Synthesis and structural characterization of a new series of ruthenium(II) complexes containing the short bite Ph_2PPy ligand. Cooperative effect between the anionic rhodium and cationic ruthenium species in the catalytic hydroformylation of styrene by $[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$

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Abstract

The reaction of $[(C_8H_{12})RuCl_2]_n$ with 3 molar equiv. of 2-(diphenylphosphino)pyridine, Ph_2PPy, in refluxing methanol, gave $[Ru(Ph_2PPy)_3Cl]Cl$ (**1**) and small amount of a red unidentified product. A *fac* structure in which one of the Ph_2PPy is η^1-coordinated and the remaining two are chelated to the ruthenium atom has been assigned to **1** on the basis of $^{31}P\{^1H\}$ NMR spectra. Solutions of **1** in chlorinated solvents afford the neutral complex $[Ru(Ph_2PPy)_2Cl_2]$ (**2**). IR and NMR spectra and X-ray analysis indicate that **2** assumes a *cis* structure in both solution and solid state. Compound **2** crystallizes with two $CDCl_3$ molecules H-bonded to the chlorine atoms of the coordination shell of each ruthenium. Crystal data: triclinic, space group $P\bar{1}$, $a=10.608(3)$, $b=14.340(4)$, $c=15.570(5)$ Å, $\alpha=102.06(2)$, $\beta=105.48(2)$, $\gamma=108.16(2)°$, $Z=2$. The structure model was refined up to $R=0.066$ for 3147 reflections with $F \geqslant 8\sigma(F)$. At 20 °C and 1 atm, compound **1** adds CO in equilibrium condition affording the dicationic compound $[Ru(CO)(Ph_2PPy)_3]Cl_2$; this cannot be isolated when operating in CO atmosphere. Treatment of **1** with 2 equiv. of CF_3COOAg in dichloromethane gave the corresponding $[Ru(Ph_2PPy)_3(CF_3COO)]CF_3COO$ (**4**) containing a small amount of $[Ru(Ph_2PPy)_2(CF_3COO)_2]$ (**5**). By reacting **1** with $[Rh(CO)_2Cl]_2$ or $[Ir(CO)_2(p\text{-toluidine})Cl]$ the complexes $[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$ (**6**) and $[Ru(Ph_2PPy)_3Cl][Ir(CO)_2Cl_2]$ (**7**) were obtained. Compounds **6** and **7** were used as catalysts in the hydroformylation of styrene. The hydroformylation reactions were performed in the temperature range 45–100 °C under 20–60 atm of a $CO+H_2$ 1:1 mixture and the reaction was generally stopped after 6 h. An almost quantitative conversion of styrene could be obtained under 50–60 atm and 75 °C in 6 h. The chemioselectivity of the reaction is satisfactory; the branched isomer aldehyde predominates in all experiments and its amount increases upon reducing the reaction temperature; at 40 atm the regioselectivity, expressed by the B/L ratio, improves from about 2.3 to 18 operating at 100 and at 45 °C. The most significant result emerges by comparison of the catalytic activity of complexes **1**, $[Rh(CO)_2Cl_2]AsPh_4$ and **6** which shows that the ionic heterobimetallic Ru–Rh complex **6** is much more active than the mononuclear complexes $[Ru(Ph_2PPy)_3Cl]Cl$ and $[Rh(CO)_2Cl_2]AsPh_4$. This was explained by a cooperative effect between the anionic rhodium and cationic ruthenium species in complex **6**. Compound **7**, as a precatalyst, showed only negligible activity.

Key words: Crystal structures; Catalysis; Ruthenium complexes; Rhodium complexes; Dinuclear complexes

Introduction

Heterobimetallic complexes have been intensively studied due in part to the promise of enhanced stoichiometric or catalytic reactivity as a result of the cooperation between the two different metal centers [1].

In a binuclear system, two metal centers in close proximity could react in a cooperative manner giving

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activation modes of organic substrate molecules different with respect to those observed with mononuclear systems. However, proofs of such a cooperative effect and of the specific role of every metal center are always difficult to attribute [2].

Furthermore there is an intrinsic difficulty in some bimetallic systems to attribute the observed activity to the bimetallic complex itself or to a mononuclear species generated under catalytic reaction conditions [2].

These considerations led us to investigate the catalytic activity, in hydroformylation reactions, of bimetallic Ru–Rh and Ru–Ir catalytic systems containing the 2-(diphenylphosphino)pyridine, Ph_2PPy, hetero-bifunctional ligand. The favorable effect of Ph_2PPy in the hydroformylation reaction of styrene has been evidenced by us using the catalytic system $[RhH(CO)(PPh_3)_3]+Ph_2PPy$, in different ratios [3].

The ionic bimetallic systems reported here, $[Ru(Ph_2PPy)_3Cl][M(CO)_2Cl_2]$ (M = Rh, Ir), have been obtained by reacting the cationic mononuclear ruthenium(II) complex $[Ru(Ph_2PPy)_3Cl]Cl$, containing one Ph_2PPy as an η^1-coordinated ligand, with $[Rh(CO)_2Cl]_2$ or $[Ir(CO)_2(p\text{-toluidine})Cl]$. Part of the work was devoted to the synthesis, characterization and multinuclear NMR structural studies of Ru^{II}–Ph_2PPy complexes; the X-ray crystal structure of the $[Ru(Ph_2PPy)_2Cl_2]$ complex is also reported. The compound $[Ru(Ph_2PPy)_3Cl]Cl$ reported here is the first example of compounds containing three short bite ligands coordinated to the metal center.

Experimental

Established methods were used to prepare the compounds *cis*-$[(C_8H_{12})RuCl_2]_n$ [4], $[Rh(CO)_2Cl]_2$ [5], $[Ir(CO)_2(p\text{-toluidine})Cl]$ [6] and Ph_2PPy [7]. All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. IR spectra were obtained as nujol mulls on KBr or CsI plates using a Perkin-Elmer FTIR 1720 spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker AMX R300 or on a Varian model Gemini-300 spectrometer.

^1H NMR spectra were referenced to internal tetramethylsilane and ^{31}P spectra to external 85% H_3PO_4; positive chemical shifts for all nuclei are to higher frequency. Conductivity measurements were made with a Radiometer CDM 3 conductivity meter. Elemental analyses were performed by REDOX s.n.c., Cologno Monzese, Milano.

Preparation of [Ru(Ph₂PPy)₃Cl]Cl (1)

To a suspension of $[(C_8H_{12})RuCl_2]_n$ (0.335 g, 1.19 mmol) in methanol (100 cm^3) was added Ph_2PPy (0.943 g, 3.59 mmol) and the mixture was stirred and refluxed for about 6 h in methanol to give an orange solution. This was concentrated and chromatographed on a neutral activated alumina column saturated with dichloromethane. A red band was eluated with CH_2Cl_2; then using methanol an orange band was separated. The orange solution was concentrated *in vacuo*; by adding diethyl ether the product was separated as a yellow–orange solid and recrystallized from dichloromethane/hexane (1:2). Yield 90% (1.038 g, 1.08 mmol). *Anal.* Calc. for $C_{51}H_{42}Cl_2N_3P_3Ru$: C, 63.68; H, 4.40; N, 4.37; Cl, 7.28. Found: C, 63.70; H, 4.41; N, 4.35; Cl, 7.29%. IR (Nujol): ν(Ru–Cl) 280 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ 47.31 ppm (dd, $^2J(P,P)$ 33.6 Hz, $^2J(P,P)$ 27.7 Hz), δ −6.53 ppm (dd, $^2J(P,P)$ 27.7 Hz, $^2J(P,P)$ 27.7 Hz) δ −7.72 ppm (t, $^2J(P,P)$ 27.7 Hz, $^2J(P,P)$ 27.7 Hz).

Preparation of cis-[Ru(Ph₂PPy)₂Cl₂] (2)

Standing a solution of **1** in chlorinated solvents for about 24 h affords the complex *cis*-$[Ru(Ph_2PPy)_2Cl_2]$ (**2**) as yellow crystals. Yield 35%. *Anal.* Calc. for $C_{34}H_{28}Cl_2N_2P_2Ru$: C, 58.46; H, 4.04; N, 4.01; Cl, 10.15. Found: C, 58.50; H, 4.06; N, 4.02; Cl, 10.18%. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ 26.4 ppm (d, $^2J(P,P)$ 32 Hz), δ −4.49 ppm (d, $^2J(P,P)$ 32 Hz).

Reaction of 1 with CO

When carbon monoxide was bubbled into a dichloromethane solution of **1**, the color turned from pale yellow to yellow; monitoring the reaction course by IR spectra the appearance of two bands for the terminal carbonyl at 2021 and 1995 cm^{-1} was observed. The CO addition is reversible and attempts to isolate the reaction product, also operating in CO atmosphere, failed. For the NMR spectra see 'Results and discussion'.

Reaction of 1 with CF₃COOAg

CF_3COOAg (0.055 g, 0.249 mmol) was added to a stirred dichloromethane solution (20 cm^3) of $[Ru(Ph_2PPy)_3Cl]Cl$ (0.120 g, 0.124 mmol). After 30 min the precipitated AgCl was separated and the solution was concentrated; diethyl ether was added to give a yellow orange solid. This was washed with petroleum ether (30 cm^3) and dried *in vacuo*. NMR spectra indicated that the product obtained is $[Ru(Ph_2PPy)_3(CF_3COO)]CF_3COO$ (**4**) with very small amounts of $[Ru(Ph_2PPy)_2(CF_3COO)_2]$ (**5**). The attempts to obtain **4** free of **5** failed. For IR and NMR see 'Results and discussion'.

Preparation of [Ru(Ph₂PPy)₃Cl][Rh(CO)₂Cl₂] (6)

To a dichloromethane solution of $[Rh(CO)_2Cl]_2$ (0.030 g, 0.078 mmol), a solution of $[Ru(Ph_2PPy)_3Cl]Cl$ (0.150 g, 0.156 mmol) was added dropwise. The resulting solution was stirred for about 2 h after which the presence of only two bands at 2070 and 1993 cm^{-1} in the IR spectrum indicated the quantitative formation of $[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$ (**6**). The solution was concentrated and petroleum ether was added to give an orange solid. This was washed with diethyl ether and dried. Yield 98% (0.180 g, 0.140 mmol). *Anal.* Calc. for $C_{53}H_{42}Cl_3N_3O_2P_3RuRh$: C, 55.06; H, 3.66; N, 3.63; Cl, 9.20. Found: C, 55.09; H, 3.64; N, 3.65; Cl, 9.22%. Ir (Nujol): ν(CO) 2063 and 1984, ν(Rh–Cl) 318 and 303, ν(Ru–Cl) 288 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) was very similar to compound **1**.

Preparation of [Ru(Ph₂PPy)₃Cl][Ir(CO)₂Cl₂] (7)

A dichloromethane solution of $[Ru(Ph_2PPy)_3Cl]Cl$ (0.127 g, 0.133 mmol) was added dropwise to a stirred solution of $[Ir(CO)_2(p\text{-toluidine})Cl]$ (0.050 g, 0.133 mmol) in the same solvent. After about 2 h, the resulting solution showed the presence of only two bands at 2055 and 1972 cm^{-1} in the IR spectrum indicating the quantitative formation of $[Ru(Ph_2PPy)_3Cl][Ir(CO)_2Cl_2]$ (**7**). The solution was concentrated and petroleum ether was added to give an orange solid. This was washed with diethyl ether and dried. Yield 99% (0.164 g, 0.132 mmol). *Anal.* Calc. for $C_{53}H_{42}Cl_3N_3O_2P_3RuIr$: C, 51.11; H, 3.40; N, 3.37; Cl, 8.54. Found: C, 51.10; H, 3.41; N, 3.35; Cl, 8.53%. IR (Nujol): ν(CO) 2048 and 1963, ν(Ir–Cl) 328 and 298, ν(Ru–Cl) 280 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) was identical to compound **1**.

Catalytic runs

All catalytic runs were performed in a 100 ml Berghoff stainless-steel autoclave equipped with gas and liquid inlets, a heating device, and magnetic stirrer. The reactions were carried out in a Teflon vessel fitted to the internal wall of the autoclave, thus preventing undesirable effects due to the metal of the reactor. The autoclave was closed and degassed through three vacuum-nitrogen cycles. A solution of the starting complex and fresh distilled styrene (in a typical experiment 0.0331 g of $[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$ and 0.35 ml of styrene), in benzene (10 ml), was introduced under nitrogen, and gases (H_2/CO 1:1) were admitted up to the desired pressure. At the end of each catalytic run, the autoclave was cooled in a cold water bath and slowly vented. A sample of the homogeneous reaction mixture was then analyzed by gas chromatography.

X-ray structure analysis and structure refinement of [Ru(Ph₂PPy)₂Cl₂]·2CDCl₃

The compound crystals were grown by freezing the $CDCl_3$ solution used for the NMR studies.

Crystal data. $C_{34}H_{28}Cl_2N_2P_2Ru\cdot 2CDCl_3$, $M=939.2$, triclinic, space group $P\bar{1}$ (No. 2), $a=10.608(3)$, $b=14.340(4)$, $c=15.570(5)$ Å, $\alpha=102.06(2)$, $\beta=105.48(2)$, $\gamma=108.16(2)°$, $U=2056(1)$ Å^3, $Z=2$, $D_c=1.51$ g cm^{-3}, $F(000)=940$, μ(Mo Kα) $=10.04$ cm^{-1}, λ(Mo Kα) $=0.71073$ Å.

A suitable crystal was mounted on a glass fiber and was completely covered by a thin film of glue to prevent the possible loss of chloroform molecules retained into the crystal packing. Then diffraction data were collected at room temperature with a Siemens R3m/v automatic four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Cell parameters were obtained from 21 accurately centered reflections with 2θ in the range 15–30°. (See also 'Supplementary material'.) A total of 8949 reflections, of which 7298 were unique ($R_{int}=6.8\%$), was collected by the variable-speed ω–2θ scan method up to 2θ value 50°, index ranges $-1\leqslant h\leqslant 13$, $-18\leqslant k\leqslant 18$, $-19\leqslant l\leqslant 19$. The intensities of three standard reflections, monitored after every 97 measurements, decreased to about 10% of the corresponding starting values.

The diffraction data were processed with the learnt-profile procedure [8] and then corrected for decay and Lorentz–polarization effects. Absorption correction was applied by fitting a pseudo-ellipsoid to the azimuthal scan data of 16 suitable reflections with high χ angles [9] (R_{int} decreased to 4.5%).

The structure was solved by standard Patterson methods and subsequently completed by a combination of least-squares technique and Fourier syntheses. The analysis of the variance in the refinement cycles clearly showed the bad quality of the diffraction data, mainly the weaker reflections and the intensities at low diffraction angles, probably due to the X-ray diffusion generated by the glue covering the surface of the crystal example. Therefore, similarly to the treatment of the solvent diffusion effects in the macromolecule studies, the refinement of the structure model was continued by the high-angle refinement technique using 3147 reflections (the observations/parameters ratio is 7.1), considering only the intensities with $F_o\geqslant 8\sigma(F_o)$ in the resolution range 2.8–0 Å.

The hydrogen atoms were generated in calculated positions by stereochemistry considerations (C–H = 0.93 Å), with a unique fixed isotropic thermal parameter ($U_{iso}=0.060$ Å^2), and during the refinement they were allowed to ride on their respective parent carbons. The structure model, with all non-hydrogen atoms anisotropic, was refined by the full-matrix least-squares technique, minimizing the function $\Sigma w(F_o^2-F_c^2)^2$, converging to $R=\Sigma|F_o-F_c|/\Sigma F_o=0.066$ and $R'=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}=0.172$ with the final weighting scheme $w^{-1}=\{\sigma^2(F_o^2)+[0.1314(\max(0.33333F_o^2)+0.66667F_c^2)]^2\}$. The last difference map showed the largest electron density residuals (max. and min. range $=\pm 1.14$ e Å^{-3}) at about 1 Å from the ruthenium atom. Other important residuals were observed around the chloroform molecules due to a rotational disorder of their Cl atoms, but attempts to interpret them as further staggered dispositions were unsuccessful. Neutral-atom scattering factors and anomalous dispersion corrections were taken into account [10].

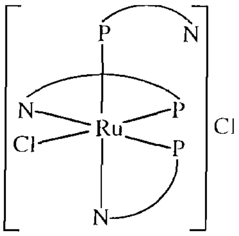
Despite the far from excellent quality of the diffraction data, the resulting structure model is well enough defined for the present discussion purposes, which mainly concern coordination of the ruthenium atom with respect to the chelating action of the diphenylphosphino-pyridine ligand.

Data reduction and structure solutions and drawings were performed with the SHELXTL-PLUS package [11], while structure refinement and final geometrical calculations were carried out with SHELXL-93 [12] and PARST program [13], respectively, on a DEC Micro Vax/3400 computer. See also 'Supplementary material'.

Results and discussion

Synthesis of Ph_2PPy–Ru^{II} complexes

The reaction of $[(C_8H_{12})RuCl_2]_n$ with 3 molar equiv. of Ph_2PPy, in refluxing methanol for about 6 h affords an orange solution from which, after chromatography, the orange compound $[Ru(Ph_2PPy)_3Cl]Cl$ (**1**) and a small amount of a red unidentified compound were separated. Compound **1** was obtained in high yield as an orange solid, soluble and air stable over long periods in methanol. Its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ solution shows three signals centered at δ 47.31 ppm (dd, ^2J(P,P) 33.6 Hz, ^2J(P,P) 27.7 Hz), δ −6.53 ppm (dd, ^2J(P,P) 33.6 Hz, ^2J(P,P) 27.7 Hz) and δ −7.72 ppm (t, ^2J(P,P) 27.7 Hz, ^2J(P,P) 27.7 Hz). The NMR spectrum of **1** is not temperature dependent in the range 238–298 K indicating that the compound is not fluxional in solution. The data are interpreted on the basis of the *fac* structure depicted below in which one of the Ph_2PPy is η^1-coordinated while the remaining two act as chelating ligands.



A large shift in the ^{31}P chemical shift is well known in four- and five-membered rings in which chelating ligands involving phosphorus atoms are coordinated to a metal atom [14]. Therefore the two signals at higher field are assigned to the phosphorus atoms of the chelating ligand according to the large shielding usually found for phosphorus atoms coordinated to a metal atom in a four-membered ring [14]. For example a difference of 55.2 ppm was found in *fac*-$[Mo(CO)_3(dppm)_2]$ (dppm = bis(diphenylphosphino)-methane) between chelated and non-chelated phosphines. [15] Further support for the postulated structure arises from the spectroscopic and X-ray data for the following compound that will be described.

To our knowledge compound **1** is the first example of a mononuclear complex where three short bite ligands, as Ph_2PPy, are coordinated to a metal center.

Standing a solution of **1** in chlorinated solvents affords the complex *cis*-$[Ru(Ph_2PPy)_2Cl_2]$ (**2**), the structure of which was established by IR and NMR spectroscopy and X-ray analysis. Compound **2** is a yellow solid, non-conducting in benzene and chlorinated solvents and air stable for extended periods of time. Figure 1 shows a perspective view of the crystal structure of **2**.

According to the shown *cis* structure, the compound displays in the IR spectrum two ν(RuCl) bands and in the $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$ solution, two doublets centered at δ 2.64 and −4.49 ppm, respectively, with a mutual coupling constant of 32 Hz. The chemical shift for the chelated ligand bonded to the ruthenium atom and the *cis* coupling constant found for this known structure represent useful parameters for determining the metal coordination sphere in the other reported compounds.

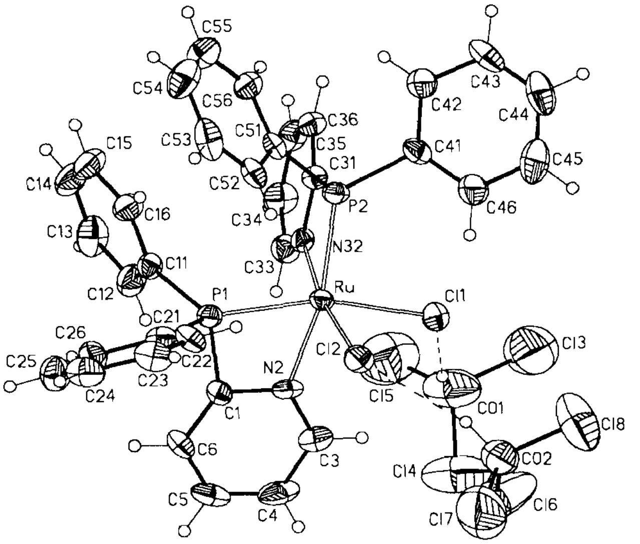
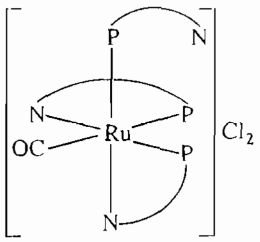


Fig. 1. Perspective view of the molecular unit showing the numbering scheme. Thermal ellipsoids are drawn at 50% of probability while hydrogen size is arbitrary. The interactions between coordinated chlorine atoms and the chloroform hydrogens are represented by dashed bonds.

When carbon monoxide was bubbled through a CH_2Cl_2 solution of **1**, at 1 atm and 20 °C, the IR spectrum shows the appearance of two bands for the terminal carbonyl at 2021 and 1995 cm^{-1}; the CO addition, in these experimental conditions, is reversible and attempts to isolate the reaction product, also operating in CO atmosphere, failed. The $^{31}P\{^1H\}$ NMR spectra of $CDCl_3$ solutions of **1** saturated with CO afford a quite similar spectrum to that found for **1**; the three phosphorus resonances are observed at δ 49.65 ppm (dd, $^2J(P,P)$ 33.6 Hz, $^2J(P,P)$ 27.7 Hz), δ -5.17 ppm (dd, $^2J(P,P)$ 33.6 Hz, $^2J(P,P)$ 27.7 Hz) and δ -5.51 ppm (t, $^2J(P,P)$ 27.7 Hz, $^2J(P,P)$ 27.7 Hz). The chemical shifts and the coupling constants reveal the presence of two chelated and one non-chelated ligand with the phosphorus atoms not involved in *trans* interaction. Furthermore the ^{13}C spectrum shows in the carbonyl region a broad signal centered at δ 199.2 ppm. The NMR data appear to contradict the results of the IR spectra; the occurrence of two $\nu(CO)$ bands indicates the presence in solution either of a dicarbonyl species, which was not evidenced in the NMR spectra, or of two monocarbonyl isomers formed very likely in a fluxional process which involves the uncoordinated pyridine nitrogen atom. It is probable that this process can be evidenced in the IR time scale but not in the NMR one. On the basis of these data a possible structure for the carbonylated product, **3**, is presented.



Treatment of **1** with 2 equiv. of CF_3COOAg in dichloromethane gave the corresponding $[Ru(Ph_2PPy)_3(CF_3COO)]CF_3COO$ (**4**) containing a small amount of $[Ru(Ph_2PPy)_2(CF_3COO)_2]$ (**5**). The attempts to obtain **4** free of **5** failed.

As the $^{31}P\{^1H\}$ NMR spectra of **4** and **5** show the same pattern of **1** and **2**, we assign to the cationic and neutral trifluoroacetate complexes **4** and **5** structures similar to **1** and **2**, respectively. Chelation of the acetato group to the ruthenium(II) center can be ruled out by the IR spectrum in which the coordinated acetato CO stretching frequency is observed at 1680br for **4** and 1672br for **5** [16].

Crystal structure of $[Ru(Ph_2PPy)_2Cl_2]\cdot 2CDCl_3$

The asymmetric unit of the cell, represented in Fig. 1, contains one ruthenium complex $[(Ph_2PPy)_2RuCl_2]$ and two $CDCl_3$ crystallization molecules coming from the solvent of the NMR solution from which the crystal was obtained. Each deuterium atom shows a relevant H interaction with a respective chlorine of the ruthenium coordination, slightly stronger for Cl(1) than for Cl(2) (2.52(1) versus 2.68(1) Å, respectively). Then the two chloroforms are quite strictly connected to the Ru bulk, however a possible rotation around the C–D bond axis continues to be allowed depending on the steric hindrance, as suggested by the van der Waals solid model and confirmed by the librational analysis of each $CDCl_3$ showing a relatively large thermal ellipsoid of the chlorines in comparison with the corresponding one of the carbon atom. The final atomic coordinates for the non-hydrogen atoms and selected bond lengths and angles are reported in Tables 1 and 2.

The complex is an almost perfect sphere with the center represented by the ruthenium atom surrounded by the two chelating diphenylphosphino-pyridine ligands and two chlorine anions each connecting one chloroform. The coordination geometry of the metal is octahedral with very large distortions mainly caused by the small bite of the two chelating ligands which determines the corresponding $\overline{\text{N–Ru–P}}$ angle markedly smaller than the expected 90° value: 68.7(3) and 69.6(3)°, respectively. The same situation is already known for a similar complex $[(Ph_2PPy)RuCl_2(CO)_2]$ [17], where the remaining ligand is enough to produce the deformation, although less important than the present one.

The Ru–Cl(2) bondlength of 2.420(3) Å is comparable with the two ruthenium–chlorine bonds reported for the complex of ref. 17, but is shorter than the corresponding distance with the Cl(1) atom, 2.473(4) Å. A similar value is found in a Pd–Ru complex with the bridging Ph_2PPy ligand [18].

A possible explanation might rise from the combination of the two different *trans* effects acting on the chlorines and of the different hydrogen interactions with the two chloroform molecules.

For each phosphine ligand it is possible to define a mean coordination plane passing through the pyridine ring and the phosphorus atom: they are arranged orthogonally around the metal center (dihedral angle = 93.7(3)°) in such a way to minimize the steric hindrance between the two ligands in the coordination shell. The ruthenium deviates 0.023(2) and 0.121(2) Å from the mean plane of the P(1)···N(2) and P(2)···N(32) ligand, respectively.

This discrepancy might be related to the equivalent difference observed in the ruthenium–nitrogen bond length, 2.13(1) versus 2.063(8) Å for N(2) and N(32) atoms, respectively, while the two Ru–phosphorus distances have about the same value corresponding to the average 2.267(4) Å. Both the Ru–N and Ru–P mean values are shorter than the corresponding distances observed in the complex $[(Ph_2PPy)RuCl_2(CO)_2]$ where

TABLE 1. Atomic coordinates (fractional × 10^4) for non-hydrogen atoms with e.s.d.s in parentheses

Atom	x	y	z
Ru	1679(1)	3139.2(7)	2111.4(7)
P(1)	2410(3)	2882(2)	874(2)
P(2)	2408(3)	4888(2)	2632(2)
Cl(1)	988(3)	2800(2)	3447(2)
Cl(2)	−809(3)	2540(2)	1166(2)
C(1)	2042(12)	1566(9)	912(7)
N(2)	1605(10)	1610(7)	1674(7)
C(3)	1185(15)	756(9)	1913(10)
C(4)	1249(17)	−146(10)	1464(13)
C(5)	1711(17)	−170(10)	717(11)
C(6)	2123(15)	678(10)	446(10)
C(11)	4296(12)	3470(9)	1100(8)
C(12)	5245(14)	3040(11)	1453(10)
C(13)	6695(15)	3602(14)	1714(11)
C(14)	7208(15)	4552(13)	1642(12)
C(15)	6265(16)	4985(11)	1281(11)
C(16)	4843(13)	4451(9)	1021(9)
C(21)	1599(13)	2740(8)	−364(8)
C(22)	397(14)	2931(9)	−685(9)
C(23)	−213(15)	2801(10)	−1626(10)
C(24)	400(18)	2496(11)	−2252(9)
C(25)	1559(17)	2269(12)	−1961(10)
C(26)	2170(14)	2396(10)	−1017(9)
C(31)	4051(12)	4848(8)	3350(8)
N(32)	3744(10)	3806(7)	3054(7)
C(33)	4724(14)	3468(10)	3440(9)
C(34)	6015(14)	4115(11)	4121(10)
C(35)	6327(13)	5145(11)	4412(9)
C(36)	5330(13)	5530(9)	4047(9)
C(41)	1776(13)	5625(9)	3419(8)
C(42)	2448(15)	6684(10)	3824(11)
C(43)	1905(19)	7187(11)	4426(10)
C(44)	752(22)	6672(16)	4572(12)
C(45)	34(18)	5624(17)	4122(14)
C(46)	560(15)	5107(11)	3556(11)
C(51)	2918(13)	5717(9)	1942(8)
C(52)	1947(14)	5469(10)	1040(9)
C(53)	2259(18)	6081(14)	489(10)
C(54)	3482(20)	6937(14)	800(14)
C(55)	4415(19)	7175(12)	1677(14)
C(56)	4151(15)	6568(10)	2239(9)
C(01)	2186(32)	1236(18)	4592(15)
Cl(3)	2133(13)	1797(8)	5718(6)
Cl(4)	1179(10)	−93(6)	4140(7)
Cl(5)	3901(12)	1508(8)	4667(9)
C(02)	−2707(19)	960(13)	2274(13)
Cl(6)	−2123(9)	111(7)	2665(12)
Cl(7)	−4071(9)	303(9)	1192(6)
Cl(8)	−3341(10)	1598(7)	3010(5)

the metal center might be more electron-rich depending on the effect of the two carbonyl groups.

TABLE 2. Selected bond lengths (Å), angles (°) and important contacts (Å)

Ru–Cl(1)	2.473(4)	Ru–Cl(2)	2.420(3)
Ru–P(1)	2.265(4)	Ru–P(2)	2.270(3)
Ru–N(2)	2.13(1)	Ru–N(32)	2.063(8)
P(1)–C(1)	1.82(1)	P(1)–C(11)	1.81(1)
P(1)–C(21)	1.83(1)	P(2)–C(31)	1.83(1)
P(2)–C(41)	1.85(2)	P(2)–C(51)	1.82(1)
C(1)–N(2)	1.38(2)	N(2)–C(3)	1.33(2)
C(31)–N(32)	1.37(1)	N(32)–C(33)	1.33(2)
N(2)···P(1)	2.48(1)	N(32)···P(2)	2.48(2)
Cl(1)···D(1)	2.52(1)	Cl(2)···D(2)	2.68(1)
Cl(1)–Ru–Cl(2)	89.1(1)		
N(2)–Ru–N(32)	96.7(4)	P(1)–Ru–P(2)	102.4(1)
P(1)–Ru–N(32)	91.7(3)	P(2)–Ru–N(2)	163.9(3)
Cl(1)–Ru–N(2)	90.1(3)	Cl(1)–Ru–N(32)	86.2(3)
Cl(2)–Ru–N(2)	90.4(3)	Cl(2)–Ru–N(32)	171.5(3)
P(1)–Ru–Cl(1)	158.4(1)	P(2)–Ru–Cl(1)	97.1(1)
P(1)–Ru–Cl(2)	95.3(1)	P(2)–Ru–Cl(2)	104.0(1)
P(1)–Ru–N(2)	68.7(3)	P(2)–Ru–N(32)	69.6(3)
Ru–N(2)–C(1)	104.5(7)	Ru–N(32)–C(31)	105.5(8)
Ru–P(1)–C(1)	86.1(4)	Ru–P(2)–C(31)	84.2(4)
P(1)–C(1)–N(2)	100.7(8)	P(2)–C(31)–N(32)	100.6(8)
C(1)–N(2)–C(3)	119(1)	C(31)–N(32)–C(33)	118(1)

It is important to note that the diphenylphosphinopyridine is a bidentate ligand which, when using both the coordination sites, could bridge two metal atoms or chelate one center. Despite the expected rigidity of the ligand fragment N–C–P, a statistical analysis using the GSTAT program on the Cambridge Structure Database shows that the N–C–P angle and N···P distance increase on going from the chelating cases (respective mean values 103° and 2.53 Å) to the bridging ones (115° and 2.58 Å, respectively), for which it is also possible to relate the distance with the inter-metal separation.

These results are in agreement with the corresponding values for the ligand found in compound **2** and in analogous ruthenium complexes [17, 18].

Reaction of 1 with [Rh(CO)$_2$Cl]$_2$ and [Ir(CO)$_2$(p-toluidine)Cl]

The mononuclear cationic complex **1** contains an uncoordinated pyridine nitrogen donor atom and strained Ph_2PPy chelating ligands and hence it should act as a metalloligand toward rhodium or iridium species which could give rise to a '$Rh(CO)_2Cl$' or '$Ir(CO)_2Cl$' fragment. This 'bridge assisted' synthetic strategy is very well established [19] and was successfully used by us in the synthesis of binuclear complexes with a Ph_2PPy bridging ligand [20]. Attempts to obtain Ru–Rh and Ru–Ir complexes containing the bridging ligand Ph_2PPy, namely $[Cl(Ph_2PPy)_2Ru(\mu\text{-}Ph_2PPy)M(CO)_2Cl]Cl$ (M = Rh, Ir), by reacting complex **1** with $[Rh(CO)_2Cl]_2$ and $[Ir(CO)_2(p\text{-toluidine})Cl]$, in the appropriate molar ratio, failed. In fact the reactions afforded the products $[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$ (**6**) and $[Ru(Ph_2PPy)_3Cl][Ir(CO)_2Cl_2]$ (**7**), respectively. Thus the reaction is similar to those of $[Rh(CO)_2Cl]_2$, $[Ir(CO)_2(p\text{-toluidine})Cl]$ and $[Ir(CO)_3Cl]_n$ with ClX (X = $AsPh_4$, N^tBu_4) [21].

Compounds **6** and **7** were obtained as yellow solids, soluble in methanol, chlorinated solvents and, to a minor extent, in benzene; they are stable in solid state over long periods. Conductivity measurements performed on methanol solutions gave values lower than those expected for 1:1 electrolytes (5×10^{-4}–10^{-4} M, 48 Ω^{-1} cm^2 mol^{-1}). The values are much lower when the concentration of the solution is increased, indicating the existence in solution of an ion pair. The structural characterization of complexes **6** and **7** in solution relies upon spectroscopic and analytical data; all attempts to obtain **6** and **7** as crystals suitable for a single-crystal X-ray analysis failed. In the IR spectrum (nujol mull) complex **6** shows ν(CO) bands at 2063 and 1984 cm^{-1} and, in the metal–chloro stretching region, bands at 318, 303 and 288 cm^{-1}. Analogously compound **7** shows ν(CO) bands at 2048 and 1963 cm^{-1}, ν(Ir–Cl) at 328 and 298 cm^{-1} and ν(Ru–Cl) at 280 cm^{-1}. The ν(CO) and ν(M–Cl) (M = Rh, Ir) bands fall at frequencies similar to those reported for $[M(CO)_2Cl_2]^-$. The $^{31}P\{^1H\}$ NMR spectra of **6** and **7** are identical to those of **1** indicating the presence of the cation $[Ru(Ph_2PPy)_3Cl]^+$.

Hydroformylation of styrene

The olefin styrene was used in the catalytic test reactions to avoid concurrent isomerization of the alkene. The hydroformylation reactions were performed in the temperature range 45–100 °C under 20–60 atm of a $CO + H_2$ 1:1 mixture and the reaction was generally stopped after 6 h. At the end of the catalytic tests with **6** the starting material was changed, as evidenced by the NMR spectra. The presence of $[Rh(CO)_2Cl_2]^-$ was inferred from the IR spectrum which remained unchanged. The results are reported in Table 3. The most significant result emerges by comparison of the catalytic activity of complexes **1**, $[Rh(CO)_2Cl_2]AsPh_4$ and **6** which shows that the ionic heterobimetallic Ru–Rh complex **6** is much more active than the mononuclear complexes $[Ru(Ph_2PPy)_3Cl]Cl$ and $[Rh(CO)_2Cl_2]AsPh_4$. The mononuclear complex $[Ru(Ph_2PPy)_3Cl]Cl$ does not show catalytic activity while the activity of $[Rh(CO)_2Cl_2]AsPh_4$ is very low (conversion at 50 atm and 75 °C about 12%) with respect to that of **6** (conversion under the same experimental conditions 94.5%). Thus the results showed a cooperative effect between the anionic rhodium and cationic ruthenium species in complex **6**. The activation mechanism of the styrene, CO and H_2 by the precatalyst **6** is quite obscure as it implies that both ruthenium and rhodium metal centers take part in the reaction. The cooperativity between metal centers and the promotional effects of one metal on another are poorly understood phenomena for binuclear complexes as well. It is very likely in a benzene solution of **6**, that the strong interaction between the cationic and anionic species evidenced by conductivity measurements (ion pair) results is further strengthened

TABLE 3.

Catalyst[a]	*P* (atm)	*T* (°C)	Conv. (%)	Selectivity[b] (%)	Regioselectivity[c]	TON[d]	TOF[e]
$[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$	20	45	30.91	95.06	1.94	3177	530
	20	75	41.21	95.22	4.11	8456	1409
	20	100	43.55	97.97	1.77	4448	741
	40	45	17.50	97.15	17.98	1806	301
	40	75	92.58	99.36	6.96	9465	1577
	40	100	97.31	98.88	2.33	9933	1656
	50	45	66.71	99.30	17.42	6823	1137
	50	75	94.50	99.52	7.67	9666	1611
	50	100	96.03	98.77	3.37	9799	1633
	60	45	34.78	98.77	20.55	3545	591
	60	75	98.68	99.62	20.06	10066	1678
	60	100	99.54	99.62	11.49	10167	1695
$[Ru(Ph_2PPy)_3Cl][Ir(CO)_2Cl_2]$	50	75	1.76	99.99		201	33
	60	75	3.40	88.27		368	61
$[Ru(Ph_2PPy)_3Cl]Cl$	60	75	1.18	63.93		134	22
$[Rh(CO)_2Cl_2][As(Ph)_4]$	50	75	12.61	71.42	~9.00	1102	184
$[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$[f]	60	75	98.32	99.42	9.61	20134	3356
	60	100	99.49	99.55	11.65	20402	3400

[a]Ratio styrene:catalyst 100:1. [b]Selectivity = [(branched aldehyde + linear aldehyde)/(branched aldehyde + linear aldehyde + ethylbenzene)]. [c][branched aldehyde/linear aldehyde]. [d]TON = [mol. of product/mol. cat.] × 100. [e]TOF = TON/reaction time (h). [f]Ratio styrene:catalyst 200:1.

by the interaction between the uncoordinated pyridine nitrogen atom of $[Ru(Ph_2PPy)_3Cl]^+$ and the rhodium center. The observed capability of the cationic ruthenium species to take up CO could be the fundamental step of the cooperative effect.

Compound **6**, as a precatalyst, displays a good catalytic activity in the hydroformylation of fresh distilled styrene; operating at a substrate-to-metal ratio of 100:1 or 200:1, an almost quantitative conversion of styrene could be obtained under 60 atm of pressure and 75–100 °C in 6 h. At high temperatures small amounts of ethylbenzene were detected. The chemioselectivity of the reaction results are satisfactory, the linear (L) and branched (B) aldehydes being more than 99% of the reaction product. The branched isomer predominates in all the experimental conditions used and its amount increases upon reducing the reaction temperature; at 40 atm the regioselectivity, expressed by the B/L ratio, improves from about 2 to 18 when operating at 100 and 45 °C. This behavior is usual in the rhodium-catalyzed hydroformylation of styrene [22, 23].

The catalytic activity decreases upon lowering the gas pressure and eventually vanishes at 1 atm, where the catalyst is otherwise still efficient. Compound **7**, as a precatalyst, showed only negligible activity. The observed difference in the catalytic activity of the systems based on **6** and **7** is in agreement with the behaviour of rhodium(I) and iridium(I) catalytic systems in hydrogenation processes [24].

Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, anisotropic temperature factors and remaining bonds and angles.

Further information on crystallographic data collection and refinement of the structure determination are reported in Table S1.

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