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Mononuclear(η^6-arene)ruthenium(II) and (η^5-pentamethylcyclopentadienyl)rhodium(III) and binuclear ruthenium(II)–platinum(II) and ruthenium(II)–rhodium(I) complexes containing 2-(diphenylphosphino)pyridine

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Abstract

The isoelectronic complexes [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] (**1**) and [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (**3**) in which 2-(diphenylphosphino)pyridine (Ph_2PPy) is *P*-monodentate, have been obtained by treating the complexes [{(η^6-C_6H_6)$RuCl_2$}$_2$], and [{(η^5-C_5Me_5)$RhCl_2$}$_2$], respectively, with Ph_2PPy in the molar ratio 1:1. Coordination of the pyridine nitrogen atom to metal in **1** and **3** has been achieved by removing one chloride with $AgPF_6$. By this route the cationic complexes [(η^6-C_6H_6)Ru(Ph_2PPy)Cl]PF_6 (**2**) and [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl]PF_6 (**4**) in which the Ph_2PPy is chelating, have been obtained. The reaction of [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] (**1**) with *cis*-[Pt(DMSO)$_2$$Cl_2$] in CH_2Cl_2 gives the ionic binuclear complex [(η^6-C_6H_6)Ru(Ph_2PPy)(μ-Cl)Pt(DMSO)Cl_2]Cl (**5a**) which was also obtained as the [PF_6]$^-$ salt, **5b**. IR, ^{1}H and ^{31}P{^{1}H} NMR spectra support structures for **5a** and **5b** with the Ph_2PPy chelated to ruthenium(II) and a chloride bridging to platinum(II). The DMSO is *S*-bonded and the geometry at platinum(II) is *cis*. Upon attempted reaction of **1** with *cis*-[Pd(^{t}BuNC)$_2$$Cl_2$] in CH_2Cl_2 at room temperature, the reagents were recovered unchanged after 7 h. The reactions of [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (**3**) with *cis*-[Pd(^{t}BuNC)$_2$$Cl_2$] and *cis*-[Pt(DMSO)$_2$$Cl_2$] afford the known *cis*-[Pd(^{t}BuNC)(Ph_2PPy)Cl_2] and *cis*-[Pt(DMSO)(Ph_2PPy)Cl_2], together with [{(η^5-C_5Me_5)$RhCl_2$}$_2$]. The reaction of [{(C_8H_{12})$RuCl_2$}$_n$] with [(η^5-C_5H_5)Rh(CO)(Ph_2PPy)] in CH_2Cl_2 in the molar ratio 1:1, is very complex. We have separated [(C_8H_{12})RuCl((μ-Cl)(μ-Ph_2PPy)Rh(η^5-C_5H_5)] (**6**) by chromatography column. The bridging Ph_2PPy is *P*-bonded to the rhodium(I). On allowing CH_2Cl_2 solution of **6** to stand, crystals of the rhodium(III) complex [(η^5-C_5H_5)$RhCl_2$(Ph_2PPy)] (**7**) are formed. Probably a very slow intramolecular redox process involving the Ru^{II}–Rh^{I} species **6** is responsible of the formation of **7**. In the complex, the 2-(diphenylphosphino)pyridine is monodentate, coordinating through phosphorus.

Keywords: Ruthenium; Platinum; Rhodium; Binuclear complexes; X-ray structure; Bridging ligand

1. Introduction

The chemistry of metal complexes containing bridging short bite ligands such as bis(diphenylphosphino) methane [1] (dppm) and 2-(diphenylphosphino)-pyridine [2] (Ph_2PPy) has been widely developed in recent years. In particular, dppm and Ph_2PPy A-frame complexes [3] with halides, hydride, CH_2, CO, S, SO_2, or a Group 11 metal as bridging group have received considerable attention.

Recently we have been interested [4] in the synthesis, structural characterization, and reactivity of d^8-d^8 homo- and hetero-binuclear complexes in which the metals are held together by only one short-bite bridging Ph_2PPy.

We have attempted the preparation of these compounds using a bridge-assisted method in which the uncoordinated pyridine nitrogen atom of a mononuclear complex, containing monodentate *P*-bonded Ph_2PPy as ligand, displaces a labile ligand from another metal to give a binuclear species.

However, this synthetic route was some times unsuccessful and only the transfer of the Ph_2PPy from one

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metal to another was achieved. For example [5], treatment of [Pd{$CH_2C(CH_3)CH_2$}(Ph_2PPy)Cl], in which the Ph_2PPy is monodentate *P*-bonded with *cis*-[Pd($^tBuNC)_2Cl_2$] in CH_2Cl_2 affords the mixed isocyanide-tertiary phosphine complex *cis*-[Pd(^{t}BuNC)(Ph_2PPy)Cl_2] and [{Pd{$CH_2C(CH_3)CH_2$}Cl}$_2$]. In this paper we report our attempts to synthesize unsymmetrical hetero-binuclear complexes containing bridging Ph_2PPy, starting from [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] and [(η^5-C_5Me_5)Rh(Ph_2PPy) Cl_2] isoelectronic complexes in which the Ph_2PPy is monodentate *P*-bonded. The reaction of [{(C_8H_{12})$RuCl_2$}$_n$] with [(η^5-C_5H_5)Rh(CO)(Ph_2PPy)] and the crystal and molecular structure of [(η^5-C_5H_5)Rh(Ph_2PPy)Cl_2] are also discussed.

2. Results and discussion

2.1. Preparation of [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] (1) and [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (3) and of the corresponding cationic complexes [(η^6-C_6H_6)Ru(Ph_2PPy)Cl]PF_6 (2) and [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl]PF_6 (4)

Treatment of [{(η^6-C_6H_6)$RuCl_2$}$_2$] with 2 equivalents of Ph_2PPy in benzene suspension led to [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] (**1**) as a red brown solid, soluble in chlorinated solvents and moderately soluble in benzene.

The compound was non-conducting in benzene, as expected for a structure in which the C_6H_6 is η^6-coordinated and the Ph_2PPy is *P*-monodentate. In accord with this, the ^1H NMR spectrum in $CDCl_3$ showed the resonance of C_6H_6 as a doublet at δ 5.57 ppm (J_{PH} = 0.648 Hz) and a distinct resonance at δ 8.82 ppm for the 6-hydrogen of the pyridine ring, as usual when the Ph_2PPy acts as monodentate *P*-bonded. This resonance is further shifted to higher frequency by the coordination of the pyridine nitrogen atom [4c]. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ solution showed a singlet at δ 25.87 ppm indicating *P*-coordination of Ph_2PPy. The η^6-C_6H_6 chemical shift and J_{PH} compare well with the values reported for η^6-C_6H_6-tertiary phosphine complexes of ruthenium(II) [6].

Coordination of the pyridine nitrogen atom to ruthenium(II) in **1** has been achieved by removing one chloride with silver ion. Treating **1** with $AgPF_6$ in the molar ratio 1:1 in CH_2Cl_2 solution resulted in the precipitation of AgCl and formation of the cationic complex [(η^6-C_6H_6)Ru(Ph_2PPy)Cl]PF_6 (**2**).

The chelation was supported by analytical, conductivity and spectroscopic $^{31}P\{^1H\}$ NMR data. A signal at δ −18.30 ppm supports the presence of chelating Ph_2PPy, consistent with the large shielding usually found for phosphorus atoms coordinated in a four-membered ring [7]. For example, a difference of about 54 ppm was found in [Ru(Ph_2PPy)$_3$Cl]Cl between chelated and η^1-*P*-coordinated Ph_2PPy [4f]. In the ^1H NMR spectrum in $CDCl_3$ solution, the C_6H_6 resonance was shifted to δ 5.84 ppm.

By reaction of [(η^5-C_5Me_5)$RhCl_2$]$_2$ with Ph_2PPy (molar ratio 1:2) in dichloromethane at room temperature [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (**3**) containing monodentate *P*-bonded Ph_2PPy, was formed as a red solid. This was non-conducting in methanol solution, and soluble in chlorinated solvents and, to a minor extent, in benzene. The ^1H and $^{31}P\{^1H\}$ NMR spectra support the structure proposed. The phosphorus resonance appeared as doublet at δ 28.85 ppm (J_{RhH} = 143.6 Hz) and the ^1H NMR spectrum showed a methyl resonance at δ 1.41 ppm (J_{PH} = 3.46 Hz) and the 6-hydrogen of the pyridine ring at δ 8.86 ppm, as expected for a structure with an uncoordinated pyridine nitrogen atom of Ph_2PPy. The X-ray molecular and crystal structure of the compound [(η^5-C_5H_5)Rh(Ph_2PPy)Cl_2], identical to **3** and obtained in a slow rearrangement process of the compound [(C_8H_{12})RuCl(μ-Cl)(μ-Ph_2PPy)Rh(η^5-C_5H_5)], **6**, is below reported.

The addition of $AgPF_6$ in the molar ratio 1:1 to a CH_2Cl_2 solution of **3** caused AgCl to precipitate and to an orange solution, giving [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl]PF_6 (**4**) as an orange solid. Conductivity measurements in methanol solution (5×10^{-4}–10^{-4} M) indicated that **4** is a 1:1 electrolyte. ^1H and $^{31}P\{^1H\}$ NMR spectra supported the formulation of **4** as a Ph_2PPy chelating species; The phosphorus resonance at δ −12.0 ppm (J_{RhP} = 116.1 Hz) was shifted to higher field, with the large shielding usually found for phosphorus atoms coordinated to a metal in a four-membered ring [7] and the 6-hydrogen of the pyridine ring resonance is shifted to higher frequency compared to **3** (δ 8.86 ppm for **3** and δ 9.0 ppm for **4**). The resonance of the η^5-C_5Me_5 methyl group appears as a doublet at δ 1.63 ppm (J_{PH} = 4.7 Hz).

2.2. Reactions in which 1 and 3 act as ligands

In the complexes **1** and **3** the pyridine nitrogen atom of the Ph_2PPy is uncoordinated and hence it should act as donor towards coordinatively unsaturated metals. This bridge-assisted synthetic strategy is very well established [8] and was successfully used by us in the synthesis of binuclear complexes with Ph_2PPy bridge [4]. The access to binuclear complexes by this synthetic strategy was sometimes frustrated because transfer of the coordinated Ph_2PPy from one metal to another occurs. This has been achieved in the reaction of [Pd{$CH_2C(CH_3)CH_2$}(Ph_2PPy)Cl] with *cis*-[Pd(^{t}BuNC)$_2Cl_2$] in which *cis* [Pd(^{t}BuNC)$_2$(Ph_2PPy)Cl] and [{Pd{$CH_2C(CH_3)CH_2$}Cl}$_2$] are formed [5]. Besides the mononuclear complexes, [Pd{$CH_2C(CH_3)CH_2$}(Ph_2PPy)Cl] and *cis*-[Pd(DMSO)(Ph_2PPy)Cl_2] (DMSO = dimethylsulfoxide) together with [{Rh(COD)(μ-Cl)}$_2$]

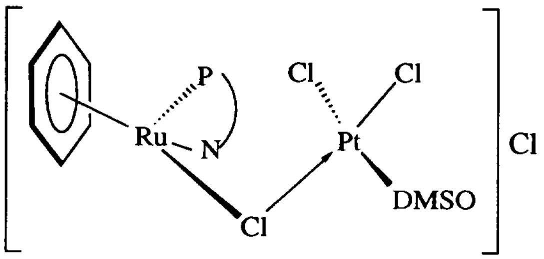
have been obtained from the reactions of [Rh(COD)-(Ph_2PPy)Cl] with [Pd{$CH_2C(CH_3)CH_2$}Cl_2] or *cis*-[Pd$(DMSO)_2Cl_2$], respectively [4b]. In all the mononuclear complexes reported here as reagents or products, the Ph_2PPy acts as monodentate *P*-donor.

The steric requirements of the Ph_2PPy when it bridges have been considered responsible for the course of these reactions and they are extremely important when the metals are square planar.

It is well known that, owing to its rigidity and small bite angle, the bridging coordination of the Ph_2PPy to d^8 square planar metals requires small ligands such as CO, halides, and $CNCH_3$ *cis* to the P atom [1b,9].

In this paper, the possibility of synthesizing unsymmetrical Ph_2PPy-bridged heterobinuclear complexes starting from the pseudo-tetrahedral species [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] and [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] with monodentate *P*-donor Ph_2PPy was considered. We tested the reactions of these species with the d^8 square-planar complexes having labile ligands, *cis*-[Pt$(DMSO)_2Cl_2$] and *cis*-[Pd(^{t}BuNC)$_2Cl_2$] to compare analogous reactions.

The reaction of [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] (**1**) with *cis*-[Pt$(DMSO)_2Cl_2$] in dichloromethane at room temperature afforded a green compound, conducting in acetone and methanol solution (10^{-4} M) as a 1 : 1 electrolyte. Analytical and spectroscopic data support its formulation as the ionic binuclear complex [(η^6-C_6H_6)Ru(Ph_2PPy)(μ-Cl)Pt(DMSO)Cl_2]Cl (**5a**).



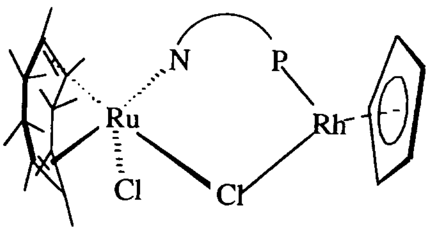
Treating **5a** with $AgPF_6$ in the molar ratio 1 : 1 gave the corresponding $[PF_6]^-$ salt, **5b**. The $^{31}P\{^1H\}$ NMR spectrum of **5a** in $CDCl_3$ solution, showed a singlet at δ −18.03 ppm, indicating that Ph_2PPy was chelated. The ^{31}P chemical shift has a value very similar to that found for **2**. The lack of platinum–phosphorus coupling confirms that the Ru–P bond was retained. In the ^1H NMR spectrum in $CDCl_3$ solution resonances at δ 6.04 and 3.42 ppm in the ratio 1 : 1 are observed for the η^6-C_6H_6 and DMSO. The value of J_{PtH} of the DMSO methyl groups was 18.60 Hz. The NMR spectra of **5b** are very similar to those of **5a**. The IR spectrum of **5a** showed ν_{PtCl} at 341 and 308 cm^{-1}, which supports a *cis* geometry at platinum. The DMSO was *S*-bonded to platinum, as shown by ν_{SO} at 1129 cm^{-1}. Probably the reaction proceeded via the ionic intermediate [(η^6-C_6H_6)Ru(Ph_2PPy)Cl][Pt(DMSO)Cl_3]. The formation of $[Pt(DMSO)Cl_3]^-$ from the reaction of *cis*-[Pt$(DMSO)_2Cl_2$] with KCl was previously described [10].

Upon attempted reaction of **1** with *cis*-[Pd(^{t}BuNC)$_2$-Cl_2] in dichloromethane solution at room temperature, the reagents were recovered unchanged after 7 h.

The reactions of [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (**3**) with *cis*-[Pd(^{t}BuNC)$_2Cl_2$] and *cis*-[Pt$(DMSO)_2Cl_2$] afforded the known *cis*-[Pd(^{t}BuNC)(Ph_2PPy)Cl_2] [5] and *cis*-[Pt(DMSO)(Ph_2PPy)Cl_2] together with [{(η^5-C_5Me_5)RhCl_2}$_2$]. Probably the reactions proceeded by formation of binuclear intermediates containing bridging Ph_2PPy. The structures were then disrupted to give the mononuclear species isolated.

Both *cis*-[Pd(^{t}BuNC)$_2Cl_2$] and *cis*-[Pt$(DMSO)_2Cl_2$] react with [(η^5-C_5H_5)Rh(Ph_2PPy)(CO)] to give the binuclear complexes [(η^5-C_5H_5)(^{t}BuNC)Rh(μ-Ph_2-PPy)Pd(^{t}BuNC)Cl]$^+$ and [(η^5-C_5H_5)RhCl(μ-Ph_2PPy)-Pt(CO)Cl], respectively. The latter reaction product is a Rh^{II}–Pt^{I} species and was formed in a process formally involving the oxidative addition of a d^8 platinum species to a rhodium(I) [4c].

In order to form a binuclear Ru–Rh complex, we have attempted the reaction of [(η^5-C_5H_5)Rh(CO)-(Ph_2PPy)] with [{(C_8H_{12})Ru-Cl_2}$_n$] in the molar ratio 1 : 1 in dichloromethane. From monitoring the reaction by IR and $^{31}P\{^1H\}$ NMR spectroscopy, it was clear that several steps occurred. Initially the reaction was very slow and the IR and $^{31}P\{^1H\}$ NMR spectra remained unchanged for some hours. Subsequently, ν_{CO} at 1942 cm^{-1} disappeared while the $^{31}P\{^1H\}$ NMR spectrum showed a new doublet at δ 47.80 (J_{RhP} = 182.42 Hz). After a long time, new doublets are observed in the $^{31}P\{^1H\}$ NMR spectra. The reaction was stopped when there remained only the species with the doublet at δ 47.80 ppm in the $^{31}P\{^1H\}$NMR spectrum together with small amounts of free $Ph_2P(O)Py$. The reaction mixture was filtered and the green solution was transferred to a chromatography column of aluminum oxide saturated with CH_2Cl_2. A green band, eluted with methanol, gave [(C_8H_{12})RuCl(μ-Ph_2PPy)(μ-Cl)Rh(η^5-C_5H_5)] (**6**).



This is a green solid, non-conducting in methanol, and soluble in chlorinated solvents and benzene. The structure proposed was supported by spectroscopic data. The doublet at δ 47.80 ppm (J_{RhP} = 182.42 Hz) observed in the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ solution is consistent with a Rh–P bond and bridging Ph_2PPy. The lack of a carbonyl stretching frequency in the IR spectrum indicates that CO was released and that one chloride is bridging. In the ^{1}H NMR spectrum in $CDCl_3$ solution, the η^5-C_5H_5 resonance was observed at δ 5.74 ppm, but the C_8H_{12} resonance was broad.

On standing for a long time, a dichloromethane solution of **6** surprisingly gave crystals of [(η^5-C_5H_5)-$RhCl_2(Ph_2PPy)$] (**7**). Thus a very slow intramolecular redox process in the species **6** occurred. This produced the rhodium (III) compound **7** and probably a ruthenium(0) species which was not isolated. Several intramolecular redox process promoted by bridging Ph_2-PPy have been reported [4b,4g,11].

2.3. Crystal structure of [(η^5-C_5H_5)$RhCl_2(Ph_2PPy)$] (7)

The asymmetric unit of the cell contains one discrete molecule of the complex (Fig. 1) which is constituted of one Rh^{III} atom coordinated to two chlorines, one 2-(diphenylphosphino)pyridine via the P atom and to one cyclopentadienyl ring by an η^5-interaction. Considering C_5H_5-ring as a single coordination centre represented by its centroid, the rhodium coordination might be described as very distorted tetrahedral (see Table 2). The deformation from the regular arrangement is mainly due to the significant bulk of the cyclopentadienyl moiety which forces the other three ligands on the same coordination side to close their interligand angles to ca. 90° while the corresponding angles with the Cp-centroid are enlarged more than 120°. Similar geometry and values are observed for analogous complexes of the $RuCl(\eta^5$-$C_5H_5)$ moiety with triphenylphosphine derivatives [12–14].

Table 1
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameter (Å$^2 \times 10^3$) for non-hydrogen atoms with e.s.d.s in parentheses; X represents the centroid of the cyclopentadienyl ring

	x	y	z	U_{eq} [a]
Rh	2548(1)	1686(1)	−992(1)	26(1)
Cl(1)	4932(1)	1851(1)	−2366(1)	38(1)
Cl(2)	2724(1)	−432(1)	−1647(1)	40(1)
C(1)	2500(4)	2958(3)	266(3)	46(1)
C(2)	1012(4)	2906(3)	368(3)	44(1)
C(3)	936(4)	1492(3)	766(3)	43(1)
C(4)	2371(4)	686(3)	968(3)	45(1)
C(5)	3334(4)	1573(4)	670(3)	46(1)
P	1432(1)	3060(1)	−2553(1)	26(1)
C(11)	−620(3)	3752(3)	−2102(2)	28(1)
C(12)	−1348(3)	5050(3)	−2664(3)	35(1)
C(13)	−2917(4)	5487(3)	−2379(3)	42(1)
C(14)	−3759(4)	4650(4)	−1547(3)	47(1)
C(15)	−3040(3)	3368(3)	−958(3)	47(1)
C(16)	−1482(3)	2928(3)	−1242(3)	39(1)
C(21)	2125(3)	4641(3)	−3156(3)	30(1)
N(22)	2039(3)	5330(3)	−2271(3)	45(1)
C(23)	2538(4)	6501(3)	−2635(4)	56(2)
C(24)	3100(4)	7006(4)	−3826(4)	61(2)
C(25)	3182(4)	6295(4)	−4729(4)	60(2)
C(26)	2669(4)	5092(3)	−4387(3)	43(1)
C(31)	1692(3)	2256(3)	−3885(2)	31(1)
C(32)	470(4)	2139(3)	−4220(3)	45(1)
C(33)	703(5)	1487(4)	−5215(3)	57(2)
C(34)	2142(4)	942(3)	−5859(3)	51(2)
C(35)	3354(4)	1073(3)	−5551(3)	47(1)
C(36)	3149(4)	1711(3)	−4555(3)	40(1)
X	2031(4)	1923(3)	608(3)	–

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

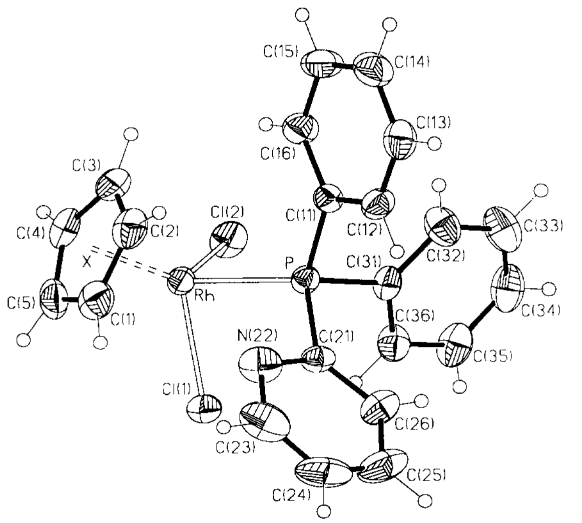


Fig. 1. Perspective view of the molecular unit showing the numbering scheme. Thermal ellipsoids are shown at 50% of probability while hydrogen size is arbitrary. The η^5-interaction of the Rh atom with the cyclopentadienyl is represented by one dashed bond with the ring centroid for clarity.

The two Rh–Cl bonds are not significantly different and the average length, 2.391(1)Å, is consistent with the value reported for the tetrahedral complexes of rhodium. The distances between the rhodium and the cyclopentadienyl carbon atoms range from 2.141 to 2.223 Å with a mean value of 2.178(4) Å and a Rh-centroid separation of 1.815(3) Å. These distances of the C_5H_5-ring from the tetrahedral Rh atom are shorter than the corresponding values observed in complexes of the $RuCl(\eta^5$-$C_5H_5)$ and $Rh(\eta^5$-$C_5H_5)$ moieties linked to triphenylphosphine derivatives. The shortening might depend on the presence of two coordinated chlorine atoms in the coordination shell. They are small and could be pack better on one side of the metal. This is further supported by the Rh–P bond length of 2.308(2) Å, significantly longer than the corresponding mean value 2.26(3) Å usually observed for complexes of triphenylphosphine derivatives *P*-linked to cyclopentadienyl rhodium and ruthenium moieties.

The Ph_2PPy is *P*-monodentate. We have already reported examples of this same ligand di-coordinated

Table 2
Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses; X represents the centroid of the cyclopentadienyl ring

Rh–Cl(1)	2.3888(8)	Rh–Cl(2)	2.3930(9)
Rh–C(1)	2.146(4)	Rh–C(2)	2.141(3)
Rh–C(3)	2.160(3)	Rh–C(4)	2.223(3)
Rh–C(5)	2.222(4)	Rh–X	1.815(3)
Rh–P	2.3089(8)	C(1)–C(2)	1.410(6)
C(1)–C(5)	1.431(4)	C(2)–C(3)	1.420(5)
C(3)–C(4)	1.416(5)	C(4)–C(5)	1.402(6)
P–C(11)	1.824(3)	P–C(21)	1.835(3)
P–C(31)	1.826(3)	C(11)–C(12)	1.391(3)
P–Rh–X	127.44(3)	Cl(2)–Rh–X	124.19(3)
Cl(1)–Rh–X	123.58(4)	Cl(1)–Rh–Cl(2)	91.07(3)
Cl(1)–Rh–P	87.20(3)	Cl(2)–Rh–P	92.37(3)
C(5)–Rh–P	148.1(1)	C(4)–Rh–P	150.5(1)
C(3)–Rh–P	112.8(1)	C(2)–Rh–P	93.32(9)
C(1)–Rh–P	110.07(9)	Cl(2)–Rh–C(5)	119.52(9)
Cl(2)–Rh–C(4)	93.28(9)	Cl(2)–Rh–C(3)	100.06(9)
Cl(2)–Rh–C(2)	136.0(1)	Cl(2)–Rh–C(1)	156.15(9)
Cl(1)–Rh–C(5)	93.4(1)	Cl(1)–Rh–C(4)	121.6(1)
Cl(1)–Rh–C(3)	156.37(9)	Cl(1)–Rh–C(2)	132.8(1)
Cl(1)–Rh–C(1)	97.8(1)	C(2)–C(1)–C(5)	107.5(3)
C(1)–C(2)–C(3)	108.3(3)	C(2)–C(3)–C(4)	107.5(3)
C(3)–C(4)–C(5)	108.6(3)	C(1)–C(5)–C(4)	107.9(3)
Rh–P–C(11)	115.40(9)	Rh–P–C(31)	117.1(1)
Rh–P–C(21)	110.6(1)	C(21)–P–C(31)	106.3(1)

via the P- and N-atoms, chelating the same metal [4f], or bridging two metal atoms [4b]. In these three coordination types, no significant differences have been observed in the ligand bite, due to the rigid P–C–N system, while the changes in the bonds to the metal are very sensitive to the coordination geometry and to the other ligands.

3. Experimental details

Established methods were used to prepare the compounds *cis*-[{(η^6-C_6H_6)$RuCl_2$}$_2$] [6] *cis*-[{(C_8H_{12})Ru-Cl_2}$_n$] [15], *cis*-[{($\eta^5C_5Me_5$)$RhCl_2$}$_2$] [16], *cis*-[Pd(^{t}Bu-NC)$_2$-Cl_2] [17], *cis*-[Pt(DMSO)$_2Cl_2$] [18], [(η^5-C_5H_5)-Rh(CO)(Ph_2PPy)] [4c], and Ph_2PPy [2]. All other reagents were purchased and used as supplied.

Solvents were dried by standard procedures. All experiments were performed under purified dinitrogen. IR spectra were obtained as Nujol mulls on KBr or CsI plates using a Perkin-Elmer FTIR 1720 spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX R300.

^1H NMR spectra were referenced to internal tetramethylsilane and $^{31}P\{^1H\}$ 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.

3.1. Preparation of [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] (1)

To a suspension of [{(η^6-C_6H_6)$RuCl_2$}$_2$] (0.536 g, 1.07 mmol) in benzene (20 cm^3) Ph_2PPy was added (0.564 g, 2.14 mmol) and the mixture was heated under reflux for 4 h. Then the solvent was removed under reduced pressure and the product was extracted with chloroform (3 × 10 cm^3). The volume of the solution was reduced to ca. 10 cm^3 and petroleum ether was added to give a red brown solid. This was washed with diethyl ether (30 cm^3) and dried in vacuo. Yield 82% (0.900 g, 1.75 mmol). Anal. Calcd. for $C_{23}H_{20}Cl_2NPRu$: C, 53.81; H, 3.93; N, 2.73; Cl, 13.81. Found: C, 53.85; H, 3.94; N, 2.75; Cl, 13.82%. IR(Nujol): ν_{RuCl} 294 and 278 cm^{-1} NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ 25.87 ppm; ^1H ($CDCl_3$) δ 5.57 ppm (d, C_6H_6, J_{PH} = 0.648 Hz).

3.2. Preparation of [(η^6-C_6H_6)Ru(Ph_2PPy)Cl]PF_6 (2)

$AgPF_6$ (0.246 g, 0.97 mmol) was added to a stirred dichloromethane solution (20 cm^3) of [(η^6-C_6H_6)Ru-(Ph_2PPy)Cl_2] (0.500 g, 0.97 mmol). After an 0.5 h the precipitated AgCl was separated by filtration and the solution was reduced in volume to ca. 10 cm^3; petroleum ether was added to give a pale green solid. This was washed with diethyl ether (30 cm^3) and dried in vacuo. Yield 92% (0.556 g, 0.89 mmol). Anal. Calcd. for $C_{23}H_{20}ClF_6NP_2Ru$: C, 44.35; H, 3.24; N, 2.25; Cl, 5.69. Found: C, 44.39; H, 3.27; N, 2.29; Cl, 5.74%. IR(Nujol): ν_{PF_6} 842 cm^{-1}, ν_{RuCl} 290 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ −18.30 ppm; ^1H ($CDCl_3$) δ 5.84 ppm (s, C_6H_6).

3.3. Preparation of [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (3)

To a suspension of [{(η^5-C_5Me_5)$RhCl_2$}$_2$] (0.300 g, 0.48 mmol) in dichloromethane (30 cm^3) Ph_2PPy was added (0.252 g, 0.96 mmol) and the mixture was stirred overnight to give an orange solution. This was concentrated (10 cm^3) and petroleum ether was added to give a red solid. This was washed with hexane (10 cm^3) and dried in vacuo. Yield 92% (0.505 g, 0.88 mmol). Anal. Calcd. for $C_{27}H_{29}Cl_2NPRh$: C, 56.66; H, 5.11; N, 2.45; Cl, 12.39. Found: C, 56.82; H, 5.15; N, 2.48; Cl, 12.51%. IR(Nujol): ν_{RuCl} 280 and 246 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ 28,85 ppm (d, J_{RhP} = 143.6 Hz); ^1H ($CDCl_3$) δ 1.41 ppm (d, CH_3, J_{PH} = 3.46 Hz).

3.4. Preparation of [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl]PF_6 (4)

To a dichloromethane solution (20 cm^3) of [(η^5-C_5-Me_5)Rh(Ph_2PPy)Cl_2] (0.500 g, 0.87 mmol), $AgPF_6$ (0.221 g, 0.87 mmol) was added. After 0.5 h the precipitated AgCl was separated by filtration and the solution was reduced to ca. 10 cm^3; petroleum ether was added to give a orange solid. This was washed with hexane (20 cm^3) and dried in vacuo. Yield 92% (0.546 g, 0.80 mmol). Anal. Calcd. for $C_{27}H_{29}ClF_6NP_2Rh$: C, 47.56; H, 4.29; N, 2.05; Cl, 5.20. Found: C, 47.61; H, 4.33; N, 2.08; Cl, 5.29%. IR(Nujol): ν_{PF_6} 842 cm^{-1}, ν_{RuCl} 279 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ −12.0 ppm (d, J_{RhP} = 116.1 Hz); ^1H ($CDCl_3$) δ 1.63 ppm (d, CH_3, J_{PH} = 4.7 Hz).

3.5. Preparation of [(η^6-C_6H_6)Ru(Ph_2PPy)(μ-Cl)Pt(DMSO)Cl_2]Cl (5a)

A dichloromethane solution (10 cm^3) of [(η^6-C_6H_6)Ru(Ph_2PPy)Cl_2] (0.610 g, 1.19 mmol) was added dropwise to a solution of *cis*-[Pt$(DMSO)_2Cl_2$] (0.408 g, 1.19 mmol) in the same solvent (10 cm^3) and the mixture was stirred for 4 h. The resulting green solution was concentrated (10 cm^3) and petroleum ether was added to give a green solid. This was separated by filtration, washed with diethyl ether and dried in vacuo. Yield 83% (0.857 g, 0.99 mmol). Anal. Calcd. for $C_{25}H_{26}Cl_4NOPPtS$: C, 35.02; H, 3.06; N, 1.63; Cl, 16.54. Found: C, 35.08; H, 3.12; N, 1.68; Cl, 16.56%. IR(Nujol): ν_{SO} 1129 cm^{-1}, ν_{PtCl} 341 and 308 cm^{-1}, ν_{RuCl} 277 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ −18.03 ppm; ^1H ($CDCl_3$) δ 6.04 ppm (C_6H_6), δ 3.42 ppm (DMSO, J_{PtH} = 18.60 Hz).

3.6. Preparation of [(η^6-C_6H_6)Ru(Ph_2PPy)(μ-Cl)Pt(DMSO)Cl_2]PF_6 (5b)

$AgPF_6$ (0.259 g, 1.02 mmol) was added to a stirred dichloromethane solution (20 cm^3) of [(η^6-C_6H_6)Ru(Ph_2PPy)(μ-Cl)Pt(DMSO)Cl_2]Cl (0.883 g, 1.02 mmol). After 0.5 h the precipitated AgCl was separated by filtration and the solution was reduced in volume to ca. 10 cm^3; petroleum ether was added to give a green solid. This was filtered, washed with diethyl ether and dried in vacuo. Yield 93% (0.917 g, 0.95 mmol). Anal. Calcd. for $C_{25}H_{26}NCl_3F_6OP_2PtS$ C, 31.05; H, 2.71; N, 1.45; Cl, 11.00. Found: C, 31.09; H, 2.77; N, 1.48; Cl, 11.05%. IR(Nujol): ν_{SO} 1155 cm^{-1}, ν_{PF_6} 838 cm^{-1}, ν_{PtCl} 340 and 303 cm^{-1}, ν_{RuCl} 275 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ −18.03 ppm; ^1H ($CDCl_3$) δ 6.04 ppm (C_6H_6), δ 3.42 ppm (DMSO, J_{PtH} = 18.60 Hz).

3.7. Reaction of [(η^5-C_5Me_5) Rh(Ph_2PPy)Cl_2] (3) with cis-[Pd(^{t}BuNC)$_2Cl_2$]

A dichloromethane solution (10 cm^3) of [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (0.500 g, 0.87 mmol) was added to a solution of *cis*-[Pd(^{t}BuNC)$_2Cl_2$] (0.292 g, 0.87 mmol) in the same solvent (10 cm^3) and the mixture was stirred for 4 h. The volume of solution was reduced to a ca. 10 cm^3 and, by addition of petroleum ether (20 cm^3), an orange precipitate was formed. This was filtered, washed with diethyl ether and dried in vacuum. $^{31}P\{^1H\}$ and ^1H NMR spectroscopy showed that the precipitate was a mixture of *cis*-[Pd(^{t}BuNC)(Ph_2PPy)Cl_2] [5] and [{(η^5-C_5Me_5)RhCl_2}$_2$].

3.8. Reaction of [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (3) with cis-[Pt$(DMSO)_2Cl_2$]

A dichloromethane solution (10 cm^3) of [(η^5-C_5Me_5)Rh(Ph_2PPy)Cl_2] (0.500 g, 0.87 mmol) was added to a solution of *cis*-[Pt$(DMSO)_2Cl_2$] (0.367 g, 0.87 mmol) in the same solvent (10 cm^3). After 3 h the colour turned from red to orange and the solution was reduced to a ca. 10 cm^3. By addition of petroleum ether (20 cm^3) an orange precipitate was formed. This was filtered, washed with diethyl ether and dried in vacuum. $^{31}P\{^1H\}$ and ^1H NMR showed that the precipitate was a mixture of *cis*-[Pt(DMSO)(Ph_2PPy)Cl_2] [4g] and [{(η^5-C_5Me_5)RhCl_2}$_2$].

3.9. Preparation of [(C_8H_{12})RuCl(μ-Ph_2PPy)(μ-Cl)Rh(η^5-C_5H_5)] (6)

A suspension of [{(C_8H_{12})RuCl_2}$_n$] (0.610 g, 2.17 mmol) in dichloromethane solution (10 cm^3) was added dropwise to a solution of [(η^5-C_5H_5)Rh(CO)(Ph_2PPy)] (1.00 g, 2.17 mmol) in the same solvent (10 cm^3). The reaction was monitored by IR and $^{31}P\{^1H\}$ NMR spectra. The IR and $^{31}P\{^1H\}$ NMR spectra remaining unchanged for several hours. After this ν_{CO} (1942 cm^{-1}) slowly disappeared while the $^{31}P\{^1H\}$ NMR spectrum showed a new doublet centred at δ 47.80 (J_{RhP} = 182.42 Hz). The reaction was stopped when the starting material (doublet δ 53.80 ppm, J_{RhP} = 199.8 Hz) had disappeared. The resulting green solution was filtered and concentrated (10 cm^3). It was then transferred to a chromatography column of aluminium oxide saturated with CH_2Cl_2. By eluting with dichloromethane/methanol (100 : 1) a small concentrate of an orange fraction (uncharacterized) was obtained. Using methanol a green fraction containing [(C_8H_{12})RuCl(μ-Ph_2PPy)(μ-Cl)Rh(η^5-C_5H_5)] was then separated. The solution was reduced to ca. 10 cm^3 and petroleum ether was added to give the product as a green solid. Yield 54% (0.609 g, 0.85 mmol). Anal. Calcd. for $C_{30}H_{31}Cl_2NPRhRu$: C, 50.65; H, 4.39; N, 1.97; Cl, 9.97. Found: C, 50.71; H, 4.41; N, 1.98; Cl, 9.98% NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ 47.80 ppm (J_{RhP} = 182.42 Hz); ^1H ($CDCl_3$) δ 5.74 ppm (C_5H_5).

3.10. X-ray structure analysis and structure refinement [RhCl_2(η^5-C_5H_5)(Ph_2PPy)]

The compound crystals were grow by freezing a CH_2Cl_2/diethyl ether solution.

Crystal data: $C_{22}H_{19}Cl_2NPRh$, $M = 502.2$, triclinic, space group $P\bar{1}$, (No. 2), $a = 9.561(2)$, $b = 10.184(2)$, $c = 11.518(2)$ Å, $\alpha = 76.14(2)$, $\beta = 72.78(2)$, $\gamma = 71.87(2)°$, $U = 1004.7(3)$ Å^3, $Z = 2$, $D_c = 1.66$ g cm^{-3}, $F(000) = 504$, μ(Mo Kα) = 1.20 cm^{-1}, λ(Mo Kα) = 0.71073 Å.

A suitable $0.20 \times 0.25 \times 0.30$ mm crystal was mounted on a Siemens R3m/v automatic four-circle diffractometer. Diffraction data were collected at room temperature using graphite-monochromatised Mo Kα radiation. Cell parameters were obtained from least-squares of the setting angles of 35 accurately centered reflections up to 2θ angle of 33°. A total of 6222 intensities were collected by the variable-speed ω–2θ scan method within to 2θ range 3.5–55° (index ranges $-3 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 14$) obtaining a data set of 4653 unique reflections ($R_{int} = 0.7\%$). No crystal decay was observed during the data collection by monitoring of three standard reflections after every 97 measurements. Diffraction intensities were evaluated by the learnt-profile procedure [19] and then corrected for Lorentz polarization effects. Absorption correction was taken into account by fitting a pseudo-ellipsoid [20] to the azimutal scan data of 25 suitable reflections with $|\chi| > 65°$ (transmission range = 0.63–0.88).

The rhodium atom was located on a super-sharpened Patterson map and then the structure was completed by a combination of least squares technique and Fourier syntheses. Hydrogen atoms, placed in calculated positions by stereochemistry considerations (C–H = 0.93 Å) and riding on their respective parent carbons, were included into the model refinement with an unique fixed isotropic thermal parameter ($U_{iso} = 0.060$ Å^2). The structure model, with all non-hydrogen atoms anisotropic, was refined by full-matrix least squares technique by minimizing the function $\Sigma w(F_o - F_c)^2$, up to convergence using 3650 observed reflections ($F \ge 6\Sigma(F)$). Final $R = \Sigma|F_o - F_c|/\Sigma F_o = 0.026$ and $wR = \Sigma w|F_o - F_c|/\Sigma wF_o = 0.026$ with the final weighting scheme $w^{-1} = \sigma^2(F_o) + 10^{-4}F_o$ and an observations to parameter ratio of 15:1. On the last difference map the highest electron density residuals (less than half electron Å^{-3}) are at about 0.5 Å from the chlorine atoms. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. [21].

Data reduction, structure solutions and refinement and drawings were performed with the SHELXTL-PLUS package [22], while final geometrical calculations were carried out with PARST program [23] on a DEC Micro Vax/3400 computer. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, anisotropic temperature factors and remaining bonds and angles.

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