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Photochemical ligand rearrangement in dirhodium(II) compounds. Structure of $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)PPh_2](\eta^2\text{-}PCCl)$ (PCCl = P(*o*-ClC_6H_4)Ph_2) ☆

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Abstract

The photochemical reaction of the adducts $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph]\cdot(P(p\text{-}XC_6H_4)_3)$ (X = H, Me, Cl), yield the compounds $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](\eta^2\text{-}PCCl)$, (PCCl = P(*o*-$ClC_6H_4$)$Ph_2$) in a ligand rearrangment reaction that involves activation of C–H and Rh–C bonds. The factors that favour this process are studied by carrying out photochemical reactions with different phosphines. The structure of $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)PPh_2](\eta^2\text{-}PCCl)$ has been determined by X-ray diffraction. $M_r = 1321.1$, orthorhombic, space group *Pbcn*, $a = 20.339(8)$, $b = 20.07(6)$, $c = 23.07(3)$ Å, $V = 9413(3)$ Å^3, $Z = 8$, $D_x = 1.86$ g cm^{-3}. Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å), μ(Mo Kα) = 13.83 cm^{-1}, $F(000) = 5280$, $T = 293$ K. Final conventional R factor = 0.062 for 4889 'observed' reflections and 500 variables. The compound contains three bridging ligands, two acetates and one metalated triphenylphosphine, and two chelating ligands, one acetate and one PCCl that acts as a P,Cl ligand, taking one equatorial (P) and one axial (Cl) coordination site. The axial Rh–Cl bond distance is 2.573(4) Å.

Keywords: Crystal structures; Photochemistry; Rhodium complexes; Carboxylate complexes; Dinuclear complexes

1. Introduction

Cyclometalation reactions on mononuclear compounds are well known [1], but the same processes involving two metal centres are much less common [2]. In recent years, we have been interested in the study of cyclometalation reactions of arylphosphines in dirhodium(II) compounds [3]. As a result of our studies, we know that $Rh_2(O_2CCX_3)_4$ (X = H, F) with arylphosphines in solution (1:2, molar ratio), undergoes stepwise orthometalation reaction of the phosphine ligands yielding the doubly metalated compounds.

Isolation and structural characterization of reaction intermediates **II** and **IV** (Scheme 1), that contain phosphines in equatorial coordination has been achieved when an *ortho*-functionalized phosphine is used [4]. With other type of phosphines these intermediates are very reactive and their preparation by thermal reactions is not feasible. We have recently found [5] that they are best achieved by photochemical irradiation of the species **I** and **III**. For the reaction of compounds of type **III**, it was observed that rearrangement of the metalated and equatorial phosphine occurs to some extent giving a mixture of compounds. Such rearrangement was enhanced by the presence of very minor amounts of acetic acid in the solution.

We present in this paper the study of the photochemical reaction of several adducts of the monometalated compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph]\cdot(H_2O)_2$ (**1**) with different phosphines. We also report in this paper the crystal structure of the compound $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)PPh_2](\eta^2\text{-}PCCl)$ (PCCl = P(*o*-ClC_6H_4)Ph_2) (**5**), an intermediate compound of type **IV**.

☆ Dedicated to Professor F.A. Cotton on his 65th birthday.

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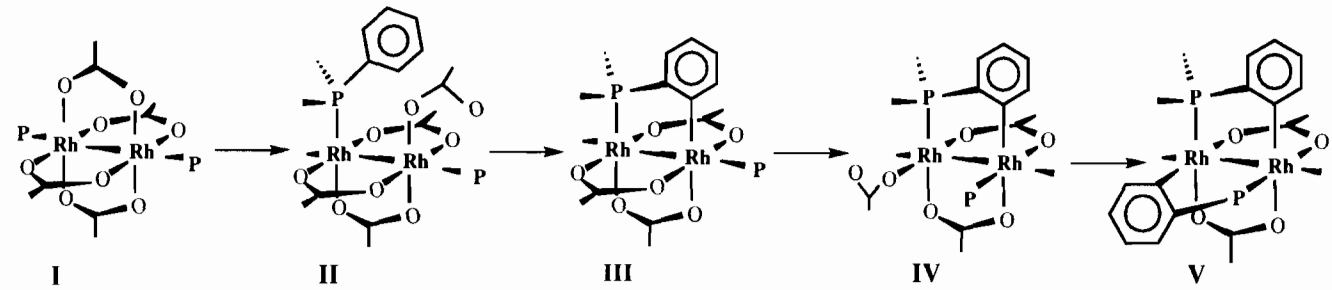


Scheme 1.

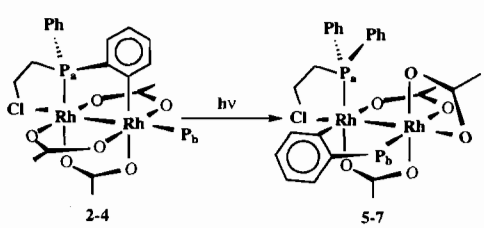
2. Results and discussion

2.1. Photochemical reaction of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph]\cdot(H_2O)_2$ (1) with $P(p\text{-}XC_6H_4)_3$ (X=H, Me, Cl)

The reaction of compound **1** with the phosphines $P(p\text{-}XC_6H_4)_3$ (X=H, Me, Cl) in 1:1 ratio, gives the adducts $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph]\cdot(P(p\text{-}XC_6H_4)_3)$ (X=H (**2**), Me (**3**), Cl (**4**)), with displacement of water from the axial positions. These compounds were characterized in solution by ^{31}P NMR spectroscopy and were not isolated. Solutions of compounds **2**, **3** and **4** in $CDCl_3$ were photochemically irradiated.

^{31}P NMR spectroscopy is a very convenient technique for monitoring these reactions since ^{31}P chemical shifts have diagnostic values for the different coordination modes of the phosphorus ligands in these dirhodium compounds [3]. So ^{31}P NMR signals from cyclometalated phosphines are in the range 10–25 ppm, ^{31}P signals from axial phosphine appear at lower chemical shift values (~ -10 ppm), while signals from equatorial phosphines appear at $\sim$40–50 ppm. The highest chemical shift values in this range correspond to equatorial functionalized phosphines that can also coordinate to an axial site of the rhodium dimer.

After irradiating solutions of compounds **2**, **3** and **4** in $CDCl_3$ for 15 min some changes are observed in the spectrum. Further irradiation gives ^{31}P NMR spectra with a very complex set of signals indicating the presence in solution of two or more products. After 4 h of irradiation the reaction is completed and only one product is present in solution. According to the ^{31}P NMR data this compound must contain one metalated and one equatorial phosphine (see Scheme 2).



Scheme 2.

The ^{31}P NMR data for the different reaction products are summarized in Table 1. All of the above mentioned results suggest that in these particular reaction conditions important ligands rearrangement takes place with Rh–C bond cleavage at the metalated phosphine PCCl and further metalation of the entering phosphine yielding compounds of formula $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(XC_6H_3)P(p\text{-}XC_6H_4)_2][\eta^2\text{-}PCCl]$ (X=H (**5**), Me (**6**), Cl (**7**)). In order to confirm this assumption the crystal structure of compound **5** was solved.

2.2. Molecular structure of $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)P(Ph_2][\eta^2\text{-}PCCl]$ (5)

Fig. 1 shows a perspective view of compound **5** and also defines the atom numbering scheme. The molecule is a dinuclear Rh(II) compound with a single bond linking the metal centres (Rh–Rh bond distance 2.529(1) Å). It also contains two cisoid bridging acetate ligands and one orthometalated triphenylphosphine. In the fourth bridging site there is one acetate in a mode of ligation that is intermediate between chelating and monodentate with a short equatorial Rh–O bond (Rh(2)–O(5)=2.038(9) Å) and a long axial Rh–O bond (Rh(2)–O(6)=2.27(1) Å.) There is also one PCCl phosphine acting as chelating ligand with P and Cl atoms in equatorial and axial positions, respectively. Bond distances and angles support the axial coordination of acetate and phosphine ligands, through O(6) and Cl(1) atoms. There are a few precedents of this arrangement of the acetate group for dirhodium(II) compounds [4a, 6]. In particular there is a closely related compound $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)P(o\text{-}BrC_6F_3)Ph]\text{-}[\eta^2\text{-}P(o\text{-}BrC_6F_4)Ph_2]$, that has been structurally characterized [4a]. In compound **5** the acetate group has a more regular coordination which is closer to a chelating mode than in the previously reported compounds ($Rh\text{–}O_{axial}$ 2.27(1) Å, versus 2.46(8) Å [6] and 2.43(2) Å [4a]; Rh–Rh–O(6) 170.8(3)°, versus 163.5(5)° [6]). The Cl atom of the phosphine has a contact distance with the Rh atom of 2.573(4) Å, which is, by all standards, a strong axial ligation. Several dirhodium(II) compounds with axial Rh–Cl bonds have been structurally characterized [7]. The distances are in the range from 2.470(1) Å [7a] to 2.5853(6) Å [7e] with Cl showing

Table 1
$^{31}P\{^1H\}$ NMR data [a]

Complex	$\delta(P_a)$	^1J(Rh–P)	^2J(Rh–P)	$\delta(P_b)$	^1J(Rh–P)	^2J(Rh–P)	^3J(P–P)
1 [b]	17.60	155	7				
2	24.2	158		−8.8	24		
3	24.3	161		−9.6	114	29	10
4	23	159	11	−13.1	113	31	11
5	52.5	181	4	18.1	143	8	
6	52.9	182	4	16.9	142	8	
7	51.8	176	4	19.5	144	7	
8	24.5	161		−11.8	113	30	10
9	19.5	151	8	45.0	182	4	
10 [c]	19.9	147	5				
11	24.7	149		−8.9	97		
12	17.3	137	9	41.8	187	4	

[a] Chemical shifts in ppm; coupling constants in Hz.
[b] Ref. [3a].
[c] Ref. [9].

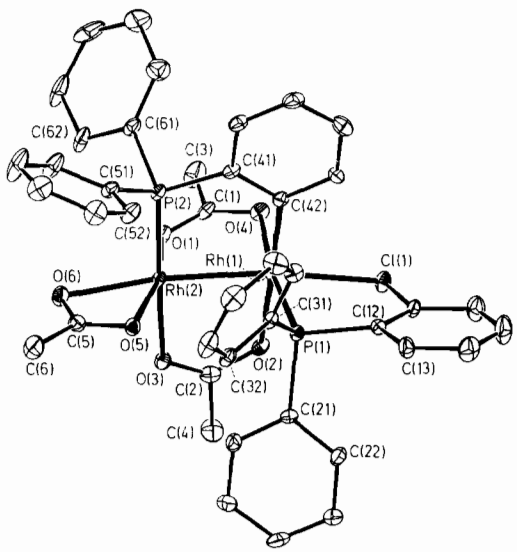


Fig. 1. Perspective view of compound 5 with the atomic numbering scheme.

deviations from the Rh–Rh bond direction which range from 0 to 12°.

The stability of compounds **5–7** must be the driving force for the observed ligand rearrangement that involves Rh–C and C–H bond activation. In order to obtain additional information about this aspect of the reaction we photolyzed the adduct $Rh_2(O_2CCH_3)_3$-$[(C_6H_4)PPh_2]\cdot[\eta^2$-PCCl] using the same experimental conditions as those described above. In this case the irradiation only produced compound **5**, and no intermediate products were observed by monitoring the reaction by ^{31}P NMR spectroscopy. This result confirms that **5** is the stable species under photochemical conditions.

We also studied the photochemical behaviour of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph]\cdot(P(p\text{-}MeOC_6H_4)Ph_2)$ (**8**). In this compound, that can be prepared by reaction of **1** with the phosphine $P(o\text{-}MeOC_6H_4)Ph_2$, the two phosphines can act as chelating ligands. The photochemical reaction of **8** in $CDCl_3$ solution was completed after 1 h, during which no intermediate products were observed by ^{31}P NMR. The only compound isolated from this reaction was $Rh_2(O_2CCH_3)_2$-$(\eta^2\text{-}O_2CCH_3)[(C_6H_4)P(o\text{-}ClC_6H_4)Ph)[\eta^2\text{-}P(o\text{-}MeOC_6H_4)Ph_2]$ (**9**), which according to the spectroscopic data has the phosphine $P(o\text{-}MeOC_6H_4)Ph_2$ in an equatorial (P) and axial (O) coordination.

We had previously observed that monometalated dirhodium compounds in a protic acid medium undergo reversible Rh–C bond cleavage [4b,8]. However the photochemical activation of this bond was not directly observed even though it was postulated in order to explain some results [8].

We have also reported $Rh_2(O_2CCH_3)_3[(o\text{-}ClC_6H_3)PPh_2]\cdot(H_2O)_2$ (**10**) [9] an isomer of **1** with the phosphine metalated at the substituted ring. We have observed [10] that in acetic acid medium, the electrophilic cleavage of the Rh–C bond is easier for compound **1** than for compound **10**. This difference of reactivity was attributed to the electronic deactivation of the Rh–C bond in **10** due to the chlorine substituent.

As an extension of this comparative study of reactivity, we have prepared the adduct $Rh_2(O_2CCH_3)_3[(o\text{-}ClC_6H_3)PPh_2]\cdot(PPh_3)$ (**11**) by standard methods. Photochemical reaction of **11** in $CDCl_3$ solution only produced rapid axial to equatorial migration of the triphenylphosphine yielding $Rh_2(O_2CCH_3)_2(\eta^2$-$O_2CCH_3)[(o\text{-}ClC_6H_3)PPh_2]\cdot(PPh_3)$ (**12**). In this case the rearrangement of the metalated and equatorial phosphines is not observed and this fact correlates well the observed differences in reactivity of the Rh–C bond in these two systems.

2.3. Exchange of acetate groups in compound 5

The ^1H NMR spectrum of compound **5** in $CDCl_3$ exhibits three singlet resonances in the methyl proton region at 1.55, 1.18 and 1.11 ppm assigned to the three different carboxylate groups. If some CD_3CO_2D is added to this solution the resonance at 1.55 ppm decreases in intensity while a new resonance at 2.01 ppm, due to free acetic acid, appears in the spectrum with increasing intensity. After 1 h the relative intensity of the signal at 1.55 ppm has decreased by two thirds of its initial value while the signals at 1.18 and 1.11 ppm maintain their intensity. This result confirms that, in compound **5**, acetic acid only exchanges with one of the acetate groups.

In order to investigate which of the acetate groups undergoes faster exchange in compound **5**, we ran additional experiments (Scheme 3). The isotopically labelled compound $Rh_2(O_2CCD_3)_{trans}(O_2CCH_3)_2$-$[(C_6H_4)PPh_2)](CD_3CO_2D)_2$ can be readily prepared following literature procedures [11]. The ^1H NMR of this compound only shows a signal at 1.25 ppm due to the two methyl groups of the *cis* acetates, which do not exchange in the conditions used. By addition of one mole of PCCl to this partially deuterated compound, the phosphine adduct $Rh_2(O_2CCD_3)_{trans}(O_2CCH_3)_2$-$[(C_6H_4)PPh_2)](CD_3CO_2D)\cdot(PCCl)$ is formed. Irradiation of this adduct for 50 min results in the formation of the isotopically labelled compound **5** (**5–d7**) that shows only two resonances in the methyl region at 1.18 and 1.11 ppm. No signal was observed at 1.55 ppm. This result supports the conclusion that the acetate group that is *trans* to the metalated phosphine is the one exchanging faster.

The kinetics of the exchange of *cis* acetate groups with acetic acid in $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2)]\cdot(CH_3CO_2H)_2$ has been recently reported [11]. An electrophilic attack at one oxygen atom of the bridging acetate group by a proton of the acetic acid was concluded to be the first and rate-determining step of the exchange process. The axially coordinated acetic acid was assumed to be responsible for the intramolecular attack. In compound **5** such an intramolecular attack is not possible since the compound does not have any available axial coordination site. The intermolecular attack must be also hindered because of the bulkiness of the equatorial phosphine. These structural features are consistent with the slower acetate exchange observed in compound **5** compared to compound $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2)](CH_3CO_2H)_2$. So, while for compound **5** only about 70% of acetate exchange is observed after 1 h, for $Rh_2(O_2CCH_3)_3$-$[(C_6H_4)PPh_2)](CH_3CO_2H)_2$ the exchange is completed in less than 5 min.

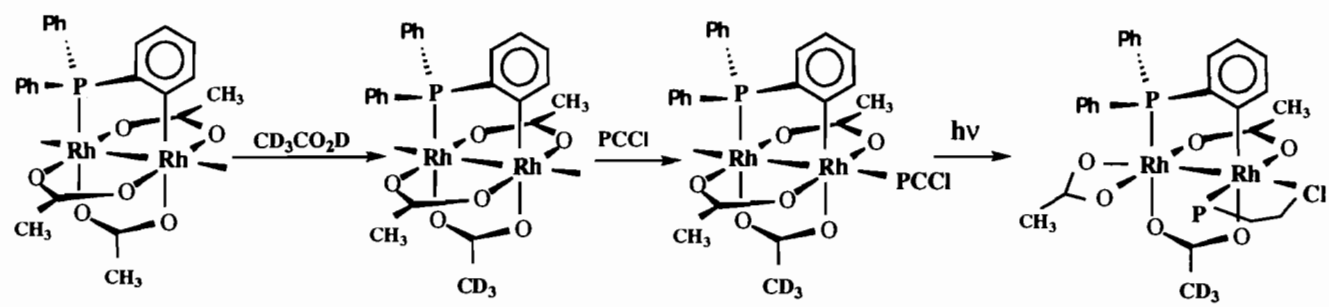
3. Experimental

3.1. Materials

$Rh_2(O_2CCH_3)_4(CH_3OH)_2$ [12], $Rh_2(O_2CCH_3)_3[(C_6$-$H_4)PPh_2]\cdot(HO_2CCH_3)_2$ [13], $Rh_2(O_2CCH_3)_3[(o\text{-}ClC_6$-$H_3)PPh_2]\cdot(HO_2CCH_3)_2$ [9] and PCCl [14] were prepared according to literature procedures. $Rh_2(O_2$-$CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_5)Ph]\cdot(HO_2CCH_3)_2$ was prepared using the same procedure described for $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2]\cdot(HO_2CCH_3)_2$ [13]. Commercial $P(C_6H_5)_3$ (Aldrich) was recrystallized from hot ethanol prior to use. $P(p\text{-}MeC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, $P(MeOC_6H_4)Ph_2$ and DO_2CCD_3 were used as purchased. Chloroform, dichloromethane and toluene were dried and degassed before use. All the reactions were carried out under Ar atmosphere using Schlenk techniques.

3.2. Preparation of $Rh(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2)][\eta^2\text{-}PCCl]$ (X=H (5), Me (6), Cl (7))

A mixture of 30 mg (0.04 mmol) of $Rh_2(O_2$-$CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph]\cdot(H_2O)_2$ and 0.04 mmol of $P(p\text{-}XC_6H_4)_3$ (X=H, Me, Cl) (1:1 molar ratio) was stirred in 5 ml of $CHCl_3$. The brown–orange solution obtained in each case was irradiated for 4 h during which time it changed to a green colour. The solvent was removed under vacuum and the solid was precipitated in CH_2Cl_2/hexane yielding $Rh_2(O_2CCH_3)_2(\eta^2$-



Scheme 3.

$O_2CCH_3)[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2)][\eta^2(o\text{-}ClC_6H_4)\text{-}PPh_2)]$ (X = H, Me, Cl), compounds.

3.2.1. $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)PPh_2)]\text{-}[\eta^2(o\text{-}ClC_6H_4)PPh_2)](CH_2Cl_2)_2$ (5)

Yield 85%. *Anal.* Found: C, 47.62; H, 3.73. Calc. for $Rh_2P_2Cl_5O_6C_{44}H_{41}$: C, 47.58; H, 3.72%. ^1H NMR ($CDCl_3$) spectrum (ppm): 1.11 (CH_3, 3H, s), 1.18 (CH_3, 3H, s), 1.55 (CH_3, 3H, s), 6.5–8 (aromatics, 28H, m). $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum: $\delta P_a = 52.5$ ppm, $^1J(Rh\text{–}P) = 181$ Hz, $^2J(Rh\text{–}P) = 4$ Hz, $\delta P_b = 18.1$ ppm, $^1J(Rh\text{–}P) = 143$ Hz, $^2J(Rh\text{–}P) = 8$ Hz. $^{13}C\{^1H\}$ NMR spectrum (ppm): 21.52 (CH_3, s), 23.35 (CH_3, s) 24.02 (CH_3, s), 120–161 (aromatics, m), 184.36 (OCO, s), 184.86 (OCO, s), 186.99 (OCO, s). The same compound was prepared by mixing 30 mg (0.04 mmol) of $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2]\cdot(H_2O)_2$ and 13 mg (0.04 mmol) of PCCl, in 20 ml of $CHCl_3$; the solution was irradiated for 1 h, changing from brown–orange to green. The solvent was removed and $Rh(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)PPh_2)][\eta^2(o\text{-}ClC_6H_4)PPh_2)]$ was precipitated in 5 ml of CH_2Cl_2/hexane (1/1). Yield 90%.

3.2.2. $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(p\text{-}MeC_6H_3)P(p\text{-}MeC_6H_4)_2)][\eta^2(o\text{-}ClC_6H_4)PPh_2)]$ (6)

Yield 87%. *Anal.* Found: C, 52.93; H, 4.23. Calc. for $Rh_2P_2Cl_5O_6C_{47}H_{47}$: C, 51.73; H, 4.25%. ^1H NMR ($CDCl_3$) spectrum (ppm): 1.13 (CH_3, 3H, s), 1.20 (CH_3, 3H, s), 1.61 (CH_3, 3H, s), 1.94 (CH_3, 3H, s), 2.22 (CH_3, 3H, s), 2.31 (CH_3, 3H, s), 6.5–8 (aromatics, 25H, m). $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum: $\delta P_a = 52.9$ ppm, $^1J(Rh\text{–}P) = 182$ Hz, $^2J(Rh\text{–}P) = 4$ Hz, $\delta P_b = 16.9$ ppm, $^1J(Rh\text{–}P) = 142$ Hz, $^2J(Rh\text{–}P) = 8$ Hz. $^{13}C\{^1H\}$ NMR spectrum (ppm): 21.25 (CH_3, s), 21.31 (CH_3, s), 21.50 (CH_3, s), 21.57 (CH_3, s), 23.31 (CH_3, s), 23.97 (CH_3, s), 120–140 (aromatics, m), 184.19 (OCO, s), 184.85 (OCO, s), 186.57 (OCO, s).

3.2.3. $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2][\eta^2(o\text{-}ClC_6H_4)PPh_2)](CH_2Cl_2)_3$ (7)

Yield 88%. *Anal.* Found: C, 41.27; H, 2.99. Calc. for $Rh_2P_2Cl_7O_6C_{45}H_{40}$: C, 41.61; H, 3.10%. ^1H NMR ($CDCl_3$) spectrum (ppm): 1.22 (CH_3, 3H, s), 1.33 (CH_3, 3H, s), 1.61 (CH_3, 3H, s), 6–8 (aromatics, 28H, m). $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum: $\delta P_a = 51.8$ ppm, $^1J(Rh\text{–}P) = 176$ Hz, $^2J(Rh\text{–}P) = 4$ Hz, $\delta P_b = 19.5$ ppm, $^1J(Rh\text{–}P) = 144$ Hz, $^2J(Rh\text{–}P) = 7$ Hz. $^{13}C\{^1H\}$ NMR spectrum (ppm): 21.71 (CH_3, s), 23.49 (CH_3, s) 23.97 (CH_3, s), 120–140 (aromatics, m), 184.93 (OCO, s), 184.99 (OCO, s), 187.22 (OCO, s).

3.3. Preparation of $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(o\text{-}ClC_6H_3)PPh_2]\cdot[PPh_3]$ (11)

A mixture of 50 mg (0.07 mmol) of $Rh_2(O_2CCH_3)_3[(o\text{-}ClC_6H_3)PPh_2]\cdot(H_2O)_2$ and 18 mg (0.07 mmol) of PPh_3 (1:1 molar ratio) was stirred in 5 ml of $CHCl_3$ under an argon atmosphere for a few minutes, yielding a red solution. After 30 min of radiation with an Hg-vapour lamp (OSRAM-125), the solution became green. The solvent was removed under vacuum and the solid was precipitated in 5 ml of CH_2Cl_2/hexane (1/1) yielding $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(o\text{-}ClC_6H_3)PPh_2]\cdot[PPh_3]\text{-}(CH_2Cl_2)$ (87% yield) as a green solid. *Anal.* Found: C, 50.96; H, 3.95. Calc. for $Rh_2P_2Cl_2O_6C_{43}H_{39}$: C, 50.34; H, 3.83%. ^1H NMR ($CDCl_3$) spectrum (ppm): 1.03 (CH_3, 3H, s), 1.26 (CH_3, 3H, s), 1.73 (CH_3, 3H, s), 6–8 (aromatics, 28H, m). $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum: $\delta P_a = 17.3$ ppm, $^1J(Rh\text{–}P) = 137$ Hz, $^2J(Rh\text{–}P) = 9.2$ Hz, $\delta P_b = 41.8$ ppm, $^1J(Rh\text{–}P) = 187$ Hz, $^2J(Rh\text{–}P) = 4$ Hz. $^{13}C\{^1H\}$ NMR spectrum (ppm): 22.65 (CH_3, s), 23.05 (CH_3, s) 23.94 (CH_3, s), 124–138 (aromatics, m), 183.76 (OCO, s), 183.82 (OCO, s), 188.64 (OCO, s).

3.4. Exchange of acetate groups with deuterated acetic acid 4 in compound 5

26 mg of compound **5** were dissolved in a $CDCl_3$/CD_3CO_2D mixture (0.5 ml/0.05 ml) inside an NMR tube. The exchange reaction was monitored by ^1H NMR spectroscopy.

The compound $Rh_2(O_2CCD_3)_{trans}(O_2CCH_3)_2[(C_6H_4)PPh_2)](CD_3CO_2D)_2$ was obtained by the procedure described in Ref. [11]. 25 mg of this product were mixed with 10 mg of PCCl (1:1 molar ratio) and dissolved in 0.6 ml of $CDCl_3$. The solution was irradiated for 50 min, following the procedure previously described.

3.5. X-ray crystallographic procedures

The molecular structure of $Rh(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)PPh_2)][\eta^2\text{-PCCl}]$ was obtained by general procedures. A detailed description is given below. The crystal parameters and basic information dealing with data collection and structure refinement are summarized in Tables 2, 3 and 4.

Green crystal, $0.26\times0.26\times0.20$ mm size. Mo Kα radiation graphite crystal monochromator, Nonius CAD4 single crystal diffractometer ($\lambda = 0.71073$ Å). Unit cell dimensions determined from the angular settings of 25 reflections with $10 < \theta < 20°$. Space group *Pbcn* from systematic absences. 9025 reflections measured, *hkl* range (0, 0, 0) to (24, 23, 27), theta limits ($0 < \theta < 25°$); ω–2θ scan technique with a variable scan rate and a maximum scan time of 60 s per reflection. Intensity checked throughout data collection by monitoring three standard reflections every 60 min. Final drift corrections between 0.98 and 1.03. On all reflections profile analysis performed [15,16]. Some double measured reflections were averaged, $R_{int} = \Sigma(|I| - \langle I\rangle)/\Sigma I = 0.050$, 8266 unique reflections and 4889 'observed' with $I > 3\sigma(I)$. Lorentz and polarization corrections applied and data reduced to $|F_o|$ values.

Table 2
Crystallographic data for $Rh_2(O_2CCH_3)_2(\eta^2\text{-}O_2CCH_3)[(C_6H_4)\text{-}PPh_2][\eta^2\text{-}PCCl]\cdot\{CHCl_3\}_2$

Formula	$Rh_2P_2Cl_7O_6C_{44}H_{39}$
Formula weight	1321.1
Space group	*Pbcn*
a (Å)	20.339(8)
b (Å)	20.07(6)
c (Å)	23.07(3)
V (Å^3)	9413(3)
Z	8
F(000)	5280
D_{calc} (Mg m^{-3})	1.86
Crystal size (mm)	0.26×0.26×0.20
μ(Mo Kα) (cm^{-1})	13.83
Data collection instrument	Nonius CAD4
Radiation, λ (Å)	Mo Kα, 0.71073
Temperature (K)	293
No. unique data	8266
Total with $I>3\sigma(I)$	4889
No. parameters	500
R [a] (for some double-measurement)	0.050
R' [b]	0.062
R_w	0.065
Largest shift/e.s.d., final cycle	0.122, 0.050 for non-disordered atoms
Largest peak (e Å^{-3})	1.40 for the disorder $CHCl_3$, 0.99 for the rest

[a] $R=\Sigma(I-\langle I\rangle)/\Sigma I$.
[b] $R'=\Sigma(|F_o|-|F_c|/\Sigma|F_o|$.

Structure solved by Patterson using the program SHELX86 [17] and expanded by DIRDIF [18]. Isotropic least-squares refinement, using SHELX76 [19,20] converged to $R=0.069$. Empirical absorption correction applied [21]. Maximum and minimum correction factors 1.12 and 0.89.

Positional parameters and anisotropic thermal parameters of the non-hydrogen atoms were refined. All hydrogen atoms were refined isotropically from their idealized geometrical positions, with a common thermal parameter. Because of the disorder found, the chloroform groups were refined as rigid groups. The final conventional agreement factors were $R=0.062$ and $R_w=0.065$ for the 4889 'observed' reflections and 500 variables. Function minimized $w(F_o-F_c)^2$, $w=1/(\sigma^2(F_o)+0.00009F_o^2)$ with $\sigma(F_o)$ from counting statistics. The maximum shift over the error ratio in the last full-matrix least-squares cycle was less than 0.122; 0.050 for non-disordered atoms. A final difference Fourier map showed no peaks higher than 1.40 e Å^{-3} on the disordered $CHCl_3$, 0.99 for the rest, nor deeper than −1.476 e Å^{-3}. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [22]. Geometrical calculations were made with PARST [23]. The plots were made using the EUCLID package [24]. All calculations were made on a MicroVax-3400 at the Scientific Computer Center, University of Oviedo.

Table 3
Fractional positional and thermal parameters (with e.s.d.s in parentheses)

Atom	*x*	*y*	*z*	U_{eq} [a] (×10^2)
Rh1	0.13099(5)	0.77702(5)	0.48511(4)	2.31(3)
Rh2	0.19642(5)	0.71260(5)	0.41061(4)	2.58(3)
Cl1	0.0451(2)	0.8187(2)	0.5586(2)	3.8(1)
P1	0.1942(2)	0.7640(2)	0.5629(1)	2.5(1)
P2	0.2400(2)	0.8077(2)	0.3803(1)	2.9(1)
O1	0.1146(4)	0.7241(5)	0.3612(4)	3.6(3)
O2	0.0799(4)	0.6817(5)	0.4949(4)	3.4(3)
O3	0.1505(4)	0.6239(5)	0.4403(4)	3.4(3)
O4	0.0643(4)	0.7982(5)	0.4176(4)	3.6(3)
O5	0.2841(4)	0.6820(5)	0.4442(4)	3.3(3)
O6	0.2650(5)	0.6491(5)	0.3560(4)	4.3(4)
C1	0.0709(7)	0.7620(8)	0.3715(6)	3.4(5)
C2	0.1022(2)	0.6279(8)	0.4723(6)	3.8(5)
C3	0.0197(8)	0.768(1)	0.3239(7)	6.5(7)
C4	0.0637(8)	0.5639(8)	0.4889(8)	5.8(7)
C5	0.3016(8)	0.6508(7)	0.3986(7)	3.8(5)
C6	0.3713(8)	0.624(1)	0.3974(7)	6.6(7)
C11	0.0936(7)	0.8354(7)	0.6185(6)	3.3(5)
C12	0.1591(7)	0.8168(7)	0.6198(6)	3.0(5)
C13	0.1976(8)	0.8336(8)	0.6696(6)	4.5(6)
C14	0.1668(9)	0.8667(9)	0.7148(7)	6.1(7)
C15	0.103(1)	0.886(1)	0.7127(8)	7.1(8)
C16	0.0660(8)	0.8706(9)	0.6638(7)	5.8(7)
C21	0.1888(6)	0.6809(7)	0.5967(6)	2.8(4)
C22	0.1596(7)	0.6710(8)	0.6509(6)	3.9(5)
C23	0.1516(9)	0.6085(8)	0.6754(7)	5.7(7)
C24	0.1738(9)	0.5552(9)	0.6466(7)	5.9(7)
C25	0.2034(9)	0.5619(8)	0.5913(7)	5.3(6)
C26	0.2118(7)	0.6253(7)	0.5681(6)	3.7(5)
C31	0.2812(6)	0.7891(7)	0.5636(5)	2.8(4)
C32	0.3300(7)	0.7420(8)	0.5617(6)	3.8(5)
C33	0.3981(8)	0.764(1)	0.5621(7)	6.1(7)
C34	0.4138(9)	0.831(1)	0.5667(8)	6.2(8)
C35	0.3643(8)	0.8756(9)	0.5684(7)	5.6(7)
C36	0.2979(7)	0.8553(7)	0.5658(6)	3.8(5)
C41	0.2260(7)	0.8756(7)	0.4297(6)	3.0(5)
C42	0.1765(7)	0.8675(7)	0.4709(5)	3.1(5)
C43	0.1587(7)	0.9239(7)	0.5024(6)	3.4(5)
C44	0.1895(8)	0.9844(7)	0.4933(7)	4.7(6)
C45	0.2401(8)	0.9903(8)	0.4543(7)	4.9(6)
C46	0.2589(8)	0.9361(7)	0.4229(6)	4.0(5)
C51	0.3289(7)	0.8080(7)	0.3679(6)	3.5(5)
C52	0.3720(8)	0.8174(8)	0.4143(7)	4.8(6)
C53	0.4373(7)	0.8165(9)	0.4062(8)	5.7(7)
C54	0.4632(8)	0.808(1)	0.3529(8)	6.6(8)
C55	0.4219(8)	0.797(1)	0.3059(8)	9.0(1)
C56	0.3564(7)	0.798(1)	0.3144(7)	6.2(7)
C61	0.2066(7)	0.8345(8)	0.3107(6)	3.8(5)
C62	0.1976(8)	0.783(1)	0.2686(6)	5.4(6)
C63	0.1713(9)	0.801(1)	0.2136(7)	8.0(9)
C64	0.1555(9)	0.870(1)	0.2041(9)	8.0(1)
C65	0.163(1)	0.919(1)	0.2450(8)	7.8(9)
C66	0.1886(9)	0.8994(9)	0.2982(8)	6.1(7)
C7	0.1279(3)	0.4171(3)	0.7982(2)	10.4(8) [a]
Cl2	0.1260(3)	0.3784(3)	0.7335(2)	7.9(3) [a,b]
Cl3	0.1809(3)	0.4843(3)	0.7920(2)	11.2(4) [a,b]
Cl4	0.0398(3)	0.4300(3)	0.8214(2)	14.4(5) [a,b]
Cl2′	0.4107(3)	1.1128(3)	0.2419(2)	26.0(2) [a,c]
Cl3′	0.3685(3)	0.9929(3)	0.3058(2)	11.9(8) [a,c]
Cl4′	0.4359(3)	1.0239(3)	0.3226(2)	15.0(1) [a,c]

(*continued*)

Table 3 (*continued*)

Atom	x	y	z	U_{eq} [a] ($\times 10^2$)
C8	−0.006(1)	1.059(1)	0.5808(9)	29.910
Cl6	0.510(1)	0.483(1)	0.5363(9)	29.910
Cl7	0.431(1)	0.592(1)	0.5674(9)	29.910
Cl8	−0.023(1)	1.033(1)	0.6515(9)	29.910

[a] $U_{eq}=\frac{1}{3}\Sigma_i U_{ii}$. Starred items: $U_{iso}\times 10^2$.
[b] Occupation factor 0.65(1).
[c] Occupation factor 0.35(1).

Table 4
Selected bond lengths (Å) and angles (°) for compound **5** with e.s.d.s in parentheses

Rh(1)–Rh(2)	2.529(1)	Rh(1)–Cl(1)	2.573(4)
Rh(1)–P(1)	2.223(4)	Rh(1)–O(2)	2.187(9)
Rh(1)–O(4)	2.106(8)	Rh(1)–C(42)	2.06(1)
Rh(2)–P(2)	2.217(4)	Rh(2)–O(1)	2.032(9)
Rh(2)–O(3)	2.134(9)	Rh(2)–O(5)	2.038(9)
Rh(2)–O(6)	2.27(1)		
Cl(1)–Rh(1)–Rh(2)	166.0(1)	P(1)–Rh(1)–Rh(2)	100.6(1)
P(1)–Rh(1)–Cl(1)	84.3(1)	O(2)–Rh(1)–Rh(2)	82.8(2)
O(2)–Rh(1)–Cl(1)	83.8(3)	O(2)–Rh(1)–P(1)	95.1(3)
O(4)–Rh(1)–Rh(2)	86.5(3)	O(4)–Rh(1)–Cl(1)	89.0(3)
O(4)–Rh(1)–P(1)	172.8(3)	O(4)–Rh(1)–O(2)	86.9(4)
C(42)–Rh(1)–Rh(2)	96.1(4)	C(42)–Rh(1)–Cl(1)	97.1(4)
C(42)–Rh(1)–P(1)	88.4(4)	C(42)–Rh(1)–O(2)	176.4(4)
C(42)–Rh(1)–O(4)	89.6(4)	P(2)–Rh(2)–Rh(1)	89.1(1)
O(1)–Rh(2)–Rh(1)	83.7(3)	O(1)–Rh(2)–P(2)	93.0(3)
O(3)–Rh(2)–Rh(1)	89.0(3)	O(3)–Rh(2)–P(2)	177.6(3)
O(3)–Rh(2)–O(1)	85.4(4)	O(5)–Rh(2)–Rh(1)	110.9(3)
O(5)–Rh(2)–P(2)	91.6(3)	O(5)–Rh(2)–O(1)	164.8(4)
O(5)–Rh(2)–O(3)	90.4(4)	O(6)–Rh(2)–Rh(1)	170.8(3)
O(6)–Rh(2)–P(2)	93.6(3)	O(6)–Rh(2)–O(1)	105.0(4)
O(6)–Rh(2)–O(3)	88.5(4)	O(6)–Rh(2)–O(5)	60.3(4)

4. Supplementary material

Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, distances, angles and least-squares-planes data and principal torsion angles have been deposited in the Crystallographic Cambridge Data Base.

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