

Synthesis of orthometallated rhodium(III) compounds. Crystal structures of $[\text{RhCl}_2\{\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-dppm})]$ and $[\text{RhCl}\{\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2\}(\eta^1\text{-PCCl})(\text{phen})](\text{SbF}_6) \cdot \text{CH}_2\text{Cl}_2$ (dppm = bis(diphenylphosphino)methane; PCCl = $\text{P}(o\text{-ClC}_6\text{H}_4)\text{Ph}_2$; phen = 1,10 phenanthroline)

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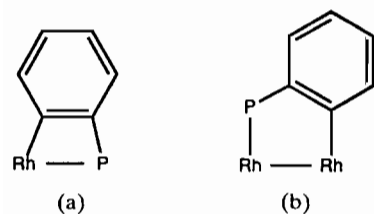
(Received January 11, 1993; revised March 18, 1993)

Abstract

Neutral and cationic rhodium(III) metallated compounds containing a four-membered ring are prepared by different synthetic methods: (i) from rhodium(I) compounds that contain the ligand $\text{P}(o\text{-ClC}_6\text{H}_4)\text{PPh}_2$, by 2c–2e intramolecular oxidative addition; (ii) from metallated dirhodium(II) compounds; (iii) by ligand substitution in $[\text{RhCl}_2\{\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2\}\{\eta^2\text{-P}(o\text{-ClC}_6\text{H}_4)\text{Ph}_2\}]$. The crystal structures of $[\text{RhCl}_2\{\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-dppm})]$ (**2**) and of the dichloromethane solvate of $[\text{RhCl}\{\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2\}\{\eta^1\text{-P}(o\text{-ClC}_6\text{H}_4)\text{Ph}_2\}(\text{phen})](\text{SbF}_6)$ (**11**) have been determined by X-ray diffraction methods. In both complexes the Rh atom is in the distorted octahedral arrangement and the metallated phosphine forms, through P and C atoms, a four-membered ring with the metal. A dppm molecule in **2** and a phen molecule in **11** act also as chelating ligands. In **11** the $\text{P}(o\text{-ClC}_6\text{H}_4)\text{PPh}_2$ phosphine behaves as a monodentate ligand.

Introduction

Organometallic rhodium(III) compounds with orthometallated P-donor ligands are quite common [1]; many of them contain a five-membered ring in the molecule. The formation of a four-membered ring is comparatively less common [1, 2]. We have synthesized and structurally characterized some metallated rhodium(III) compounds with a four-membered ring (Scheme 1(a)) by using orthohalogenated phosphines [3]. In these reactions the metallation is produced by



Scheme 1.

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1c–2e oxidative addition involving cleavage of the C–halogen bond of the phosphine [4].

The preparation of dirhodium(II) compounds containing orthometallated phosphines as bridging ligand (Scheme 1(b)) has been also reported [5]; the reaction seems to occur by a proton transfer from one phenyl ring of the phosphine to one acetate group [5c]. The reactivity of some of these compounds has been briefly explored [6].

We have also prepared, by a different synthetic approach, some dirhodium(II) compounds containing one metallated phosphine bridging the rhodium atoms. The complex $[\text{Rh}(\text{pz})(\text{CO})(\text{PCBr})_2]$ (pz = pyrazolyl or substituted pyrazolyl, $\text{PCBr} = \text{P}(o\text{-BrC}_6\text{F}_4)\text{Ph}_2$) undergoes orthometallation by a 2c–2e oxidative addition reaction yielding $[\text{Rh}_2(\text{pz})_2\{\mu\text{-}(\text{C}_6\text{F}_4)\text{PPh}_2\}_2\text{Br}(\text{CO})(\eta^2\text{-PCBr})]$ [7].

We wanted to explore a synthetic route for the preparation of metallated rhodium compounds in oxidation state I or II from the easily available metallated rhodium(III) compounds. The crystal structures of $\text{RhCl}_2\{\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-dppm})$ (**2**) and $[\text{RhCl}\{\eta^2-$

$(C_6H_4)PPh_2\{\eta^1-P(o-ClC_6H_4)Ph_2\}(phen)](SbF_6) \cdot CH_2Cl_2$ (**11**) are also reported.

Results

We have recently reported that $RhCl_2\{\eta^2-(C_6H_4)PPh_2\}(\eta^2-PCCl)$ (**1**) ($PCCl = P(o-ClC_6H_4)Ph_2$) reacts [3f] with stoichiometric amounts of dppm in dichloromethane at room temperature with displacement of the $PCCl$ ligand, yielding $RhCl_2\{\eta^2-(C_6H_4)PPh_2\}(\eta^2-dppm)$ (**2**) in high yield. The reaction with bis(diphenylphosphino)ethane (dppe) gave a compound of similar formulation $RhCl_2\{\eta^2-(C_6H_4)PPh_2\}(\eta^2-dppe)$ (**3**) [3f]. The large ${}^2J(P-P')$ coupling constant values (c. 500 Hz) observed in the ${}^{31}P$ NMR spectra (see Table 1) indicate that, in the three compounds, the phosphorus of the metallated phosphine is *trans* to one of the phosphorus atoms of the diphosphine ligand. Smaller ${}^2J(P-P')$ coupling constant values (c.

10–50 Hz), corresponding to *cis* coupling, were also observed.

An alternative route has been tested for the preparation of compounds **2** and **3**. It involves 1c–2e oxidative addition reaction of rhodium(I) species of formula $RhCl(\eta^1-PCCl)(\eta^2-P-P)$ ($P-P = dpmm$ (**4**), dppe (**5**)) which can be easily obtained from $RhCl(\eta^2-PCCl)(\eta^1-PCCl)$ [3f], by phosphine substitution reaction. Based on the ${}^{31}P$ NMR spectra we assign a square planar arrangement to the rhodium atom in compounds **4** and **5** with the $PCCl$ acting as monodentate ligand. Both **4** and **5** undergo thermal oxidative-addition with cleavage of the C–Cl bond of the phosphine to give compounds **2** and **3** in high yield.

Cotton and Dumbar have reported the preparation and X-ray structure of $[Rh_2Cl_2(\mu-dmpm)_2\{\mu-(C_6H_4)PPh_2\}_2]$ ($dmpm = bis(dimethylphosphino) methane$) by reacting $[Rh_2(O_2CCH_3)_2\{(C_6H_4)PPh_2\}_2(HO_2CCH_3)_2]$ with four moles of $ClSiMe_3$ followed by addition of $dmpm$ [6a]. We have tried this reaction

TABLE 1. ${}^{31}P$ NMR data for rhodium(I) and rhodium(III) synthesized compounds

| Compounds ^a | $\delta(PC)^b$ (ppm) | $\delta(PCCl)^b$ (ppm) | $\delta(P-P)^b$ (ppm) | ${}^2J(P-P')$ (Hz) |
|---|-------------------------|---------------------------|--------------------------------------|--|
| $RhCl_2(\eta^2-PC)(\eta^2-PCCl)$ | –31.1(121) | | 44.2(130) | 25 |
| $RhCl_2(\eta^2-PC)(\eta^2-dppm)$ | P_a –50.5(74) | | P_b –29.1(87) P_c –19.8(116) | P_a-P_b 527 P_a-P_c 18 P_b-P_c 54 |
| $RhCl_2(\eta^2-PC)(\eta^2-dppe)$ | P_a –50.2(72) | | P_b 39.8(103) P_c 48.1(132) | P_a-P_b 493 P_a-P_c 24 P_b-P_c 12 |
| $RhCl(\eta^1-PCCl)(\eta^2-dppm)$ | | P_a 30.2(133) | P_b –41.3(123) P_c –19.5(160) | P_a-P_b 385 P_a-P_c 32 P_b-P_c 103 |
| $RhCl(\eta^1-PCCl)(\eta^2-dppe)$ | | P_a 25.7(130) | P_b 39.8(143) P_c 53.1(158) | P_a-P_b 360 P_a-P_c 48 P_b-P_c 26 |
| $RhCl_2(\eta^2-PC')(\eta^2-dppm)$ Isomer 1 | P_a –54.2(74) | | P_b –29.7(85) P_c –16.4(118) | P_a-P_b 523 P_a-P_c 17 P_b-P_c 56 |
| Isomer 2 | P_a –57.6(75) | | P_b –32.2(84) P_c –12.3(115) | P_a-P_b 531 P_a-P_c 19 P_b-P_c 56 |
| $RhCl_2(\eta^2-PC'')(\eta^2-dppm)$ | P_a –61.4(76) | | P_b –32.7(84) P_c –10.6(117) | P_a-P_b 534 P_a-P_c 18 P_b-P_c 56 |
| $[RhCl(\eta^2-PC)(\eta^2-dppm)](SbF_6)$ | P_a –43.8 (70) | | P_b –22.6(91) P_c –5.0(126) | P_a-P_b 421 P_a-P_c 15 P_b-P_c 61 |
| $[RhCl(\eta^2-PC)(\eta^2-dppe)](SbF_6)^c$ | P_a –46.7(70) | | P_b 56.8(129) P_c 61.4(99) | P_a-P_b 371 P_a-P_c 22 P_b-P_c 76 |
| $[RhCl(\eta^2-PC)(PCCl)(CH_3CN)_x](SbF_6)$ | –34.4(108) | 48.7(131) | | 24 |
| $[RhCl(\eta^2-PC)(\eta^1-PCCl)(bipy)](SbF_6)$ | –34.6(111) | 43.3(120) | | 24 |
| $[RhCl(\eta^2-PC)(\eta^1-PCCl)(phen)](SbF_6)$ | –35.1(111) | 44.6(121) | | 24 |

^aKey: $PC = (C_6H_4)PPh_2$; $PC' = (C_6H_4)PMePh$; $PC'' = (C_6H_4)PMe_2$. ^bPositive shifts are downfield from aqueous H_3PO_4 85%. Values of ${}^1J(Rh-P)$ in Hz, are in parentheses. ^cSolvent CH_2Cl_2/CH_3CN .

with three metallated compounds $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\mu\text{-PC}')_2$ ($\text{PC}' = (\text{C}_6\text{H}_4)\text{PPh}_2$, $(\text{C}_6\text{H}_4)\text{PPhMe}$, $(\text{C}_6\text{H}_4)\text{PMe}_2$) and using *dppm* as diphosphine ligand. In all these reactions, oxidation to rhodium(III) occurs to some extent and compounds of the type $\text{RhCl}_2(\eta^2\text{-PC})(\eta^2\text{-P-P})$ are identified in the reaction mixture by ^{31}P NMR techniques. Yellow mononuclear rhodium(III) compounds and red dirhodium(II) compounds were isolated by chromatographic methods.

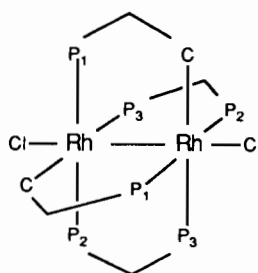
The yellow compounds gave elemental analyses and spectroscopic data consistent with the formula $\text{RhCl}_2(\eta^2\text{-PC}')(\eta^2\text{-dppm})$, PC' being $(\text{C}_6\text{H}_4)\text{PPh}_2$ (**2**), $(\text{C}_6\text{H}_4)\text{PMePh}$ (**6**) and $(\text{C}_6\text{H}_4)\text{PMe}_2$ (**7**). The ^{31}P NMR spectrum of **2** shows three sets of signals in the high field region, -19 to -50 ppm, consistent with the presence of two chelating ligands, *dppm* and metallated phosphine. The values of the $^1J(\text{Rh-P})$ coupling constants in the range 74 to 116 Hz are normal for a rhodium(III) octahedral configuration. The high value of the $^2J(\text{P-P}')$ coupling constant, 527 Hz, is indicative of the presence of two phosphorous nuclei in a *trans* disposition.

The other two compounds containing metallated PMePh_2 and PMe_2Ph ligands show very similar spectroscopic results and accordingly we assign to these compounds a structure as for **2**. Compound **6** exhibits in solution ^{31}P NMR signals that have to be attributed to a second isomer (intensity ratio 3:1). The values of the chemical shifts and $^1J(\text{Rh-P})$ coupling constants are very similar in both sets of signals. This fact and the lack of signal splitting for the compounds with metallated PPh_3 and PMe_2Ph phosphines strongly suggest that the two isomers are due to the presence of a chiral center at the P atom of the metallated phosphine.

We have also spectroscopically detected [8] that in the preparation of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2\{(\text{C}_6\text{H}_4)\text{PMePh}\}_2(\text{HO}_2\text{CCH}_3)_2]$ a mixture of three isomers was obtained in solution. A related compound of one of these isomers with pivalate instead of acetate groups was crystallographically identified [5e].

Based on the spectroscopic data the red compounds are likely to be rhodium(II) binuclear species with a structure comparable to that of the already cited compound $\text{Rh}_2\text{Cl}_2(\text{dmpm})_2\{(\text{C}_6\text{H}_4)\text{PPh}_2\}_2$ [6a]. The ^{31}P NMR spectra of these red species show three complex sets of signals assignable to the three magnetically different P nuclei present in the structure of the type shown in Scheme 2. Signals for P_2 and P_3 appear at $\delta = 12$ and 6 ppm and the chemical shift for P_1 shift depends on the metallated phosphine: $\delta = -11$ ppm for $(\text{C}_6\text{H}_4)\text{PPh}_2$, -20 ppm for $(\text{C}_6\text{H}_4)\text{PMePh}$, -33 for $(\text{C}_6\text{H}_4)\text{PMe}_2$.

The data so obtained indicate that dirhodium(II) complexes can be oxidized to rhodium(III) species with the metallated phosphine changing from bridging to



Scheme 2.

chelating coordination mode. Looking for synthetic methods yielding cyclometallated rhodium(II) species we found [3f] that the chemical or electrochemical reduction of complex **1**, results in the cleavage of the metal-carbon bond. It was reasonable to assume that the reduction of cationic orthometallated rhodium(III) compounds could be done at lower potential values (c. 0.5–1.0) than the analogous neutral species thus preserving the metallacycle.

In order to test these arguments we have prepared some cationic rhodium(III) complexes by ligand substitution reactions in compounds **1–3**.

The reaction of $\text{RhCl}_2\{\eta^2\text{-(C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-P-P})$ ($\text{P-P} = \text{dppm}$ (**2**), *dppe* (**3**)) with AgSbF_6 (1:1 molar ratio) in CH_2Cl_2 yields cationic species $[\text{RhCl}\{\eta^2\text{-(C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-P-P})](\text{SbF}_6)$, ($\text{P-P} = \text{dppm}$ (**8**), *dppe* (**9**)) in high yield. The ^{31}P NMR spectrum for compound **8** is similar to that of the neutral analogue. However for compound **9** a well defined ^{31}P NMR spectrum is only obtained in the presence of CH_3CN .

Reaction of $[\text{RhCl}_2\{\eta^2\text{-(C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-PCCl})]$ [3e] with one mole of AgSbF_6 in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ at room temperature gave, after elimination of the AgCl precipitate, a yellow solution. The ^{31}P NMR spectrum of this solution showed two doublets of doublets centered at $\delta = -34.4$ ppm ($^1J(\text{Rh-P}) = 108$ Hz) and $\delta = 48.7$ ppm ($^1J(\text{Rh-P}) = 131$ Hz) with a $^2J(\text{P-P}')$ coupling constant of 24 Hz. These spectroscopic data are consistent with the fact that the P atoms of $(\text{C}_6\text{H}_4)\text{PPh}_2$ and PCCl ligands remain bonded to the rhodium atom in a mutual *cis* configuration. We tentatively formulate this solvated species as $[\text{RhCl}\{\eta^2\text{-(C}_6\text{H}_4)\text{PPh}_2\}(\text{PCCl})(\text{NCCH}_3)_x](\text{SbF}_6)$ but all the efforts to isolate it as a crystalline solid were unsuccessful.

Reaction of this solvated species with 2,2'-bipyridine (*bipy*) or 1,10-phenanthroline (*phen*) gave the compounds $[\text{RhCl}\{\eta^2\text{-(C}_6\text{H}_4)\text{PPh}_2\}(\eta^1\text{-PCCl})(\text{bipy})](\text{SbF}_6)$ (**10**) and $[\text{RhCl}\{\eta^2\text{-(C}_6\text{H}_4)\text{PPh}_2\}(\eta^1\text{-PCCl})(\text{phen})](\text{SbF}_6)$ (**11**) in high yield. The same two compounds were obtained by direct reaction of **1** with one mole of AgSbF_6 in dichloromethane solution in the presence of equimolecular amounts of bipyridine or phenanthroline. The ^{31}P NMR spectra of these compounds exhibit two different phosphorus environments; the low

field signals centered at $\delta=43.3$ ppm ($^1J(\text{Rh-P})=120$ Hz) and $\delta=44.6$ ppm ($^1J(\text{Rh-P})=121$ Hz) for **10** and **11**, respectively, are assigned to a PCCl ligand in a monodentate coordination mode. The high field signals at $\delta=-34.6$ ppm ($^1J(\text{Rh-P})=111$ Hz) and $\delta=-35.1$ ppm ($^1J(\text{Rh-P})=111$ Hz), respectively, are assigned to metallated phosphines [9]. The $^2J(\text{P-P}')$ coupling constant values (24 Hz) are indicative of a *cis* disposition of two P nuclei in both compounds. The same results were obtained when **1** was reacted with an excess of AgSbF_6 . Only in the presence of an appropriate ligand such as *N,N'*-ethylenebis(salicylideneiminato), salen, was the second chlorine atom released obtaining the dicationic dinuclear complex $[(\text{Rh}(\eta^2\text{-C}_6\text{H}_4\text{PPh}_2)(\eta^2\text{-PCCl})_2(\text{salen}))(\text{SbF}_6)_2]$, which contains the salen ligand in an unusual bis-bidentate mode of coordination [3g].

Table 2 gives the reduction potential values for the synthesized rhodium(III) compounds. All the compounds show a two-electron irreversible reduction process except for **10** and **11** that show two consecutive mono-electronic reduction processes. Rhodium(III) compounds usually reduce directly to rhodium(I) species; an ECEC mechanism with halide dissociation has been proposed for this process [10]. In some cases, as for $[\text{Rh}(\text{bipy})_3]^{3+}$, two consecutive reduction peaks have been detected at high sweep rates [11]. However the intermediate rhodium(II) species was unstable, due to a disproportionation to rhodium(I) and rhodium(III) compounds [12], and could not be characterized.

Compound **10** shows by cyclic voltammetry in THF (NBu_4PF_6 as supporting electrolyte and Pt electrode) two mono-electronic reduction processes A_1 ($E_p = -0.38$ V) and A_2 ($E_p = -0.62$ V) (see Fig. 1). At a sweep rate of 0.1 V s^{-1} , the corresponding anodic peaks A'_1 and A'_2 are detected in the reverse sweep, the ΔE_p value ($\Delta E_p = E_p(A_1) - E_p(A'_1)$) for the first redox couple

TABLE 2. Reduction potential values^a for the synthesized rhodium(III) compounds

| Compound | A_1 (V) | A_2 (V) |
|--|--------------------|--------------------|
| $[\text{RhCl}_2(\eta^2\text{-PC})(\eta^2\text{-PCCl})]$ | -0.98 ^b | |
| $[\text{RhCl}_2(\eta^2\text{-PC})(\eta^2\text{-dppm})]$ | -1.48 ^b | |
| $[\text{RhCl}_2(\eta^2\text{-PC})(\eta^2\text{-dpppe})]$ | -1.70 ^b | |
| $[\text{RhCl}(\eta^2\text{-PC})(\eta^2\text{-dppm})](\text{SbF}_6)$ | -1.04 ^b | |
| $[\text{RhCl}(\eta^2\text{-PC})(\eta^2\text{-dpppe})](\text{SbF}_6)$ | -1.10 ^b | |
| $[\text{RhCl}(\eta^2\text{-PC})(\text{PCCl})(\text{CH}_3\text{CN})_x](\text{SbF}_6)$ | -0.40 ^b | |
| $[\text{RhCl}(\eta^2\text{-PC})(\eta^1\text{-PCCl})(\text{bipy})](\text{SbF}_6)$ | -0.38 | -0.62 ^c |
| $[\text{RhCl}(\eta^2\text{-PC})(\eta^1\text{-PCCl})(\text{phen})](\text{SbF}_6)$ | -0.38 | -0.62 ^c |

^aPotential values obtained containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte and referenced to the saturated calomel electrode (SCE). In all cases platinum was employed as electrode and THF as solvent. $v=100 \text{ mV/s}$.

^bAssigned to a bi-electronic irreversible reduction process from Rh(III) to Rh(I). 2 F/mol by coulometry. ^cAssigned to consecutive mono-electronic reduction process. $\Delta E_p(A_1)=0.06 \text{ V}$, $\Delta E_p(A_2)=0.10 \text{ V}$.

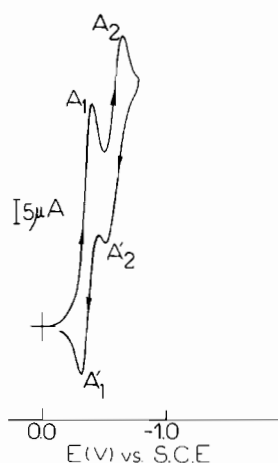


Fig. 1. Cyclic voltammogram for $[\text{RhCl}(\eta^2\text{-C}_6\text{H}_4\text{PPh}_2)(\eta^1\text{-PCCl})(\text{bipy})](\text{SbF}_6)$ (**10**). Scan rate 100 mV s^{-1} and 0.2 mol dm^{-3} $[\text{NBu}_4^+]\text{PF}_6^-$ in THF.

is very close to 0.060 V, corresponding to a reversible system. However, for the second reduction process, a higher ΔE_p value ($\Delta E_p = E_p(A_2) - E_p(A'_2) \sim 0.1 \text{ V}$) is observed. This fact can be tentatively interpreted assuming that a chemical reaction (probably the dissociation of one chloride ion) is coupled to the electrochemical reduction for the second process [13]. Very similar electrochemical behaviour is observed for compound **11**.

The reversibility of the first reduction process can be attributed to the π -delocalizing ability of bipyridine and phenanthroline ligands. The electrochemical behaviour of the cationic solvated species $[\text{RhCl}(\eta^2\text{-C}_6\text{H}_4\text{PPh}_2)(\text{PCCl})(\text{CH}_3\text{CN})_x](\text{SbF}_6)^+$, that reduces in an irreversible way supports this interpretation. In addition to that the paramagnetic mononuclear rhodium(II) species are in general fairly unstable in solution [14], while the species generated by electrochemical reduction of **10** at -0.40 V (A_1 peak) is stable enough to be detected by ESR spectroscopy. The observation of a complicated set of very close signals in the ESR spectrum of the reduced sample strongly supports that the electron must have strong ligand character (bipy) excluding the delocalization to the P nuclei that would involve higher coupling values [15a]. This fact is in agreement with the electrochemical behaviour observed for other polypyridine complexes of iridium and ruthenium where after successive reduction processes the electrons are localized on the pyridine ligands [15b, c].

In the light of the electrochemical data obtained for complexes **10** and **11** we can estimate the value of the equilibrium constant for the reaction $\text{Rh(III)} + \text{Rh(I)} \rightarrow 2\text{Rh(II)}$. We have determined the equilibrium constant from [16] the equation $K = \exp[(E_2^\circ - E_1^\circ)F/RT]$, where E_1° and E_2° are the

standard potentials related to the Rh(III)/Rh(II) and Rh(II)/Rh(I) couples. Considering the processes as reversible the difference $E_2^\circ - E_1^\circ$ can be substituted by $\Delta E_{1/2}$ and the above mentioned equation can be expressed as $K = \exp(\Delta E_{1/2}/25.69)$ at 298 K with $\Delta E_{1/2}$ given in mV. According to that the constant obtained is 5.2×10^3 , reflecting a relative thermodynamic stability for the intermediate Rh(II) species.

We have also tried the chemical and the electrochemical reduction of complexes **10** and **11**. Addition of equimolecular amounts of cobaltocene to a dichloromethane solution of complex **10**, at 0 °C, gave after a few minutes a yellow–orange solution and a black powder. The ^{31}P NMR spectrum of the filtered solution consists of two sets of signals. The first centered at $\delta = -46$ ppm ($^1J(\text{Rh}-\text{P}) = 71$ Hz) assignable to a metallated phosphine and the second at $\delta = 21$ ppm assignable to a PCCl ligand. Similar results were obtained by electrochemical reduction after consumption of 1 F/mol. The same ^{31}P NMR signals were detected after refluxing **10** in ethanol for several hours. The high value of $^2J(\text{P}-\text{P}') = 465$ Hz clearly indicates a *trans* disposition for the phosphorous atoms whereas the $^1J(\text{Rh}-\text{P})$ is in the range for a rhodium(III) complex. According to these data we assume that the reduction is followed by an isomerization from *cis* to *trans* of the ligands following a still obscure reaction pathway. Similar results can be obtained in the reduction of **11**.

Crystal and molecular structure of $[\text{RhCl}_2\{\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-dppm})]$ (**2**)

A view of the complex **2** is shown in Fig. 2 together with the atomic numbering scheme. Selected bond distances and angles are also given in Table 3.

The distorted octahedral coordination geometry around the Rh atom involves two chlorine atoms in *cis* position, the P(1) and C(2) atoms from the chelating metallated phosphine, and the P(2) and P(3) atoms from the chelating dppm ligand.

The Rh–Cl bond lengths of 2.423(3) and 2.488(3) Å are significantly different; this could be due to the stronger *trans* influence of C(2) (*trans* to Cl(2)) with respect to P(3) atom (*trans* to Cl(1)) [3e, g]. The three Rh–P bond lengths fall in a rather large range, 2.268(3)–2.347(3) Å, the longest two being associated with the P(1) and P(2) atoms. It may be that the P(1) and P(2) atoms, which are mutually *trans*, exert a large *trans* influence on each other [17].

The chelating $(\text{C}_6\text{H}_4)\text{PPh}_2$ and dppm ligands form with the Rh atom two four-membered rings. Both these ligands can also act as bridging ligands in rhodium compounds. The strongest distortions have been found, of course, in the bond angles when they chelate [3, 17, 18]. There are considerable strains in the two four-

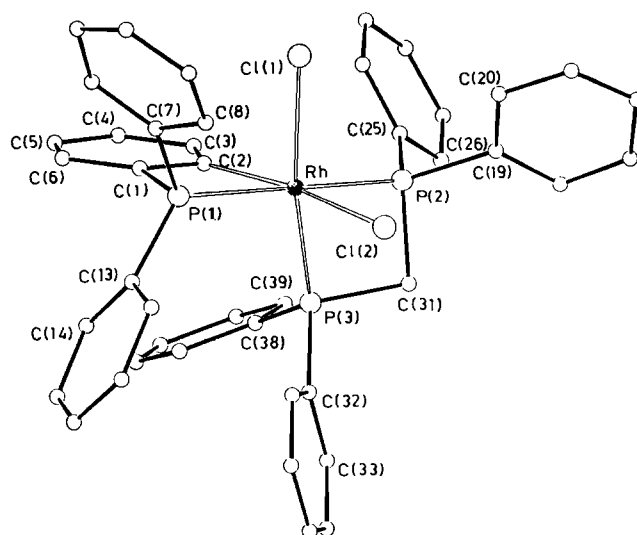


Fig. 2. Molecular structure of the complex $\text{RhCl}_2(\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2)(\eta^2\text{-dppm})$ (**2**) including the atomic numbering scheme.

TABLE 3. Selected bond distances (Å) and angles (°) for $[\text{RhCl}_2(\eta^2-(\text{C}_6\text{H}_4)\text{PPh}_2)(\eta^2\text{-dppm})]$ (**2**)

| | | | |
|-----------------|-----------|----------------|-----------|
| Rh–Cl(1) | 2.423(3) | Rh–Cl(2) | 2.488(3) |
| Rh–P(1) | 2.347(3) | Rh–P(2) | 2.317(3) |
| Rh–P(3) | 2.268(3) | Rh–C(2) | 2.066(11) |
| P(1)–C(1) | 1.812(13) | P(1)–C(7) | 1.804(12) |
| P(1)–C(13) | 1.809(11) | P(2)–C(19) | 1.825(11) |
| P(2)–C(25) | 1.810(10) | P(2)–C(31) | 1.843(10) |
| P(3)–C(31) | 1.846(10) | P(3)–C(32) | 1.812(10) |
| P(3)–C(38) | 1.842(14) | | |
| P(3)–Rh–C(2) | 91.1(3) | P(2)–Rh–C(2) | 105.6(3) |
| P(2)–Rh–P(3) | 72.6(1) | P(1)–Rh–C(2) | 68.9(3) |
| P(1)–Rh–P(3) | 105.2(1) | P(1)–Rh–P(2) | 174.2(1) |
| Cl(2)–Rh–C(2) | 168.6(3) | Cl(2)–Rh–P(3) | 89.3(1) |
| Cl(2)–Rh–P(2) | 85.4(1) | Cl(2)–Rh–P(1) | 100.0(1) |
| Cl(1)–Rh–C(2) | 89.1(3) | Cl(1)–Rh–P(3) | 166.9(1) |
| Cl(1)–Rh–P(2) | 94.7(1) | Cl(1)–Rh–P(1) | 87.1(1) |
| Cl(1)–Rh–Cl(2) | 93.2(1) | Rh–P(1)–C(13) | 127.0(4) |
| Rh–P(1)–C(7) | 120.2(4) | Rh–P(1)–C(1) | 82.4(4) |
| Rh–P(2)–C(31) | 93.4(4) | Rh–P(2)–C(25) | 121.5(4) |
| Rh–P(2)–C(19) | 122.1(4) | Rh–P(3)–C(38) | 118.0(4) |
| Rh–P(3)–C(32) | 123.9(4) | Rh–P(3)–C(31) | 94.9(4) |
| Rh–C(2)–C(1) | 105.5(8) | Rh–C(2)–C(3) | 136.5(9) |
| P(1)–C(1)–C(2) | 103.2(8) | P(1)–C(1)–C(6) | 131.7(9) |
| P(2)–C(31)–P(3) | 94.8(5) | | |

membered rings, the two strongest observed distortions in the octahedral coordination around the rhodium atom involving the rather narrow C(2)–Rh–P(1) and P(2)–Rh–P(3) bite angles, 68.9(3) and 72.6(1)°. The four-membered ring of the metallated phosphine is planar (maximum deviation from the mean plane 0.02(1) Å for C(1)) as found in other orthometallated aryl phosphines containing four-membered rings [3e, g], whereas if the metallation does not involve an aryl

group the four-membered chelate ring is not planar as found, for example, for the MCH_2CMe_2P framework ($M = Rh, Ir, Pd, Pt$) [19]. The value of the $Rh-C(2)$ bond length, 2.066(11) Å, is comparable to those found for other $Rh(III)-C(sp^2)$ (2.00–2.06 Å) [19a].

In the dppm ligand the $P(2)-C(31)-P(3)$ bond angle, 94.8(5)°, is far from the value found in rhodium complexes with monodentate dppm ligand, 114.4(4)° [20], but is comparable to the values found when chelating (95.4°) [18d, 21]. In binuclear rhodium complexes, where dppm is a bridging group, this angle is about 109° [22]. The four-membered chelating ring is not planar, the $C(31)$ deviates by 0.41(1) Å from the plane passing through the $Rh, P(2)$ and $P(3)$ atoms.

Crystal and molecular structure of $[RhCl\{\eta^2-(C_6H_4)PPh_2\}(\eta^1-PCCl)(phen)](SbF_6) \cdot CH_2Cl_2$ (11)

In the crystals of **11** $[RhCl\{\eta^2-(C_6H_4)PPh_2\}(\eta^1-PCCl)(phen)]^+$ cations, SbF_6^- anions and dichloromethane molecules of solvation are present. A view of the cationic complex is shown in Fig. 3 together with the atomic numbering scheme. Selected bond distances and angles are given in Table 4.

The rhodium atom exhibits a distorted octahedral coordination geometry involving a terminal chlorine atom, the $P(2)$ and $C(14)$ atoms from the chelating metallated phosphine, the $N(1)$ and $N(2)$ atoms from the chelating phenanthroline and the $P(1)$ atom of the monodentate $P(o-C_6H_4)PPh_2$ ligand. The chelating $(C_6H_4)PPh_2$ and phen ligands form with the rhodium atom a four- and a five-membered ring, respectively;

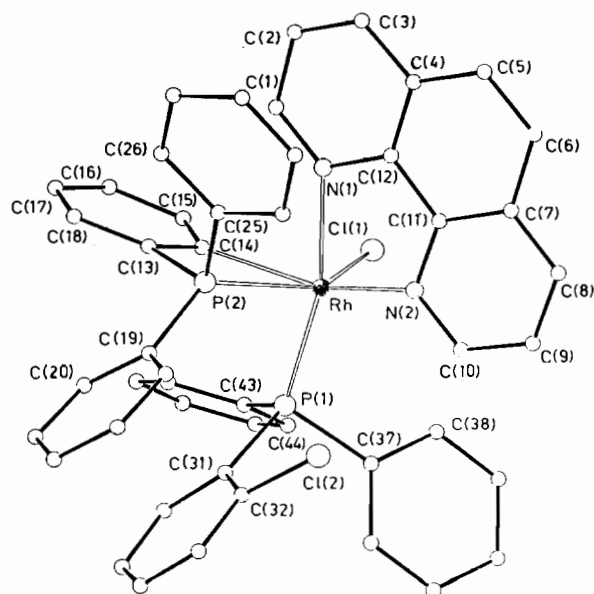


Fig. 3. Molecular structure of the complex $[RhCl\{\eta^2-(C_6H_4)PPh_2\}(\eta^1-PCCl)(phen)](SbF_6)$ (**11**) including the atomic numbering scheme.

TABLE 4. Selected bond distances (Å) and angles (°) for $[RhCl\{\eta^2-(C_6H_4)PPh_2\}(\eta^1-PCCl)(phen)](SbF_6) \cdot CH_2Cl_2$ (**11**)

| | | | |
|------------------|----------|------------------|----------|
| Rh–Cl(1) | 2.423(2) | Rh–P(1) | 2.370(3) |
| Rh–P(2) | 2.372(2) | Rh–N(1) | 2.152(6) |
| Rh–N(2) | 2.223(5) | Rh–C(14) | 2.001(7) |
| Cl(2)–C(32) | 1.731(7) | P(1)–C(31) | 1.850(7) |
| P(1)–C(37) | 1.838(7) | P(1)–C(43) | 1.844(6) |
| P(2)–C(13) | 1.793(6) | P(2)–C(19) | 1.818(7) |
| P(2)–C(25) | 1.832(7) | N(1)–C(1) | 1.359(9) |
| N(1)–C(12) | 1.344(8) | N(2)–C(10) | 1.349(9) |
| N(2)–C(11) | 1.373(9) | | |
| N(2)–Rh–C(14) | 165.1(2) | N(1)–Rh–C(14) | 87.8(2) |
| N(1)–Rh–N(2) | 77.5(2) | P(2)–Rh–C(14) | 68.8(2) |
| P(2)–Rh–N(2) | 107.6(2) | P(2)–Rh–N(1) | 86.2(2) |
| P(1)–Rh–C(14) | 92.4(2) | P(1)–Rh–N(2) | 102.4(2) |
| P(1)–Rh–N(1) | 174.1(2) | P(1)–Rh–P(2) | 99.4(1) |
| Cl(1)–Rh–C(14) | 93.3(2) | Cl(1)–Rh–N(2) | 87.7(2) |
| Cl(1)–Rh–N(1) | 85.2(2) | Cl(1)–Rh–P(2) | 160.4(1) |
| Cl(1)–Rh–P(1) | 88.9(1) | Rh–P(1)–C(43) | 112.0(2) |
| Rh–P(1)–C(37) | 118.6(2) | Rh–P(1)–C(31) | 118.7(2) |
| Rh–P(2)–C(25) | 114.2(2) | Rh–P(2)–C(19) | 135.8(2) |
| Rh–P(2)–C(13) | 82.1(2) | Rh–N(1)–C(12) | 114.9(4) |
| Rh–N(1)–C(1) | 126.0(5) | Rh–N(2)–C(11) | 110.0(4) |
| Rh–N(2)–C(10) | 129.9(5) | P(2)–C(13)–C(18) | 136.9(5) |
| P(2)–C(13)–C(14) | 101.5(5) | Rh–C(14)–C(13) | 107.5(5) |
| Rh–C(14)–C(15) | 131.0(5) | | |

the strongest distortions in the octahedral coordination around rhodium are due to the narrow bite angles, 68.8(2)° for $(C_6H_4)PPh_2$ and 77.5(2)° for phen. The value of the bite angle for $(C_6H_4)PPh_2$ in **11** is practical equal to that found in **2**.

The $Rh-N(1)$ bond distance, 2.152(6) Å, is significantly shorter than the $Rh-N(2)$ one, 2.223(5) Å; this could be due to the relative *trans* influence of $C(14)$, *trans* to $N(2)$, with respect to $P(1)$, *trans* to $N(1)$, as already found in some related complexes [3d, e]. In $[(\eta^5-C_5Me_5)Rh(phen)Cl](ClO_4)$, one of the few $Rh(III)$ –phen complexes structurally characterized [23], the $Rh-N$ bond distances were found to be 2.109(3) and 2.128(3) Å, but the coordination around Rh is distorted tetrahedral (the centroid of the pentamethylcyclopentadienyl ring occupying a coordination site).

The $N(1)C(12)C(11)N(2)$ moiety of the pentaatomic chelating ring is planar with the Rh atom deviating the 0.117(2) Å from the mean plane through it. The phen ligand as a whole is roughly planar (maximum deviations from the mean plane 0.06(1) Å for $C(3)$ and $C(8)$).

The $Rh-P(1)$ and $Rh-P(2)$ bond lengths, 2.370(3) and 2.372(2) Å, involving the metallated phosphine and the $P(o-C_6H_4)PPh_2$ ligand, are practically equal and considerably longer than those reported for $Rh(III)$ complexes containing aryl orthometallated phosphines. The value of the $Rh-Cl$ bond distance, 2.423(2) Å, is slightly longer than the one found in

$[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{phen})\text{Cl}](\text{Cl}(\text{O}_4))$ [23] and falls in the range of those reported for related complexes [3e, g]. It is to note that the $\text{P}(o\text{-ClC}_6\text{H}_4)\text{PPh}_2$ ligand acts as monodentate in contrast with what found in other related complexes where it acts as bidentate ligand [3e, g]. As in **2** the four-membered ring of the metallated phosphine is planar (maximum deviation from the mean plane 0.04(1) Å for C(13)).

Experimental

General comments

Chemical reactions were carried out under dry argon by Schlenk-line procedures. All solvents were reagent grade and were dried and distilled before use. $[\text{RhCl}_2\{\eta^2\text{-}(\text{C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-PCCl})$ (**1**) [3e], $[\text{RhCl}_2\{\eta^2\text{-}(\text{C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-dppm})]$ (**2**) [3f], $[\text{RhCl}_2\{\eta^2\text{-}(\text{C}_6\text{H}_4)\text{PPh}_2\}(\eta^2\text{-dppe})]$ (**3**) [3f] and $[\text{RhCl}(\eta^2\text{-PCCl})(\eta^1\text{-PCCl})]$ [3f] were prepared by published procedures. Doubly metallated compounds $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2\{(\text{C}_6\text{H}_4)\text{PPh}_2\}_2(\text{HO}_2\text{CCH}_3)_2]$ [5a] and $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2\{(\text{C}_6\text{H}_4)\text{PMePh}\}_2(\text{HO}_2\text{CCH}_3)_2]$ [5e], were prepared according to literature procedures. The analogous compound with PMe_2Ph , $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2\{(\text{C}_6\text{H}_4)\text{PMe}_2\}_2(\text{HO}_2\text{CCH}_3)_2]$ was prepared in the same way as the above compounds. Silica gel (70–230 mesh, 60 Å) was used to pack chromatographic columns. Phosphines and chlorotrimethylsilane were used as purchased. The ^{31}P NMR were recorded on a Bruker AC-200 FT spectrometer, operating at 81.015 MHz, with 85% H_3PO_4 as external reference. ^{31}P NMR data are given in Table 1. The electrochemical experiments were carried out in a three-electrode cell; the working and auxiliary electrodes were platinum, the reference electrode was a saturated calomel electrode electrically connected to the solution by a 'salt bridge' containing a saturated solution of the supporting electrolyte and the solvent. Cyclic voltammograms were obtained with a programming function generator 305 HQ instrument connected to a Amel potentiostat, and were recorded on a Riken-Denshi F-35 x-y recorder. The solvent used was tetrahydrofuran which had been freshly distilled from sodium benzophenone. The supporting electrolyte, NBu_4PF_6 , was recrystallized from ethanol and dried at 80 °C under vacuum for 48 h. Potential-controlled electrolysis was carried out in a three-compartment cell separated by fritted glass. Working and auxiliary electrodes were platinum mesh. The charge transferred was calculated by recording intensity versus time and carrying out a further integration. The system was calibrated against cobaltocene; ESR spectra were recorded on a Bruker ER 200 D spectrometer working with X-band (9.4–9.8 GHz). In order to prove the presence of paramagnetic species, we carried out simultaneous ESR and electrochemical experiments.

The electrolysis was performed by placing a special flat cell inside the microwave cavity of the X-band spectrometer. We used the Willmad and Glass Co. electrolytic cell assembly for ESR studies. The tetrahydrofuran solutions were degassed for 15 min to avoid the scavenging effect of the dissolved oxygen.

Synthesis of $[\text{RhCl}(\eta^1\text{-PCCl})(\eta^2\text{-P-P})]$

($\text{P-P} = \text{dppm}$ (**4**), dppe (**5**))

To a solution of the complex $[\text{RhCl}(\eta^2\text{-PCCl})(\eta^1\text{-PCCl})]$ (75 mg, 0.103 mmol) in dichloromethane was added the corresponding phosphine, dppm or dppe (0.103 mmol). The solution colour changed rapidly from red to yellow and was stirred for 2 h. After evaporation of solvent the resulting oil was recrystallized in dichloromethane:hexane to give compound **4** (yield 74%) or **5** (yield 77%). *Anal.* Found: C, 63.7; H, 4.2. Calc. for $\text{C}_{43}\text{H}_{36}\text{Cl}_2\text{P}_3\text{Rh}$ (**4**): C, 63.0; H, 4.4%. Found: C, 64.0; H, 4.3. Calc. for $\text{C}_{44}\text{H}_{38}\text{Cl}_2\text{P}_3\text{Rh}$ (**5**): C, 63.3; H, 4.6%.

Synthesis of compounds $[\text{RhCl}_2(\eta^2\text{-}(\text{C}_6\text{H}_4)\text{PPh}_2)(\eta^2\text{-P-P})]$ ($\text{P-P} = \text{dppm}$ (**2**), dppe (**3**))

A solution of complex **4** or **5** (0.122 mmol) in 96% ethanol was refluxed for 2 h yielding a yellow suspension which was filtered and the product **2** (yield 85%) or **3** (yield 82%) was washed with hexane.

Synthesis of $[\text{RhCl}_2(\eta^2\text{-PC}')(\eta^2\text{-dppm})]$ ($\text{PC}' = (\text{C}_6\text{H}_4)\text{PPh}_2$ (**2**), $(\text{C}_6\text{H}_4)\text{PMePh}$ (**6**), $(\text{C}_6\text{H}_4)\text{PMe}_2$ (**7**))

0.1 mmol of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\mu\text{-PC}')_2(\text{HO}_2\text{CCH}_3)_2]$ was dissolved in dried tetrahydrofuran to give a blue solution. The solution was slightly heated and 0.2 mmol of chlorotrimethylsilane was added giving a green solution which was refluxed for 5 min and 0.2 mmol of dppm were added yielding a red–orange solution. After refluxing for 30 min the solution was stirred for 5 h at room temperature. The solvent was evaporated and the crude product was redissolved in dichloromethane:hexane (1:1). The solution was chromatographed in a column (30 × 1 cm) packed with silica gel in hexane. Elution with dichloromethane:hexane (6:1) separated a red band which probably contained dinuclear dirhodium(II) compound (see discussion). On further elution with acetone a yellow band of compound **2**, **6** or **7** was obtained. The fraction was concentrated under vacuum and addition of hexane gave compound **2** (yield 47%), **6** (yield (60%) or **7** (yield 40%). *Anal.* Found: C, 60.4; H, 4.5. Calc. for $\text{C}_{38}\text{H}_{34}\text{Cl}_2\text{P}_3\text{Rh}$ (**6**): C, 60.2; H, 4.5%. Found: C, 57.1; H, 4.7. Calc. for $\text{C}_{33}\text{H}_{32}\text{Cl}_2\text{P}_3\text{Rh}$ (**7**): C, 57.0; H, 4.7%.

TABLE 5. Fractional atomic coordinates with e.s.d.s in parentheses for the non-hydrogen atoms of $[\text{RhCl}_2(\eta^2\text{-C}_6\text{H}_4)\text{PPh}_2](\eta^2\text{-dppm})$ (**2**)

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|-------|------------|-------------|-------------|
| Rh | 0.36671(6) | 0.20648(6) | 0.14103(3) |
| Cl(1) | 0.4357(2) | 0.0402(2) | 0.1483(1) |
| Cl(2) | 0.4990(2) | 0.2711(2) | 0.0909(1) |
| P(1) | 0.2375(2) | 0.1538(2) | 0.0514(1) |
| P(2) | 0.4812(2) | 0.2588(2) | 0.2347(1) |
| P(3) | 0.3229(2) | 0.3637(2) | 0.1578(1) |
| C(1) | 0.1694(9) | 0.1229(8) | 0.1093(5) |
| C(2) | 0.2374(7) | 0.1530(8) | 0.1647(5) |
| C(3) | 0.2061(9) | 0.1440(8) | 0.2189(6) |
| C(4) | 0.1061(9) | 0.1051(9) | 0.2137(6) |
| C(5) | 0.0372(10) | 0.0781(10) | 0.1586(6) |
| C(6) | 0.0668(9) | 0.0833(10) | 0.1029(5) |
| C(7) | 0.2595(9) | 0.0470(8) | 0.0083(5) |
| C(8) | 0.3452(10) | 0.0476(9) | -0.0169(5) |
| C(9) | 0.3625(11) | -0.0317(10) | -0.0518(6) |
| C(10) | 0.2992(12) | -0.1098(11) | -0.0608(7) |
| C(11) | 0.2150(11) | -0.1175(11) | -0.0302(7) |
| C(12) | 0.1942(10) | -0.0348(10) | 0.0024(7) |
| C(13) | 0.1566(9) | 0.2308(8) | -0.0096(6) |
| C(14) | 0.0656(11) | 0.2744(11) | -0.0019(7) |
| C(15) | 0.0112(13) | 0.3405(13) | -0.0532(10) |
| C(16) | 0.0470(17) | 0.3626(14) | -0.1043(9) |
| C(17) | 0.1384(16) | 0.3227(12) | -0.1075(6) |
| C(18) | 0.1956(12) | 0.2542(10) | -0.0617(6) |
| C(19) | 0.6227(8) | 0.2545(8) | 0.2483(5) |
| C(20) | 0.6673(8) | 0.1755(9) | 0.2233(5) |
| C(21) | 0.7773(11) | 0.1720(10) | 0.2362(7) |
| C(22) | 0.8399(11) | 0.2423(11) | 0.2739(7) |
| C(23) | 0.7917(11) | 0.3210(12) | 0.2946(7) |
| C(24) | 0.6824(10) | 0.3281(10) | 0.2823(7) |
| C(25) | 0.4658(8) | 0.2209(7) | 0.3100(4) |
| C(26) | 0.4871(9) | 0.2826(8) | 0.3611(5) |
| C(27) | 0.4843(10) | 0.2446(10) | 0.4202(6) |
| C(28) | 0.4624(9) | 0.1477(9) | 0.4268(5) |
| C(29) | 0.4429(9) | 0.0848(9) | 0.3756(5) |
| C(30) | 0.4437(9) | 0.1220(8) | 0.3175(5) |
| C(31) | 0.4451(8) | 0.3895(7) | 0.2196(5) |
| C(32) | 0.3023(7) | 0.4605(7) | 0.0992(5) |
| C(33) | 0.2851(8) | 0.5592(9) | 0.1190(5) |
| C(34) | 0.2707(10) | 0.6333(9) | 0.0748(7) |
| C(35) | 0.2739(11) | 0.6126(10) | 0.0124(6) |
| C(36) | 0.2886(11) | 0.5171(10) | -0.0051(6) |
| C(37) | 0.3048(9) | 0.4409(8) | 0.0388(5) |
| C(38) | 0.2158(9) | 0.3828(7) | 0.1942(6) |
| C(39) | 0.2374(12) | 0.3874(9) | 0.2602(6) |
| C(40) | 0.1500(19) | 0.3953(11) | 0.2838(10) |
| C(41) | 0.0461(16) | 0.3963(12) | 0.2457(11) |
| C(42) | 0.0313(13) | 0.3920(13) | 0.1848(11) |
| C(43) | 0.1139(9) | 0.3826(10) | 0.1525(8) |

*Synthesis of compounds $[\text{RhCl}(\eta^2\text{-PC})(\eta^2\text{-P-P})](\text{SbF}_6)$ (*P-P* = *dppm* (**8**), *dppe* (**9**))*

0.2 mmol of compounds **2** or **3** was dissolved in dichloromethane, under argon atmosphere, and 0.2 mmol of AgSbF_6 was added. The mixture was stirred for 10 h and the AgCl precipitate was separated by filtration. The solution was evaporated to dryness under

TABLE 6. Fractional atomic coordinates with e.s.d.s in parentheses for the non-hydrogen atoms of $[\text{RhCl}(\eta^2\text{-C}_6\text{H}_4)\text{PPh}_2](\eta^1\text{-PCCl})(\text{phen})](\text{SbF}_6) \cdot \text{CH}_2\text{Cl}_2$ (**11**)

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|-------|------------|------------|------------|
| Rh | 0.7815(1) | 0.8369(1) | 0.8871(1) |
| Cl(2) | 0.5976(1) | 0.6568(1) | 0.7668(2) |
| Cl(1) | 0.7966(1) | 0.9058(1) | 1.0825(1) |
| P(1) | 0.7782(1) | 0.7149(1) | 0.9783(1) |
| P(2) | 0.8242(1) | 0.7921(1) | 0.6933(1) |
| N(1) | 0.7862(4) | 0.9536(3) | 0.8225(4) |
| N(2) | 0.6134(4) | 0.8613(3) | 0.8797(4) |
| C(1) | 0.8734(6) | 0.9974(4) | 0.7934(6) |
| C(2) | 0.8693(6) | 1.0754(4) | 0.7503(7) |
| C(3) | 0.7769(7) | 1.1059(4) | 0.7403(7) |
| C(4) | 0.6848(6) | 1.0618(4) | 0.7760(6) |
| C(5) | 0.5857(7) | 1.0926(5) | 0.7679(8) |
| C(6) | 0.4964(7) | 1.0485(5) | 0.8064(8) |
| C(7) | 0.5046(5) | 0.9690(4) | 0.8427(6) |
| C(8) | 0.4177(5) | 0.9224(5) | 0.8788(7) |
| C(9) | 0.4293(5) | 0.8455(5) | 0.9107(7) |
| C(10) | 0.5287(5) | 0.8168(5) | 0.9112(6) |
| C(11) | 0.6031(5) | 0.9372(4) | 0.8478(5) |
| C(12) | 0.6930(5) | 0.9849(3) | 0.8149(5) |
| C(13) | 0.9551(5) | 0.8168(4) | 0.7540(6) |
| C(14) | 0.9369(5) | 0.8408(3) | 0.8722(5) |
| C(15) | 1.0200(5) | 0.8715(4) | 0.9518(6) |
| C(16) | 1.1209(5) | 0.8775(5) | 0.9084(7) |
| C(17) | 1.1385(6) | 0.8515(5) | 0.7893(7) |
| C(18) | 1.0571(5) | 0.8221(4) | 0.7110(6) |
| C(19) | 0.8202(5) | 0.6967(4) | 0.6088(6) |
| C(20) | 0.9025(6) | 0.6475(4) | 0.6280(6) |
| C(21) | 0.9074(7) | 0.5756(5) | 0.5578(7) |
| C(22) | 0.8247(9) | 0.5515(6) | 0.4701(8) |
| C(23) | 0.7439(8) | 0.6010(5) | 0.4505(7) |
| C(24) | 0.7402(6) | 0.6736(5) | 0.5180(6) |
| C(25) | 0.7899(5) | 0.8581(4) | 0.5783(5) |
| C(26) | 0.8702(7) | 0.8941(5) | 0.5083(7) |
| C(27) | 0.8447(9) | 0.9488(6) | 0.4229(8) |
| C(28) | 0.7379(11) | 0.9657(6) | 0.4086(9) |
| C(29) | 0.6621(8) | 0.9298(6) | 0.4745(8) |
| C(30) | 0.6884(6) | 0.8747(5) | 0.5614(6) |
| C(31) | 0.7774(5) | 0.6217(4) | 0.8830(5) |
| C(32) | 0.6983(5) | 0.5975(4) | 0.7968(6) |
| C(33) | 0.6948(6) | 0.5226(5) | 0.7300(7) |
| C(34) | 0.7668(7) | 0.4723(5) | 0.7488(7) |
| C(35) | 0.8480(7) | 0.4931(4) | 0.8401(8) |
| C(36) | 0.8534(6) | 0.5672(4) | 0.9046(6) |
| C(37) | 0.6688(5) | 0.6890(4) | 1.0720(6) |
| C(38) | 0.6348(6) | 0.7467(5) | 1.1537(7) |
| C(39) | 0.5597(6) | 0.7246(5) | 1.2352(7) |
| C(40) | 0.5165(6) | 0.6452(6) | 1.2368(7) |
| C(41) | 0.5485(6) | 0.5877(6) | 1.1533(8) |
| C(42) | 0.6234(6) | 0.6097(5) | 1.0716(6) |
| C(43) | 0.8897(5) | 0.7119(4) | 1.0862(5) |
| C(44) | 0.8759(6) | 0.7139(5) | 1.2086(6) |
| C(45) | 0.9629(8) | 0.7121(5) | 1.2893(7) |
| C(46) | 1.0603(6) | 0.7085(4) | 1.2507(7) |
| C(47) | 1.0771(6) | 0.7065(4) | 1.1278(8) |
| C(48) | 0.9911(5) | 0.7082(4) | 1.0446(7) |
| Sb | 0.3418(1) | 0.7333(1) | 0.5291(1) |
| F(1) | 0.3196(4) | 0.7277(3) | 0.3616(4) |
| F(2) | 0.3664(7) | 0.7367(5) | 0.6935(5) |

(continued)

TABLE 6. (continued)

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|-------|------------|------------|------------|
| F(3) | 0.4772(7) | 0.7624(9) | 0.5133(7) |
| F(4) | 0.2098(7) | 0.6880(9) | 0.5396(8) |
| F(5) | 0.3721(9) | 0.6295(4) | 0.5170(7) |
| F(6) | 0.2938(12) | 0.8293(5) | 0.5385(8) |
| C(49) | 0.7457(12) | 0.4061(11) | 0.1793(10) |
| Cl(3) | 0.6712(3) | 0.3795(2) | 0.0445(3) |
| Cl(4) | 0.8712(3) | 0.4331(3) | 0.1686(3) |

vacuum and the product was redissolved with dichloromethane and precipitated with hexane, yielding a yellow solid **8** (yield 79%) or **9** (yield 82%). *Anal.* Found: C, 50.0; H, 3.4. Calc. for $C_{43}H_{36}P_3ClRhSbF_6$ (**8**): C, 50.6; H, 3.5%. Found: C, 50.5; H, 3.6. Calc. for $C_{44}H_{38}P_3ClRhSbF_6$ (**9**): C, 51.1; H, 3.7%.

*Synthesis of [RhCl(η^2 -PC)(η^1 -PCCl)(N-N)](SbF₆) (N-N = bipyridine (**10**), phenanthroline (**11**))*

To a dichloromethane solution of $[RhCl_2\{\eta^2-(C_6H_4)PPh_2\}(\eta^2-PCCl)$ (**1**) (150 mg, 0.205 mmol) and 4,4'-bipyridine or 1,10-phenanthroline (0.205 mmol), $AgSbF_6$ (71 mg, 0.205 mmol) was added. The mixture was stirred vigorously and after 12 h a white precipitate of $AgCl$ was separated by filtration from a light yellow solution. This solution was concentrated to half of the initial volume under vacuum. Addition of 10 ml of n-hexane caused the formation of a yellow oil, which was washed with three portions of 10 ml of n-hexane and dissolved with 5 ml of dichloromethane. Slow diffusion of n-hexane gave after four days yellow crystals of complexes **10** and **11** suitable for X-ray diffraction methods. Yield: compound **10**: 200 mg, 90%; compound **11**: 210 mg, 86%. *Anal.* Found: C, 48.64; H, 3.23; N, 2.38. Calc. for $C_{46}H_{36}N_2P_2Cl_2RhSbF_6 \cdot CH_2Cl_2$ (**10**): C, 48.08; H, 3.32; N, 2.48%. Found: C, 49.05; H, 3.20; N, 2.18. Calc. for $C_{48}H_{36}N_2P_2Cl_2RhSbF_6 \cdot CH_2Cl_2$ (**11**): C, 49.13; H, 3.18; N, 2.34%.

Crystal structure determination of the complexes

$[RhCl_2\{\eta^2-(C_6H_4)PPh_2\}(\eta^2-dppm)]$ (**2**) and $[RhCl_2\{\eta^2-(C_6H_4)PPh_2\}(\eta^1-PCCl)(phen)](SbF_6) \cdot CH_2Cl_2$ (**11**)

A yellow well formed single crystal of **2**, grown from a dichloromethane/hexane solution, and a yellow well formed single crystal of **11**, grown from a dichloromethane/methanol/hexane solution, were used for the X-ray analyses.

Crystal data for 2

$C_{43}H_{36}Cl_2P_3Rh$, $M_r = 819.49$, monoclinic, space group $P2_1/c$, $a = 13.317(5)$, $b = 13.561(5)$, $c = 22.132(7)$ Å, $\beta = 106.10(2)^\circ$, $V = 3840(2)$ Å³ (by least-squares refinement from the θ values of 30 accurately measured reflections with θ in the range 10.2–17.4°, $\lambda = 0.71073$

Å), $Z = 4$, $D_c = 1.417$ g cm⁻³, $F(000) = 1672$, $\mu(Mo K\alpha) = 7.30$ cm⁻¹.

Crystal data for 11

$C_{48}H_{36}Cl_2F_6N_2P_2RhSb \cdot CH_2Cl_2$, $M_r = 1197.26$, triclinic, space group $P\bar{1}$, $a = 12.810(4)$, $b = 16.946(8)$, $c = 11.314(6)$ Å, $\alpha = 93.86(1)$, $\beta = 92.50(1)$, $\gamma = 94.35(1)^\circ$, $V = 2440(2)$ Å³ (by least-squares refinement from the θ values of 30 accurately measured reflections with θ in the range 10.1–15.6°, $\lambda = 0.71073$ Å), $Z = 2$, $D_c = 1.629$ g cm⁻³, $F(000) = 1188$, $\mu(Mo K\alpha) = 12.33$ cm⁻¹.

Data were collected at room temperature on a Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo K α radiation and the $\theta/2\theta$ scan mode. All reflections with θ in the range 3–24° for both **2** and **11** were measured; of 6140 (**2**) and 7513 (**11**) independent reflections, 3398 (**2**) and 5580 (**11**), having $I > 2\sigma(I)$, were considered observed and used in the analyses. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collections.

The structures were solved by Patterson and Fourier methods, and refined by full-matrix (**2**) and blocked-matrix (**11**) least-squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. A dichloromethane molecule of solvation was found in the crystals of **11**. All hydrogen atoms of **2** were placed at their calculated positions (C–H = 1.00 Å) and introduced in the final structure factors calculation with a fixed isotropic thermal parameter ($U = 0.09$ Å²). All hydrogen atoms (except five) of **11** were located in the Fourier difference synthesis, but not refined; all were introduced in the final structure factors calculation with a fixed isotropic thermal parameter ($U = 0.09$ Å²). A weighting scheme $w = [\sigma^2(F_o + gF_o^2)]^{-1}$ was used in the last cycles of refinement with $g = 0.009$ (**2**) and 0.019 (**11**) at convergence. Final R and R' values were 0.0568 and 0.0627 (**2**) and 0.0464 and 0.0554 (**11**). The SHELX-76 and SHELXS-86 systems of computer programs were used [24]. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 25. Final atomic coordinates for the non-hydrogen atoms are given in Tables 5 (**2**) and 6 (**11**). All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Parma.

Supplementary material

Additional data available from the authors or from the Cambridge Crystallographic Data Centre comprise H atom coordinates and thermal parameters for both compounds **2** and **11**.

Acknowledgements

We thank the C.I.C.Y.T., Spain, and Ministero dell'Università e della Ricerca Scientifica e Tecnologica, Italy, for financial support.

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