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# A new structural type of dinuclear rhodium(II) compounds: synthesis by serendipity and design; catalytic behaviour in carbene transfer reactions †

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The compound $[Rh_2(\mu\text{-}O_2CCH_3)_3(O_2CCH_3)][\eta^2\text{-}(o\text{-}CH_3OC_6H_4)P(C_6H_5)_2]$ **1**, having one phosphine acting as a chelating, equatorial (P)–axial(O), ligand has been structurally characterized. A new family of structurally related dirhodium(II) compounds of general formula $[Rh_2(\mu\text{-}O_2CR)_2(X)_2\{\eta^2\text{-}(o\text{-}YC_6H_4)P(C_6H_5)_2\}_2]$ (R = $CH_3$, X = $CH_3CO_2$, Y = $CH_3O$ **2**; R = $CF_3$, X = $CF_3CO_2$, Y = $CH_3O$ **3**; R = $CH_3$, X = Cl **4** or R = $CH_3$, X = Cl, Y = $CH_3O$ **5**) has been synthesized. All these compounds are structurally related; they have two orthofunctionalized phosphines acting as equatorial (P) and axial (Cl, O) donor ligands and two bridging carboxylates. The two remaining equatorial sites around the rhodium atoms are occupied by two monodentate carboxylates (**2**, **3**) or two chlorine atoms (**4**, **5**). Compounds **4** and **5** have been structurally characterized by X-ray methods. Compound **4**, initially obtained in low yield by serendipity, was also prepared in moderate yield from rhodium acetate and $P(o\text{-}ClC_6H_4)(C_6H_5)_2$ in the presence of a stoichiometric amount of $Me_3SiCl$. Compounds **2** and **3** were prepared by treating the corresponding rhodium tetracarboxylate with two moles of $P(o\text{-}CH_3OC_6H_4)(C_6H_5)_2$ and **5**, obtained by serendipity, was best synthesized from the reaction of **2** and two moles of $Me_3SiCl$.

## Introduction

The reaction of rhodium acetate and triphenylphosphine to form a bis-cyclometallated compound of formula $[Rh_2(\mu\text{-}O_2CCH_3)_2\{\mu\text{-}(C_6H_4)P(C_6H_5)_2\}_2]\cdot 2HO_2CCH_3$ (Chart 1, **A**) was first reported by Cotton and co-workers[1] in 1985. Dinuclear compounds with bridging metallated phosphines were rare at that time and this reaction represented a synthetic method of general application for the preparation of metallated rhodium(II) compounds.

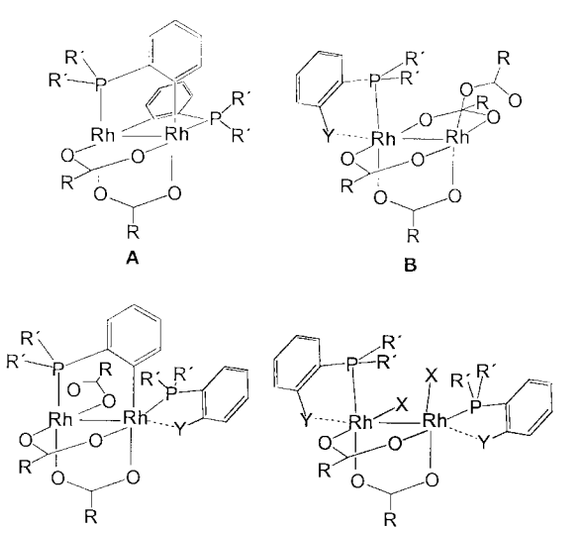



**Chart 1**

When orthofunctionalized phosphines were used in this reaction different intermediates could be isolated and structurally characterized.[2] In these studies the orthofunctionalized phosphines of formula $P(o\text{-}YC_6H_4)(C_6H_5)_2$, Y = Cl (PCCl) or $CH_3O$ (PCOMe), have been particularly useful, due to their ability to act as bidentate P,Cl or P, O donors, allowing the isolation of reaction intermediates of type **B** and **C** (Chart 1).[3]

We describe in this paper the synthesis and characterization of new rhodium compounds with a new type of structure **D**. They contain two orthofunctionalized phosphines, PCCl or PCOMe, in an equatorial–axial chelating mode and they have the formula $[Rh_2(\mu\text{-}O_2CR)_2(X)_2\{\eta^2\text{-}(o\text{-}YC_6H_4)P(C_6H_5)_2\}_2$, (R = $CH_3$, X = $CH_3CO_2$, Y = $CH_3O$; R = $CF_3$, X = $CF_3CO_2$, Y = $CH_3O$, R = $CH_3$, X = Y = Cl or R = $CH_3$, X = Cl, Y = $CH_3O$. The catalytic behaviour of these compounds in cyclopropanation reactions is also described.

## Results

### Synthesis of dinuclear rhodium(II) compounds, $[Rh_2(\mu\text{-}O_2CR)_2(X)_2(\eta^2\text{-PCOMe})_2]$ (R = $CH_3$, X = $CH_3CO_2$ 2; R = $CF_3$, X = $CF_3CO_2$ 3**

Earlier work showed that $Rh_2(O_2CCH_3)_4$ and PCOMe react, in a 1:1 molar ratio, to form the adduct $Rh_2(O_2CCH_3)_4\cdot$PCOMe that, under UV irradiation, readily rearranged to form the compound $[Rh_2(\mu\text{-}O_2CCH_3)_3(\eta\text{-}O_2CCH_3)(\eta^2\text{-PCOMe})]$, **1**, in quantitative yield.[4] We report here a single crystal X-ray study that confirms the structure **B** for this compound (Chart 1). This was the first time that a compound with this structure was

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3493/

**Table 1** $^{31}P$-{$^{1}H$} NMR Data.[a]

| Compound | $\delta$(P)[b] | $^{1}J_{Rh\text{-}P}$ | $^{2}J_{Rh\text{-}P}$ | $^{3}J_{P\text{-}P}$ | $^{1}J_{Rh\text{-}Rh}$ |
|---|---|---|---|---|---|
| **1** | 38.2 | 161 | 4 | | |
| **2** | 32.7 | 165 | −5 | 0 | −20 |
| **3** | 33.0 | 158 | −5 | 0 | −21 |
| **4** | 33.7 | 153 | −5 | 0 | −23 |
| **5** | 29.7 | 158 | −5 | 0 | −21 |
| **6** | 37.6 | 152 | | | |
| **7**[c] | 45.8 | 177 | 4 | | |
| **8**[d] | 46.2 | 181 | | | |

[a] Chemical shifts in ppm; coupling constants in Hz. [b] Equatorial phosphine. [c] For metallated phosphine: $\delta$(P) 13.2, $^{1}J_{Rh\text{-}P}$ 153, $^{2}J_{Rh\text{-}P}$ 8 Hz. [d] For metallated phosphine: $\delta$(P) 10.8, $^{1}J_{Rh\text{-}P}$ 148, $^{2}J_{Rh\text{-}P}$ 8 Hz.

formed by direct reaction of rhodium carboxylate and the phosphine ligand. A structurally analogous compound with bipyridine has been prepared by direct reaction of rhodium carboxylate and bipyridine.[5] The synthesis of a similar compound with PCCl was reported[2e] by a different route: electrophilic Rh–C bond cleavage in the corresponding monometallated compound.

We also observed, that irradiation of compound **1** in the presence of an equimolar amount of PCOMe gave a new compound $[Rh_2(\mu\text{-}O_2CCH_3)_2(\eta\text{-}O_2CCH_3)_2(\eta^2\text{-}PCOMe)_2]$, **2**, that has two chelating PCOMe phosphines and structure **D** (Chart 1). The direct photochemical reaction of $Rh_2(O_2CCH_3)_4$ and two moles of PCOMe was not a convenient route for the preparation of **2**, as other products of type **C** were also formed. The characterization of **2** was based on spectroscopic data. The $^{31}P$ NMR spectrum (Table 1) showed a second order signal centered at $\delta$ 32.7, that corresponds to the AA′ part of a AA′XX′ system. This high value of the chemical shift is characteristic of phosphines in equatorial co-ordination.[2a,3,4b] The $^{1}H$ and $^{13}C$ NMR spectra indicated the presence of two different acetates, but only one environment for the PCOMe phosphine. No evidence of metallated carbon was observed in the $^{13}C$ NMR spectrum.[6] All these spectroscopic data suggested for **2** one structure of type **D**, with two chelating phosphines partially displacing two carboxylates in the rhodium acetate.

The compound PCOMe also reacted with $Rh_2(O_2CCF_3)_4$ to form $[Rh_2(O_2CCF_3)_2(\eta\text{-}O_2CCF_3)_2(\eta^2\text{-}PCOMe)_2]$, **3**, that according to the NMR data has the same structure as **2**. Photochemical irradiation was not required in this case and the reaction was completed after stirring for two hours at room temperature. This higher reactivity of rhodium trifluoroacetate compared to rhodium acetate was observed in reactions with other arylphosphines.[7,8]

### Synthesis of dinuclear rhodium(II) compounds, $[Rh_2(\mu\text{-}O_2CCH_3)_2(Cl)_2\{\eta^2\text{-}(o\text{-}YC_6H_4)P(C_6H_5)_2\}_2]$ (Y = Cl **4** or $CH_3O$ **5**)

In order to explore the utility of this synthetic method we tried the reaction of PCCl and $[Rh_2(O_2CCH_3)_4(CH_3OH)_2]$ (1:1 molar ratio), under thermal or photochemical conditions. The major products were species resulting from the cyclometallation of the PCCl phosphine, identified by $^{31}P$ NMR spectroscopy. However in the spectrum there was one multiplet signal of minor intensity, centered at $\delta$ 33.7, that could not be structurally assigned. Careful manipulation of the sample allowed the isolation of small amounts of a crystalline yellow-orange compound, that was characterized by single crystal X-ray methods as $[Rh_2(\mu\text{-}O_2CCH_3)_2(Cl)_2(\eta^2\text{-}PCCl)_2]$, **4**. This compound showed a second order $^{31}P$ NMR spectrum (Table 1) that was fitted to the AA′ part of a AA′XX′ system ($\delta$ 33.72, $^{1}J_{Rh\text{-}P}$ = 153, $^{2}J_{Rh\text{-}P} = -5$, $^{3}J_{P\text{-}P} = 0$ and $^{1}J_{Rh\text{-}Rh} = -23$ Hz).

Analogous reaction with PCOMe gave small amounts of a similar product of formula $[Rh_2(\mu\text{-}O_2CCH_3)_2(Cl)_2\{\eta^2\text{-}(o\text{-}CH_3OC_6H_4)P(C_6H_5)_2\}_2]$, **5**, also characterized by X-ray crystallography.

**Table 2** Selected bond distances (Å) and angles (°) for compound **4**

| | | | |
|---|---|---|---|
| Rh(1)–Rh(2) | 2.5692(14) | Rh(2)–P(13) | 2.2466(16) |
| Rh(1)–P(33) | 2.2474(15) | Rh(2)–Cl(32) | 2.5916(15) |
| Rh(1)–Cl(52) | 2.5870(18) | Rh(2)–Cl(3) | 2.3154(14) |
| Rh(1)–Cl(4) | 2.3243(18) | Rh(2)–O(11) | 2.050(3) |
| Rh(1)–O(7) | 2.049(3) | Rh(2)–O(8) | 2.112(3) |
| Rh(1)–O(12) | 2.102(3) | | |
| | | | |
| Cl(52)–Rh(1)–Rh(2) | 164.94(3) | Rh(1)–Rh(2)–Cl(32) | 165.22(3) |
| P(33)–Rh(1)–O(7) | 92.38(10) | P(13)–Rh(2)–O(11) | 91.10(10) |
| P(33)–Rh(1)–O(12) | 169.37(10) | P(13)–Rh(2)–O(8) | 169.33(9) |
| Cl(4)–Rh(1)–O(7) | 172.24(10) | Cl(3)–Rh(2)–O(11) | 173.64(9) |

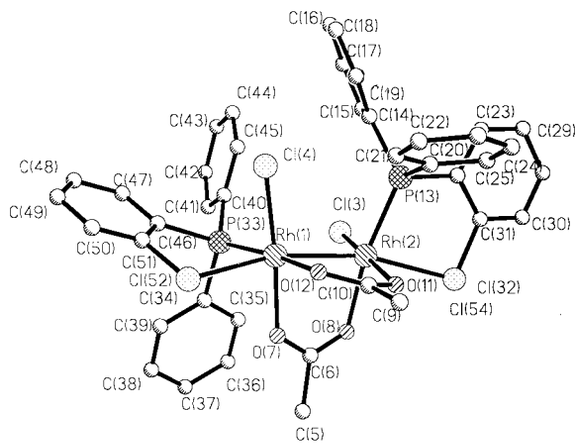



**Fig. 1** Molecular view of $[Rh_2(\mu\text{-}O_2CCH_3)_2(Cl)_2\{\eta^2\text{-}(o\text{-}ClC_6H_4)P(C_6H_5)_2\}_2]$ **4**.

The $^{31}P$ NMR spectra for compounds **2–5** were very similar, giving good evidence of all having the same structure **D**.

We have obtained compounds **4** and **5** in higher yields using properly designed synthetic methods. It is known[9] that $ClSiMe_3$ is an excellent reagent for the substitution of carboxylates by chloride in rhodium(II). Thus, the reaction of rhodium acetate with $ClSiMe_3$ (2 moles) at 50 °C for 30 min followed by addition of PCCl (2 moles) and further stirring of the mixture for 12 h at room temperature gave **4** in high yield (75%). Heating must be avoided in the last reaction step to prevent the formation of cylometallated products.

We also tried the analogous reaction of rhodium acetate with $ClSiMe_3$ and PCOMe in order to prepare compound **5**. This reaction was slow and only gave the desired compound in 30% yield after 2 h of irradiation. Compound **5** was obtained in 60% yield from **2** and $ClSiMe_3$ in stoichiometric amounts at 50 °C.

### Structural results

The crystal structures for compounds **1**, **4** and **5** have been determined by X-ray procedures. A perspective drawing of compound **4** is shown in Fig. 1, and important bond distances and angles are listed in Table 2. The overall structure is based on that of the rhodium acetate dimer where two cisoid acetate bridges have been replaced by two phosphines and two chlorine atoms. Each PCCl phosphine is acting as a chelating ligand, at one equatorial (P) and one axial (Cl) site of the dirhodium. As expected, the average equatorial Rh–Cl bond distance (2.319 Å) is considerably shorter than the axial one (2.5893 Å). This co-ordination mode was observed in other rhodium(II) compounds with this and other orthofunctionalized phosphines.[2e,3,4] The Rh–Rh distance, 2.5692(14) Å, is longer than that of rhodium acetate and reflects the presence of only two bridging ligands in the dinuclear unit.

A perspective drawing of compound **5** is shown in Fig. 2 and important bond distances and angles are listed in Table 3. The overall structure is similar to that described for compound **4**,

**Table 3** Selected bond distances (Å) and angles (°) for compound **5**

| | | | |
|---|---|---|---|
| Rh(1)–Rh(2) | 2.5605(11) | Rh(2)–Cl(2) | 2.318(3) |
| Rh(1)–Cl(1) | 2.322(3) | Rh(2)–O(3) | 2.094(7) |
| Rh(1)–P(1) | 2.234(3) | Rh(2)–P(2) | 2.247(3) |
| Rh(1)–O(1) | 2.111(7) | Rh(2)–O(6) | 2.298(7) |
| Rh(1)–O(4) | 2.061(6) | Rh(2)–O(2) | 2.058(7) |
| Rh(1)–O(5) | 2.342(7) | | |
| O(5)–Rh(1)–Rh(2) | 170.3(2) | O(6)–Rh(2)–Rh(1) | 165.5(2) |
| O(4)–Rh(1)–P(1) | 90.6(2) | O(2)–Rh(2)–P(2) | 94.5(2) |
| O(4)–Rh(1)–Cl(1) | 171.6(2) | O(2)–Rh(2)–Cl(2) | 172.8(2) |
| O(5)–Rh(1)–Cl(1) | 86.2(2) | O(6)–Rh(2)–Cl(2) | 90.7(2) |

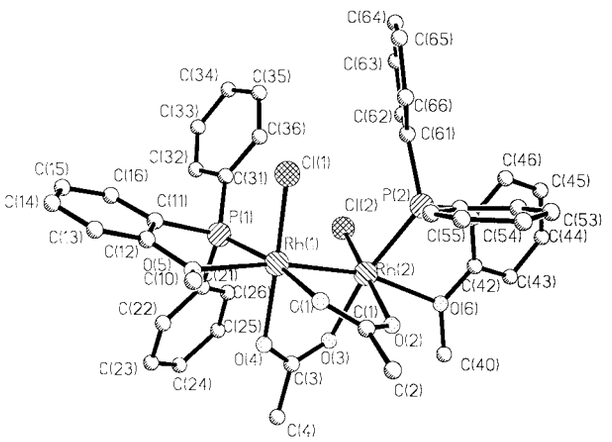



**Fig. 2** Molecular view of $[Rh_2(\mu\text{-}O_2CCH_3)_2(Cl)_2\{\eta^2\text{-}(o\text{-}OCH_3C_6H_4)P(C_6H_5)_2\}_2]$ **5**.

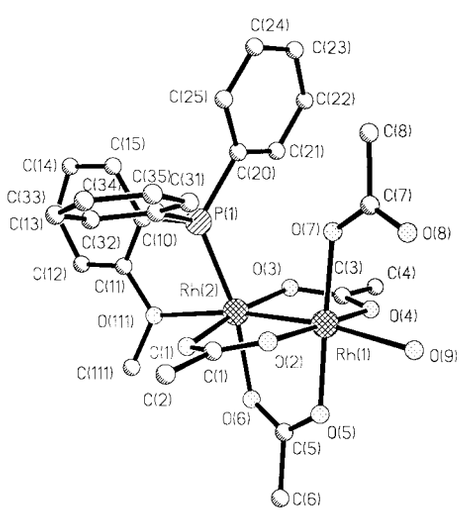



**Fig. 3** Molecular view of $[Rh_2(\mu\text{-}O_2CCH_3)_3(O_2CCH_3)\{\eta^2\text{-}(o\text{-}CH_3OC_6H_4)P(C_6H_5)_2\}]$ **1**. Atom O(9) corresponds to a water molecule.

as is the Rh–Rh bond distance 2.5605(11) Å. The phosphines co-ordinate in the same chelating mode observed in **4** for PCCl. The equatorial Rh–O bond distances (2.1 Å) are also shorter than the axial ones (2.3 Å).

There are in the literature some dinuclear rhodium (II) compounds with chlorine ligands in axial[9,10] or bridging[9b,11] disposition but rhodium(II) compounds with equatorial chlorides are rare.[10b,c,11] In most cases the chloride ligand arises from $Me_3SiCl$, HCl or LiCl used in the reaction. It seems very likely that in the reactions yielding compounds **4** and **5** by serendipity the chlorines were extracted from the $CHCl_3$ used as reaction solvent, as in the absence of it, these compounds were not formed at all.

A perspective drawing of compound **1** is shown in Fig. 3 and important bond distances and angles are listed in Table 4. The

**Table 4** Selected bond distances (Å) and angles (°) for compound **1**

| | | | |
|---|---|---|---|
| Rh(1)–Rh(2) | 2.439(3) | Rh(2)–O(1) | 2.071(14) |
| Rh(1)–O(2) | 2.019(11) | Rh(2)–O(6) | 2.089(12) |
| Rh(1)–O(7) | 2.037(11) | Rh(2)–O(3) | 2.063(12) |
| Rh(1)–O(4) | 2.058(14) | Rh(2)–P(1) | 2.235(10) |
| Rh(1)–O(9) | 2.248(12) | Rh(2)–O(111) | 2.353(10) |
| Rh(1)–O(5) | 2.015(12) | | |
| O(5)–Rh(1)–Rh(2) | 87.1(4) | P(1)–Rh(2)–Rh(1) | 106.47(11) |
| O(4)–Rh(1)–O(9) | 91.5(6) | O(6)–Rh(2)–P(1) | 167.3(3) |
| O(5)–Rh(1)–O(7) | 178.0(4) | O(1)–Rh(2)–P(1) | 89.0(3) |
| O(2)–Rh(1)–O(4) | 174.1(5) | O(1)–Rh(2)–O(111) | 89.3(5) |

quality of the crystal was not very good and consequently the data collected were poor. However the refinement was sufficiently good ($R = 10\%$) unambiguously to establish the relative situation of the ligands around the dinuclear unit. The overall structure is based on that of the rhodium acetate dimer where one acetate group has been partially replaced by one PCOMe phosphine. The phosphine co-ordinates in a chelating mode acting as an equatorial (P) and axial(O) ligand. The Rh–Rh distance is 2.439(3)Å, considerably shorter than in **4** or **5**.

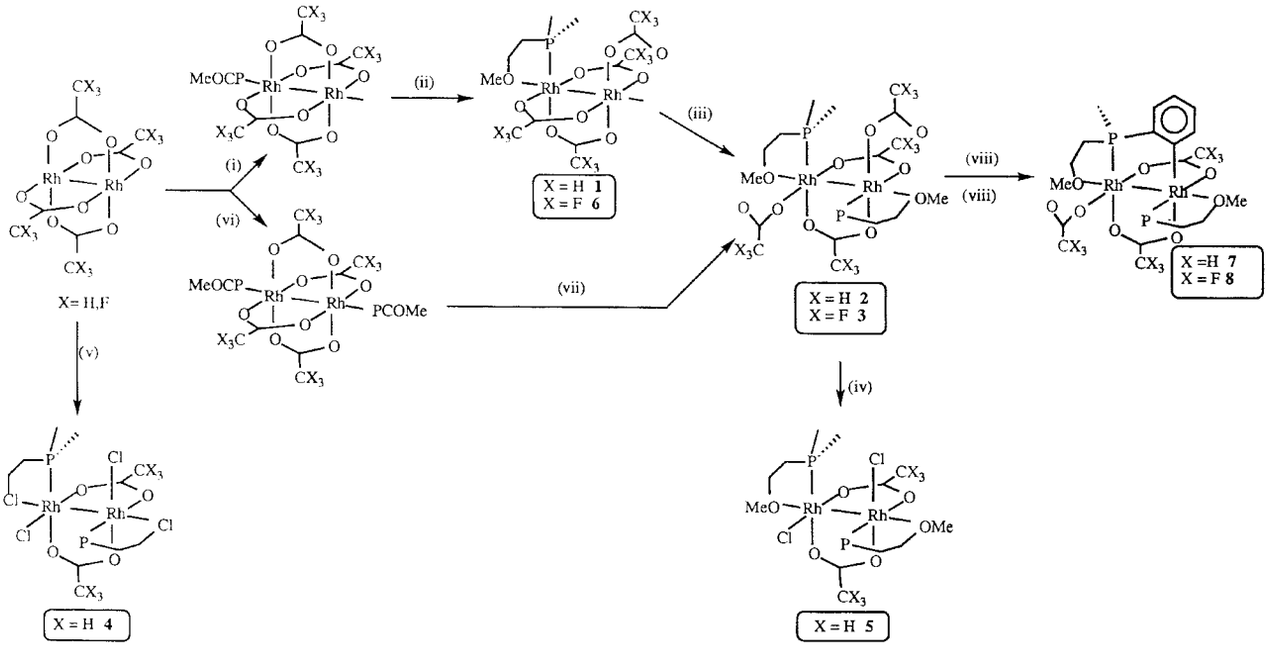
## Discussion

It is remarkable that in the reaction of $Rh_2(O_2CCF_3)_4$ and PCOMe the intermediate $[Rh_2(\mu\text{-}O_2CCF_3)_3(O_2CCF_3)(\eta^2\text{-PCOMe})]$ **6**, structurally analogous to **1**, was not observed and, independently of the Rh : P ratio used, 1 : 1 or 1 : 2, **3** was the only species detectable by $^{31}P$ NMR spectroscopy in the reaction mixture. We observed that **6** was formed on treating $[Rh_2(O_2CCH_3)_3\{(C_6H_4)P(o\text{-}CH_3OC_6H_4)(C_6H_5)\}]$[4b] with $CF_3CO_2H$; this reaction involves simultaneous exchange of acetates by trifluoroacetate groups and electrophilic Rh–C bond cleavage. We confirmed that **6** readily reacts with PCOMe to form **3**.

The fact that compounds **2** and **3** are isolable and do not readily undergo cyclometallation, might be attributed to the ability of PCOMe to exhibit intramolecular (P,O) co-ordination that makes the metallation reaction less favorable. However, when **2** was heated in toluene solution at 90 °C for 24 h only one of the equatorial phosphines was metallated yielding $[Rh_2(\mu\text{-}O_2CCH_3)_2(O_2CCH_3)[(C_6H_4)(o\text{-}CH_3OC_6H_4)P(C_6H_5)](\eta^2\text{-PCOMe})]$ **7** as the only reaction product (Scheme 1). The $^{31}P$ NMR spectrum of this compound is consistent with the existence of one bridging (metallated) and one chelating (non-metallated) phosphine (Table 1). The $^1H$ NMR spectrum also shows two resonances, $\delta$ 3.93 and 4.26, due to the two different methoxy groups of the phosphines.

Compound **3** is also stable in solution at moderate temperatures (< 50 °C). The cyclometallation reaction was only completed after heating at 90 °C for 24 h or after stirring in $CF_3CO_2H$ for 9 d. The resulting product was formulated as $[Rh_2(\mu\text{-}O_2CCF_3)_2(O_2CCF_3)[(C_6H_4)(o\text{-}CH_3OC_6H_4)P(C_6H_5)](\eta^2\text{-PCOMe})]$, **8**. The spectroscopic data indicate that in solution **8** exists as two species in equilibrium. Their ratio changes with the amount of $CF_3CO_2H$ in solution, suggesting that they differ in the mode of co-ordination of the $CF_3CO_2^-$ group, as monodentate (equatorial) or chelating (equatorial–axial). Examples of these two co-ordination modes have been found[2,3] for similar rhodium(II) species.

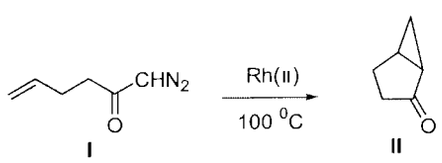
In contrast to the ability shown by PCOMe to stabilize compounds with structure **D**, all the efforts to prepare bis-equatorial compounds with PCCl in high yield failed. Apparently, in this case, the axial rhodium–chlorine interaction is weak and does not prevent cyclometallation of this ligand. Thus, $Rh(O_2CCH_3)_4$ (or $Rh_2(O_2CCF_3)_4$) reacted with PCCl, at room temperature, to give a complex mixture of cyclometallated compounds of type **C**.



**Scheme 1** X = H, (i) 1 mol of PCOMe; (ii) *hv* (ref. 4); (iii) 1 mol of PCOMe, *hv*; (iv) 2 mol of $Me_3SiCl$, 50 °C; (v) 2 mol $Me_3SiCl$, 50 °C, 2 mol PCCl, RT; (viii) 90 °C, 24 h. X = F, (vi) 2 mol PCOMe; (vii) 2 h, RT; (viii) 90 °C, 24 h.

### Catalysis

Compound **2** completely transformed the α-diazo ketone **I** (Scheme 2) upon heating the reaction mixture for 1 h; a 56%



**Scheme 2**

yield of the cyclopropanation product **II** was observed (Table 5). In the case of **3** 20% of diazo compound was recovered unchanged under these conditions and ketone **II** was only obtained in 28% yield. However, **4** and **5** did not react after heating for 3 h. These results indicate that at high temperature there is cleavage of the axial Rh–O bonds in **2** and **3**, allowing the diazo compound to reach the catalytic center. The order of reactivity observed for compounds **2** and **3** is opposite to the general observation (compounds with acetate groups are usually less active than the analogues with trifluoroacetates). This observation suggests that the total substitution of acetates by more electron withdrawing groups such as trifluoroacetates strengthens the axial Rh–$OCH_3$ bond in **3**, reducing the activity of this catalyst. Exchanging the monodentate acetates by chlorides, apparently has even a more pronounced effect and makes the products **4** and **5** even less reactive.

## Experimental

### General comments

Compounds $Rh_2(O_2CCF_3)_4$,[3a,12] $[Rh_2(\mu\text{-}O_2CCH_3)_3(O_2CCH_3)(\eta^2\text{-}PCOMe)]$[4] $[Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}CH_3OC_6H_4)(C_6H_5)]$[4] and PCCl[13] were prepared according to literature methods. Comercially available $[Rh(O_2CCH_3)_4(CH_3OH)_2]$ (Pressure Chemical Co.), PCOMe (Strem Chemicals), $CF_3CO_2H$ (Fluorochem) and $CH_3CO_2H$ were used as purchased. All solvents were of analytical grade. Chloroform and toluene were dried and degassed before use; acetic acid was only degassed. The NMR spectra were recorded in $CDCl_3$ on Bruker AC-200, Varian-300 and Varian-400 spectrophotometers; chemical shifts being relative to TMS ($^1H$, $^{13}C$), 85% $H_3PO_4$ ($^{31}P$) or $CFCl_3$($^{19}F$).

**Table 5** Catalytic results from cyclopropanation reactions

| Catalyst | *t*/h | Diazo **I** recovered (%) | Yield of **II** (%) |
|---|---|---|---|
| **2** | 1 | <2 | 56 |
| **3** | 1 | 20 | 28 |
| **4** | 3 | >99 | — |
| **5** | 3 | >99 | — |

### Synthesis of compounds

**$[Rh_2(\mu\text{-}O_2CCH_3)_2(O_2CCH_3)_2(\eta^2PCOMe)_2]$ 2.** Compound **1**[4] (100 mg, 0.14 mmol) was dissolved in 100 ml of $CHCl_3$ and 40 mg (0.14 mmol) of PCOMe were added. The solution was stirred for 30 min. After irradiation for 1 h with an Hg-vapour lamp (OSRAM-125) the solution became green-yellow. The solvent was removed under vacuum, the residue extracted with 5 mL of 1:1 $CH_2Cl_2$–hexane and the extract transferred to a column (2 × 30 cm, silica gel, hexane). Elution with $CH_2Cl_2$–hexane–acetone (10:10:2) separated a minor green band that was discarded. Further elution with hexane–acetone (1:1) gave a green-yellow band. The solution was evaporated to dryness and the residue dissolved in 3 mL of $CH_2Cl_2$; slow addition of hexane gave 106 mg (76% yield ) of compound **2**. NMR: $^{31}P\text{-}\{^1H\}$, AA′XX′ system, $\delta$ 32.65, $^1J_{Rh\text{-}P} = 165$, $^2J_{Rh\text{-}P} = -5$, $^3J_{P\text{-}P} = 0$ and $^1J_{Rh\text{-}Rh} = -20$ Hz; $^1H$, $\delta$ 1.02 (s, $CH_3$, 6 H), 1.28 (s, $CH_3$, 6 H), 4.27 (s, $CH_3$, 6 H) and 6.5–7.5 (aromatics, m, 28 H); $^{13}C$, $\delta$ 22.66 (s, $CH_3$), 23.06 (s, $CH_3$), 57.81 (s, $OCH_3$), 112.39 (s, aromatics), 122.02 (m, aromatics), 127–135 (m, aromatics), 163.96 (s, aromatic, C bonded to $OCH_3$) and 180.16 (s, OCO). Found: C, 52.30; H, 4.70. $C_{46}H_{46}O_{10}P_2Rh_2\cdot H_2O$ requires C, 52.89; H, 4.63%.

**$[Rh_2(\mu\text{-}O_2CCF_3)_2(O_2CCF_3)_2(\eta^2\text{-}PCOMe)_2]$ 3.** (a) A mixture of 100 mg (0.14 mmol) of $Rh_2(O_2CCF_3)_4$ and 89 mg (0.30 mmol) of PCOMe in $CHCl_3$ was stirred for two hours. The resulting green-yellow solution was evaporated under reduced

pressure and the crude oil obtained dissolved in 5 ml of 1:1 $CH_2Cl_2$–hexane and chromatographed on a column (2 × 30 cm, silica–gel, hexane). After elution with $CH_2Cl_2$–hexane (1:1) a green-yellow band was collected from which 140 mg (78% yield) of compound **3** were obtained. NMR: $^{31}$P-{$^1$H}, AA′XX′ system, $\delta$ 32.98, $^1J_{Rh\text{-}P}$ = 158, $^2J_{Rh\text{-}P}$ = −5, $^3J_{P\text{-}P}$ = 0 and $^1J_{Rh\text{-}Rh}$ = −21 Hz; $^1$H, $\delta$ 4.23 (s, $CH_3$, 6 H), 6.77 (t, $J$ = 9, aromatics, 2 H), 6.97 (t, $J$ = 8 Hz, aromatics, 2 H), 7.15–7.36 (m, aromatics, 14 H) and 7.44–7.58 (m, aromatics, 10 H); $^{13}$C, $\delta$ 57.98 (s, $CH_3O$, 2C), 112.04 (aromatics, d, $J$ = 6, 2 C), 112.61 ($CF_3$, q, $J$ = 291, 4 C), 119.43 (aromatic C bonded to P, d, $J$ = 54, 2 C), 122.34 (aromatics, d, $J$ = 8, 2 C), 126.31 (aromatic C bonded to P, d, $J$ = 59, 2 C), 127.06 (C aromatic bonded to P, d, $J$ = 57, 2 C), 128.42 (aromatics, d, $J$ = 12, 4 C), 128.66 (aromatics, d, $J$ = 11, 4 H), 131.00 (aromatics, d, $J$ = 3, 2 C), 131.26 (aromatics, d, $J$ = 2, 2C), 132.86 (aromatics, d, $J$ = 10, 4 C), 134.02 (aromatics, s, 2 C), 134.24 (aromatics, s, 2 C), 134.51 (aromatics, d, $J$ = 10, 4 C), 161.80 (C aromatic bonded to $CH_3O$, d, $J$ = 8, 2C), 163.40 (OCO, q, $J$ = 37, 2C) and 171.91 (OCO, q, $J$ = 42 Hz, 2 C); $^{19}$F, $\delta$ −74.74 (s) and −75.04 (s). Found: C, 44.17; H, 2.81. $C_{23}H_{17}O_5F_6PRh$ requires C, 44.47; H, 2.76%.

Compound **6** (b) (100 mg, 0.10 mmol) dissolved in 100 ml of $CHCl_3$ was stirred with 30 mg ( 0.10 mmol) of PCOMe for 30 min. After further irradiation for 30 min with an Hg-vapour lamp (OSRAM-125) the resulting green-yellow solution was manipulated as described to obtain 100 mg (73% yield) of **3**.

**[$Rh_2$(μ-$O_2CCH_3$)$_2$(Cl)$_2${η$^2$-(*o*-$ClC_6H_4$)P($C_6$.$H_5$)$_2$}$_2$] 4.** *(a) By serendipity*. To 40 mL of 10:4 toluene–$CH_3CO_2H$ 600 mg of [$Rh_2(O_2CCH_3)_4(CH_3OH)_2$] (1.19 mmol) were added. The mixture was refluxed under an argon an atmosphere until complete dissolution and 348 mg of PCCl (1.19 mmol), dissolved in 20 mL of 1:3 $CHCl_3$–toluene, were added. The solution immediately changed from blue to brown-red. It was refluxed for 30 min and changed to blue. The solvent was removed under vacuum, the resulting crude oil dissolved in 5 mL of 1:1 $CH_2Cl_2$–hexane and the resulting solution chromatographed on a column (2 × 30 cm, silica gel, hexane). After elution with $CH_2Cl_2$–hexane (1:1) a minor yellow band separated that was discarded. Increasing polarity ($CH_2Cl_2$–hexane–acetone, 10:10:1) gave an orange band . Other products obtained with more polar solvents were not characterized. The eluted orange solution was evaporated under reduced pressure to give a yellow residue that after crystallization from $CH_2Cl_2$–hexane gave compound **4** as a yellow-brown solid (49 mg, yield 10%). NMR: $^{31}$P-{$^1$H}, AA′XX′ system, $\delta$ 33.7, $^1J_{Rh\text{-}P}$ = 153, $^2J_{Rh\text{-}P}$ = −5, $^3J_{P\text{-}P}$ = 0 and $^1J_{Rh\text{-}Rh}$ = −23); $^1$H, $\delta$ 1.60 (s, $CH_3$, 6 H), 6.63 (t, $J$ = 8, aromatics, 2 H), 7.16 (m, aromatics, 8 H), 7.45 (s, aromatics, 10 H) and 7.68 (m, aromatics, 8 H); $^{13}$C, $\delta$ 22.5 (s, $CH_3$), 125.0–138.0 (m, aromatics) and 186.5 (s, OCO).

(*b*) A mixture of 100 mg (0.198 mmol) of [$Rh_2$($O_2$C-$CH_3$)$_4$($CH_3OH$)$_2$] and 42.25 mg of $Me_3SiCl$ (0.376 mmol) was stirred for one hour at 50 °C; 123 mg of PCCl (0.436) were added to the resulting brown-green solution and the mixture was stirred at room temperature for 12 h. The solvent was removed under vacuum, the resulting crude oil dissolved in 5 mL of 1:1 $CH_2Cl_2$–hexane and chromatographed on a column (2 × 30 cm, silica gel, hexane). The column was washed with $CH_2Cl_2$. Further elution with $CH_2Cl_2$–acetone (4:1) gave an orange band from which compound **4** was isolated in 75% yield.

**[$Rh_2$(μ-$O_2CCH_3$)$_2$(Cl)$_2${η$^2$-(*o*-$CH_3OC_6H_4$)P($C_6H_5$)$_2$}$_2$] 5.** *(a) By serendipity.* To 70 mL of degassed toluene–$CH_3CO_2H$ (5:2) 200 mg of [$Rh_2(O_2CCH_3)_4(CH_3OH)_2$] (0.39 mmol) were added. The mixture was refluxed until complete dissolution and 231 mg of PCCl (0.79 mmol) dissolved in 10 mL of $CHCl_3$ were added. After refluxing for 90 min the solution changed from red-brown to blue. After evaporation in vacuum, the residue was extracted with 5 mL of 1:1 $CH_2Cl_2$–hexane and transferred to a column (2 × 30 cm, silica gel, hexane). After elution with $CH_2Cl_2$–hexane–acetone (10:10:1) a minor orange band separated. The orange solution was evaporated under reduced pressure to give an orange solid that after crystallization from $CH_2Cl_2$–hexane gave compound **5** (8 mg, yield 2%). NMR: $^{31}$P-{$^1$H}, AA′XX′ system, $\delta$ 29.74, $^1J_{Rh\text{-}P}$ = 158, $^2J_{Rh\text{-}P}$ = −5, $^3J_{P\text{-}P}$ = 0 and $^1J_{Rh\text{-}Rh}$ = −21 Hz).

(*b*) Compound **2** (100 mg, 0.097 mmol) was dissolved in 100 ml of $CHCl_3$ and 21 mg of $Me_3SiCl$ (0.184) were added. The mixture was stirred for 30 min at 50 °C. The yellow solution obtained was evaporated to dryness. Following procedure (a) compound **5** was isolated in 60% yield.

**[$Rh_2$(μ-$O_2CCF_3$)$_3$($O_2CCF_3$){η$^2$-(*o*-$CH_3OC_6H_4$)P($C_6H_5$)$_2$}] 6.** The compound [$Rh_2(O_2CCH_3)_3$[($C_6H_4$)P(*o*-$CH_3OC_6H_4$)($C_6H_5$)] (100 mg, 0.15 mmol) was dissolved in $CF_3CO_2H$ and was stirred for two days at room temperature. The green solution obtained was evaporated to dryness and the residue dissolved in 5 mL of 1:1 $CH_2Cl_2$–hexane and chromatographed on a column (2 × 30 cm, silica gel, hexane). After elution with $CH_2Cl_2$–hexane–acetone (20:20:1) a green band separated. Removal of the solvent gave a crude oil which was recrystallized from $CH_2Cl_2$–hexane yielding 110 mg of compound **6** (78% yield). NMR: $^{31}$P-{$^1$H}, $\delta$ 37.6, $^1J_{Rh\text{-}P}$= 152; $^1$H, $\delta$ 4.60 (1 $CH_3$, 3 H) and 6.80–7.80 (aromatics, 14 H); $^{19}$F NMR, $\delta$ −74.2 (3F), −74.65 (3F) and −75.0 (6F). Found: C, 33.24; H, 2.05. $C_{27}H_{17}O_9F_{12}PRh_2\cdot H_2O$ requires C, 33.50%; H, 1.98%.

### X-Ray crystallography

An Enraf-Nonius CAD 4 diffractometer was employed for data collection on **1** and **4**. The structure of **1** was solved by direct methods using the program SHELXS 86 and refined by means of full-matrix least squares procedures using SHELXL 93.[14] The structure of **4** was also solved by direct methods using SHELXS 97 and refined by full-matrix least squares methods on $F^2$ with SHELXL 97.[15] For data collection on crystals of compound **5** a Siemens SMART CCD diffractometer was used. The structure was solved by direct methods and refined on $F^2$ for all reflections using SHELXTL V 5.05.[16] In all cases the positions of non-hydrogen atoms were deduced from Fourier-difference maps and refined anisotropically. Hydrogen atoms were placed in geometrically generated positions and refined riding on the carbon atom to which they are attached.

**Complex 1.** *Crystal data.* $C_{27}H_{31}O_{10}PRh_2$, $M$ = 752.31, monoclinic, space group $P2_1/c$, $a$ = 10.751(6), $b$ = 16.282(6), $c$ = 17.22(2) Å, $\beta$ = 105.20(6)°, $V$ = 2908(3) Å$^3$, $T$ = 293 K, $Z$ = 4, $\mu$(Mo-Kα) = 1.244 mm$^{-1}$. Final conventional $R$ = 0.1078 for 4998 'observed' reflections and 365 variables.

Owing to the poor quality of the crystals we could not refine the structure further (based on $F$ and 2$\sigma$($I$) cut-off). On the other hand no crystal deterioration was observed during data collection nor strong disorder in the presence of solvents. Nevertheless the molecular structure is well established. Multiple attempts to make better crystals were unsuccessful.

**Complex 4.** *Crystal data.* $C_{42}H_{36}Cl_{10}O_4P_2Rh_2$, $M$ = 1226.97, triclinic, space group $P\bar{1}$, $a$ = 13.398(6), $b$ = 13.623(5), $c$ = 14.538(5) Å, $\alpha$ = 77.40(5), $\beta$ = 84.25(5), $\gamma$ = 69.69(4)°, $V$ = 2427.7(17) Å$^3$, $T$ = 293 K, $Z$ = 2, $\mu$(Mo-Kα) = 1.336 mm$^{-1}$, 8941 reflections measured, 8538 unique ($R_{int;}$ = 0.0182) which were used in all calculations. The final $R$ was 0.0352.

**Complex 5.** *Crystal data.* $C_{43.50}H_{43}Cl_5O_6P_2Rh_2$, $M$ = 1106.79, monoclinic, space group $P2_1/n$, $a$ = 17.9125(10), $b$ = 13.0427(8), $c$ = 19.6074(12) Å, $\beta$ = 94.8900(10)°, $V$ = 4564.2(5) Å$^3$, $T$ = 293 K, $Z$ = 4, $\mu$(Mo-Kα) = 1.132 mm$^{-1}$, 16640 reflections measured, 6475 unique ($R_{int}$ = 0.0553) which were used in all calculations. The final $R$ was 0.076.

CCDC reference number 186/1576.

See http://www.rsc.org/suppdata/dt/1999/3493/ for crystallographic files in .cif format.

### Catalytic experiments

All the catalytic reactions were performed by addition of the corresponding rhodium(II) complex (1 mol%) in 1 ml of $CH_2Cl_2$ to an anhydrous dichloromethane solution containing the diazo compound. The mixture was stirred at 100 °C in a sealed tube. After cooling, the reaction mixture was filtered through a short plug of silica gel to remove the catalyst and the solvent removed under reduced pressure. The residue was analysed by $^1H$ and $^{13}C$ NMR spectroscopy.

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## References

1 A. R. Chakravarty, F. A. Cotton, D. A. Tocher and J. H. Tocher, *Organometallics*, 1985, **4**, 8.

2 (*a*) F. Barceló, F. A. Cotton, P. Lahuerta, R. Llusar, M. Sanaú, W. Schwotzer and M. A. Ubeda, *Organometallics*, 1986, **5**, 808; (*b*) F. Barceló, F. A. Cotton, P. Lahuerta, M. Sanaú, W. Schwotzer and M. A. Ubeda, *Organometallics*, 1987, **6**, 1105; (*c*) F. A. Cotton, P. Lahuerta, J. Payá, F. Barceló and M. A. Ubeda, *Inorg. Chem.*, 1988, **27**, 1010.

3 (*a*) P. Lahuerta, J. Payá, X. Solans and M. A. Ubeda, *Inorg. Chem.*, 1992, **31**, 385; (b) P. Lahuerta, E. Peris, M. A. Ubeda, S. García-Granda, F. Gómez-Beltran and M. R. Díaz, *J. Organomet. Chem.*, 1993, **455**, C10; (*c*) A. Garcia-Bernabé, P. Lahuerta, M. A. Ubeda, S. García-Granda and P. Pertierra, *Inorg. Chim. Acta*, 1995, **229**, 203.

4 (*a*) C. J. Alarcón, P. Lahuerta, E. Peris, M. A. Ubeda, A. Aguirre, S. García-Granda and F. Gómez-Beltrán, *Inorg. Chim. Acta*, 1997, **254**, 177; (*b*) C. J. Alarcón, F. Estevan, P. Lahuerta, M. A. Ubeda, G. González, M. Martínez and S. E. Stiriba, *Inorg. Chim. Acta*, 1998, **278**, 61.

5 S. P. Perlepes, J. C. Huffman, J. Matonic, K. R. Dunbar and G. Chistou, *J. Am. Chem. Soc.*, 1991, **113**, 2770.

6 F. Estevan, unpublished work.

7 P. Lahuerta, M. A. Ubeda, J. Payá, S. García-Granda and F. Gómez-Beltrán, *Inorg. Chim. Acta*, 1993, **205**, 91.

8 F. Estevan, P. Lahuerta, E. Peris, M. A. Ubeda, S. García-Granda, F. Gómez-Beltrán, E. Pérez-Carreño, G. González and M. Martínez, *Inorg. Chim. Acta*, 1994, **218**, 189.

9 (*a*) F. A. Cotton, K. R. Dunbar and M. G. Verbruggen, *J. Am. Chem. Soc.*, 1987, **109**, 5498; (*b*) F. A. Cotton, K. R. Dunbar and C. T. Eagle, *Inorg. Chem.*, 1987, **26**, 4127.

10 (*a*) J. L. Bear, C. L. Yao, R. S. Lifsey, J. D. Korp and K. M. Kadish, *Inorg. Chem.*, 1991, **30**, 336; (*b*) Y. Fuchita, Y. Ohta, K. Hiraki, M. Kawatani and N. Nishiyama, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 3767; (*c*) J. A. Jenkins, J. P. Ennet and M. Cowie, *Organometallics*, 1988, **7**, 1845; (*d*) V. M. Miskowski, R. F. Dallinger, G. G. Chistoph, D. E. Morris, G. H. Spies and W. H. Woodruff, *Inorg. Chem.*, 1987, **26**, 2127; (*e*) F. A. Cotton and M. Matusz, *Inorg. Chim. Acta*, 1988, **143**, 45; (*f*) T. Glowiak, H. Pasternak and F. Pruchnik, *Acta. Crystallogr.*, *Sect. C.*, 1987, **43**, 1036; (*g*) F. A. Cotton and K. R. Dunbar, *J. Am. Chem. Soc.*, 1987, **109**, 3142; (*h*) F. A. Cotton and T. R. Felhouse, *Inorg. Chem.*, 1980, **19**, 320.

11 A. T. Baker, W. R. Tikkanen, W. C. Kaska and P. C. Ford, *Inorg. Chem.*, 1984, **23**, 3254.

12 S. A. Johnson, H. R. Hunt and H. M. Neumann, *Inorg. Chem.*, 1963, **2**, 960.

13 E. A. Hart, *J. Chem. Soc.*, 1960, 3324.

14 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986; SHELXL 93, University of Göttingen, 1993.

15 G. M. Sheldrick, SHELXS 93, SHELXL 97, University of Göttingen, 1997.

16 SHELXTL V. 5.05 AXS, Siemens, Madison, WI, 1996.

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