36)	4.34 (4.28)	1.28 (1.21)
5a	2125			
6a	2153	58.98 (59.24)	5.15 (5.14)	2.22 (2.30)
6b	2133	61.72 (61.2)	4.21 (4.33)	2.52 (2.23)
7a	2155	53.86 (54.35)	4.69 (4.17)	2.06 (2.11)
7b	2141	55.92 (56.27)	4.02 (3.98)	1.75 (2.05)
8	2153	58.34 (58.47)	4.72 (5.07)	2.21 (2.27)
9	2159	54.1 (53.70)	4.90 (4.66)	2.19 (2.09)

[a] Measured in CH_2Cl_2. [b] Calculated values given in parentheses.

phorus spectrum has the same pattern as **1b**, indicating that both compounds have the same arrangement for the four phosphorus atoms. **2b** is also unstable in solution, being readily converted to the cationic derivative **3b** on standing at room temperature.

It must be noted that the possibility of assigning a cationic bis(isocyanide) structure for **1a**, **1b** and **2b** can be ruled out in view of the isolation of **6a** and **6b**, as described below, and also in view of the absence of any bis(isocyanide) compound in the final product.

The mechanisms described above for the formation of complexes of type **3**, imply ring-opening and -closing processes of a chelating dppm. However, another mechanism implying the dissociation of a chloride group from *trans*-$[RuCl_2(dppm)_2]$ to give the cationic pentacoordinated intermediate $[RuCl(dppm)_2]^+$ [8], which could easily add an isocyanide molecule to complete the formation of complexes of type **3**, cannot be excluded, although we have not detected any pentacoordinated species during the course of these reactions.

2.2. Reaction of *trans*-$[RuCl_2(dppm)_2]$ with an excess of isocyanide. Synthesis of *trans*-$[RuCl(CNR)_2(dppm)(dppm\text{-}P)]PF_6$ and *trans*-$[Ru(CNR)_2(dppm)_2](PF_6)_2$

The treatment of *trans*-$[RuCl_2(dppm)_2]$ with an excess of isocyanide (approximately 12 equivalents) gave a quite different result than the 1:1 stoichiometric reaction described above. The formation of the intermediates **1a** and **1b** corresponding to the ring-opening of a dppm ligand is also observed as the first step, but, after more reaction time, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture reveals the progressive formation of another species in which the ring-opening of the second dppm ligand has taken place, with coordination of another isocyanide molecule (complexes **5a** and **5b** in Scheme 1). Depending on the reaction time, these new species are mixed with different amounts of *trans*-$[RuCl_2(dppm)_2]$ and complexes of types **1**, **2** and **3**. This makes their spectroscopic characterization difficult, and, of course, precludes their isolation as pure samples. With these limitations, we assign for complexes **5a** and **5b** the formula *trans,trans,trans*-$[RuCl_2(CNR)_2(dppm\text{-}P)_2]$, mainly on the basis of the following data: (i) the IR spectrum of dichloromethane solutions of the reaction mixture with a high percentage of **5a**, which shows a new νCN band at 2125 cm^{-1}, thus supporting the trans arrangement of the two isocyanide ligands; (ii) the $^{31}P\{^1H\}$ NMR spectrum of **5a** consisting of two virtual triplets due to a deceptively simple AA'XX' spin system (one of them appearing at a similar frequency as free dppm). The same pattern has been found in other complexes containing two mutually trans monohapto dppm ligands [9]. The phosphorus spectrum of **5b** appears as two apparent doublets of doublets, a pattern similar to those found in other complexes of this type [10].

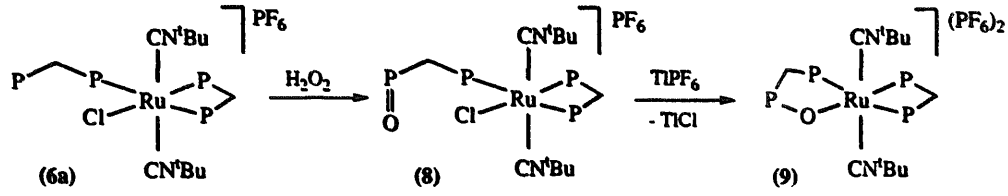
In contrast, the addition of a halogen abstractor to the above reaction mixture gave rise to the formation of new cationic ruthenium(II) complexes with chelating dppm. Thus, the treatment with $NaPF_6$ affords, after 12 h of stirring in dichloromethane at room temperature, complexes **6a** and **6b**, together with small amounts of the monoisocyanide complexes of type **4**. Complexes of type **6** were isolated as pure samples by recrystallization from dichloromethane–diethyl ether solutions, and the analytical and spectroscopic data are in accordance with their formulation as *trans*-$[RuCl(CNR)_2(dppm)(dppm\text{-}P)]PF_6$. The phosphorus spectra have the same patterns as those of complexes of types **1** and **2b**, typical for a mer arrangement of a chelating and a monodentate diphosphine ligand. In the ^1H NMR spectra the methylene protons of the chelating dppm appear as triplet at δ 4.5 (**6a**) and δ 4.9 (**6b**), whereas those corresponding to the monodentate dppm give doublets of doublets at δ 3.2 (**5a**) and δ 3.6 (**5b**).

In order to achieve the substitution reaction of the remaining chloride ligand by the free phosphorus atom of the monohapto dppm, complexes of type **6** were treated with a large excess of $NaPF_6$ in dichloromethane. However, no changes were observed in the reaction mixtures after several days of stirring at room temperature. With the aim of making the dissociation process of the chloride ion from ruthenium easier, a more polar

Table 2
NMR data for compounds 1–9 [a,b]

Compound	$^{31}P\{^1H\}$ NMR										^1H NMR, δ (ppm), J (Hz) [c]
	δ (ppm) [d]				Coupling constants (Hz)						
	P_A	P_B	P_C	P_D	$^2J_{AB}$	$^2J_{AC}$	$^2J_{CD}$	$^2J_{BC}$	$^4J_{BD}$	$^4J_{AD}$	
1a [d]	−24.0 (dd)	−0.30 (ddd)	27.1 (ddd)	−27.0 (dd)	33	29	41	328	7		
1b	−27.5 (t)	−0.59 (ddd)	26.3 (ddd)	−26.5 (dd)	29	29	49	324	6		
2a	−22.5 (ddd)	−13.5 (ddd)	27.3 (ddd)	−3.17 (ddd)	36	30	45	294	22	23	
2b	−0.12 (dd)	−16.7 (ddd)	23.6 (dt)	−28.0 (dd)	42	24	24	358	12		
3a,4a	−9.9 (s)										0.35 (s, CH_3, ^{t}Bu) 5.0 (m, CH_2)
4a,4b	−11.3 (s)										5.1 (m, CH_2)
5a	27.9 (at)	−28.0 (at)			$^2J_{(P_AP_B)} + {}^4J_{(P_APB')} = 48$						
5b	26.0 (add)	−26.1 (add)			$^2J_{(P_AP_B)} + {}^4J_{(P_APB')} = 64$						
6a	2.70 (dd)	−23.4 (ddd)	21.7 (ddd)	−28.6 (dd)	44	19	35	278	7		4.5 (t, $^2J_{PH}$ = 10, CH_2, dppm) [e] 3.2 (dd, $^2J_{PH}$ = 5.5, $^2J_{PH}$ = 2, CH_2, dppm-*P*) 0.24 (s, CH_3, ^{t}Bu)
6b	1.46 (dd)	−22.7 (dd)	22.0 (ddd)	−27.5 (d)	45	19	49	271			4.9 (t, $^2J_{PH}$ = 11, CH_2, dppm) 3.6 (dd, $^2J_{PH}$ = 7, $^2J_{PH}$ = 2, CH_2, dppm-*P*) 5.1 (aq, lines separation = 4.5 Hz, CH_2) 0.43(s, CH_3, ^{t}Bu)
7a [f]	−11.5 (s)										
7b	−12.4 (s)										5.3 (aq, lines separation = 4.6 Hz, CH_2)
8	1.31 (dd)	−20.6 (ddd)	20.2 (ddd)	23.0 (dd)	43	19	29	280	11		4.7 (t, $^2J_{PH}$ = 10, CH_2, dppm) 4.0 (dd, $^2J_{PH}$ = 9.4, $^2J_{PH}$ = 7, CH_2, dppmO) 0.68 (s, CH_3, ^{t}Bu)
9	11.3(dd)	−15.4 (ddd)	43.0 (ddd)	68.9 (dd)	53	19	27	263	14		5.1 (t, $^2J_{PH}$ = 11, CH_2, dppm) 3.8 (t, $^2J_{PH}$ = 9.6, CH_2, dppmO) 0.42 (s, CH_3, ^{t}Bu)

[a] In CD_2Cl_2 solutions. [b] Abbreviations: s = singlet, d = doublet, dd = doublet of doubles, ddd = doublet of doublet of doublets, t = triplet, m = multiplet, add = apparent doublet of doublets, at = apparent triplet, aq = apparent quintet. [c] Resonances for phenyl hydrogens are not given. [d] In the $^{13}C\{^1H\}$ a broad doublet at δ = 153.5 ppm ($^2J_{transP-C}$ = 107 Hz) for the *C*NR carbon is observed. [e] In $CDCl_3$ solution. [f] In the $^{13}C\{^1H\}$ the P_2CH_2 carbon appears as an apparent quintet at δ = 49 ppm (lines separation = 14 Hz).



Scheme 2.

reaction solvent was used. Indeed, the treatment of **6a** and **6b** with $NaPF_6$ in methanol afforded the desired product *trans*-$[Ru(CNR)_2(dppm)_2](PF_6)_2$ (**7a** and **7b**).

The appearance of only one νCN band in the IR spectra and a singlet in the phosphorus spectra support the proposed structure for complexes of type **7**. Interestingly, the ^1H NMR spectra gave an apparent quintet at about δ 5 for the methylene protons of the dppm, due to a deceptively simple A_4X_4 spin system, with all nuclei being magnetically inequivalent. Also of note is the $^{13}C\{^1H\}$ NMR spectra for the methylene carbon atoms, consisting of an apparent quintet at about δ 45, due to a deceptively simple AX_4 spin system (there is only one ^{13}C atom per molecule, due to the very low natural abundance of ^{13}C) with all nuclei being magnetically inequivalent.

It must be noted that it is not possible to transform **4a** and **4b** into **7a** and **7b**, even in the presence of an excess of isocyanide and $NaPF_6$, in methanol as solvent. Other, more powerful, halogen abstractors, such as silver salts, lead to the ring-opening of a chelating dppm giving a complex mixture of species, so far uncharacterized.

2.3. Synthesis of ruthenium(II) complexes with mixed ligands dppm and dppmO (dppmO = $P(Ph)_2CH_2P(O)(Ph)_2$)

The isolation of complexes of type **6** opens the possibility of obtaining mixed ligand dppm/dppmO ruthenium(II) derivatives, by taking advantage of the selective oxidation of the free phosphorus atom of the monohapto dppm ligand in these complexes, when treated with the appropriate oxidation agent. Thus, the reaction of **6a** with an excess of hydrogen peroxide in acetone as solvent affords *trans*-$[RuCl(CN^tBu)_2(dppm)(dppmO\text{-}P)]PF_6$ (**8**) in quantitative yield (see Scheme 2). The oxidation of the uncoordinated phosphorus atoms (P_D) is clearly shown by a considerable change toward high frequencies (51.6 ppm) in its ^{31}P resonance. The corresponding ^1H NMR spectrum shows the methylene protons of the chelating dppm as a triplet at δ 4.7, whereas those of the dppmO ligand appear as a doublet of doublets at δ 4.04.

Finally, the treatment of **8** with $TlPF_6$ as a halogen abstractor, allowed us to obtain the dicationic complex *trans*-$[Ru(CN^tBu)_2(dppm)(dppmO)](PF_6)_2$ (**9**) (see Scheme 2), with all spectroscopic and analytical data being in accordance with this formulation. When comparing the $^{31}P\{^1H\}$ NMR data of **8** and **9**, the most drastic changes are observed for the P_D and P_C phosphorus resonances of the dppmO ligand, which are shifted toward high frequencies 46 ppm and 23 ppm respectively, in complex **9**. This is due to two main effects: the electronic changes produced by the coordination of the oxygen atom, and the positive ring contribution effect that is usually undergone by the phosphorus atoms belonging to five-member rings, as reviewed by Garrou [11]. Interestingly, complex **9** can be considered as being derived from **7a**, in which an oxygen atom has been inserted into a phosphorus ruthenium bond. This produces important electronic changes in the complex, as revealed by a comparison of the spectroscopic data of **7a** and **9** (Tables 1 and 2), which anticipates some differences in their chemical behaviour; this matter will be studied in the future.

3. Experimental details

All reactions were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Solvents were dried and purified by standard techniques and distilled under nitrogen prior to use. The FT IR spectra were recorded on a Perkin–Elmer 1720-X spectrometer. Proton, ^{13}C and ^{31}P NMR spectra were measured with Bruker AC-300 and AC-200 instruments. Chemical shifts are given in ppm, relative to internal $SiMe_4$ (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P). The C, H and N analyses were performed on a Perkin–Elmer 240B elemental analyser.

The complex *trans*-$[RuCl_2(dppm)_2]$ [3], phenyl isocyanide [12] and dppm [13] were prepared as described elsewhere. All other reagents were obtained from commercial sources and used without further purification.

3.1. Preparation of trans-[RuCl(CN'Bu)(dppm)$_2$]Cl (3a) and trans-[RuCl(CN'Bu)(dppm)$_2$]PF$_6$ (4a)

A solution containing *trans*-$[RuCl_2(dppm)_2]$ (0.5 g, 0.53 mmol) and 50 ml of CH_2Cl_2 was treated with CN^tBu (0.07 ml, 0.061 mmol) and allowed to stir for 5 days. The addition of 50 ml of hexane caused the

formation of a pale yellow microcrystalline precipitate, which was collected by filtration, washed with hexane and dried in vacuo. Yield, 0.4 g; 78%.

The interchange of the anion by addition of a twofold excess of $NaPF_6$ to a solution of **3a** in CH_2Cl_2–EtOH (1:1), gave **4a** in an essentially quantitative yield.

3.2. Preparation of trans-[RuCl(CNPh)(dppm)$_2$]Cl (3b) and trans[RuCl(CNPh)(dppm)$_2$]PF$_6$ (4b)

These complexes were prepared similarly to **3a** and **4a**, starting from *trans*-[$RuCl_2$(dppm)$_2$] (0.25 g, 0.26 mmol), CNPh (0.03 g, 0.28 mmol) and 30 ml of CH_2Cl_2. Yield for **3b**, 0.23 g; 85%.

3.3. Preparation of trans-[RuCl(CN^{t}Bu)$_2$(dppm)(dppm-P)]PF$_6$ (6a)

To a solution containing *trans*-[$RuCl_2$(dppm)$_2$] (0.5 g, 0.53 mmol) in 100 ml of CH_2Cl_2 were added CN^{t}Bu (0.75 ml, 6.6 mmol) and $NaPF_6$ (0.2 g, 1.19 mmol). The reaction mixture was stirred for 18 h and then filtered through Celite. The solution was layered with 100 ml of diethyl ether and stored at room temperature for 24 h. The pale orange crystals which precipitated were filtered, washed with Et_2O and dried in vacuo. Yield, 0.47 g; 73%.

3.4. Preparation of trans-[RuCl(CNPh)$_2$(dppm)(dppm-P)]PF$_6$ (6b)

To a solution containing *trans*-[$RuCl_2$(dppm)$_2$] (0.04 g, 0.042 mmol) in 10 ml of CH_2Cl_2 were added CNPh (0.027 g, 0.26 mmol) and $NaPF_6$ (0.027 g, 0.16 mmol). The reaction mixture was stirred for 11 h and then filtered through Celite. The solution was then layered with 10 ml of hexane. Once the diffusion was finished, some colourless crystals of **4b** appeared which were separated by filtration. The remaining solution was once again layered with 20 ml of hexane. A pale orange precipitate corresponding to **6b** was obtained. This was washed with hexane and dried in vacuo. Yield, 0.018 g; 35%.

3.5. Preparation of trans-[Ru(CN^{t}Bu)$_2$(dppm)$_2$](PF$_6$)$_2$ (7a)

A suspension of **6a** (0.25 g, 0.20 mmol) and $NaPF_6$ (0.050 g, 0.30 mmol) in 40 ml of methanol was stirred for 7 days. The reaction mixture was then evaporated to dryness and the remaining residue extracted with 50 ml of CH_2Cl_2 and filtered through Celite. The solution was evaporated to dryness, and the white solid residue stirred with hexane, filtered and dried in vacuo. Yield, 0.24 g; 94%.

3.6. Preparation of trans-[Ru(CNPh)$_2$(dppm)$_2$](PF$_6$)$_2$ (7b)

This complex was prepared similarly to **7a** from **6b** (0.10 g, 0.08 mmol) and $NaPF_6$ (0.02 g, 0.12 mmol). Yield, 0.10 g; 91%.

3.7. Preparation of trans-[RuCl(CN^{t}Bu)$_2$(dppm)(dppmO-P)]PF$_6$ (8)

To a solution of **6a** (0.08 g, 0.07 mmol) in 10 ml of acetone, an excess of hydrogen peroxide was added (0.03 ml of a 30% aqueous solution, 0.26 mmol). The reaction mixture was heated with stirring at 45 °C for 5 h. The solution was then filtered through Celite and 20 ml of hexane added to obtain a white solid material, which was filtered and dried in vacuo. Yield, 0.08 g; 93%.

3.8. Preparation of trans-[Ru(CN^{t}Bu)$_2$(dppm)(dppmO)](PF$_6$)$_2$ (9)

An excess of $TlPF_6$ (0.050 g, 0.14 mmol) was added to a solution of **8** (0.07 g, 0.06 mmol) in 10 ml of CH_2Cl_2. The reaction mixture was stirred for 24 h. The solution was then filtered through Celite, and the addition of 20 ml of hexane produced a white precipitate which was filtered and dried in vacuo. Yield, 0.072 g; 89%.

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