

# The donor properties of 1,8-bis(diphenylphosphino)-3,6-dioxaoctane towards cationic rhodium(I) salts revisited. X-Ray structural characterization of a quadridentate mode of bonding

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## Abstract

The  $[(\text{dppoo})\text{Rh}(\text{COD})]^+$  cation ( $\text{dppoo} = (\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_2)_2$ ) reacts with chloroform at room temperature to give  $[\text{RhCl}_2(\text{dppoo})]^+$ , whose structure has been established by X-ray structural determination on  $[\text{RhCl}_2(\text{dppoo})][\text{PF}_6]$ . The  $\text{dppoo}$  ligand adopts a planar  $\eta^4$  mode of bonding, the two chlorine atoms being in the *trans* position.  $[(\text{dppoo})\text{Rh}(\text{COD})][\text{ClO}_4]$  (**2**) reacts with dihydrogen at atmospheric pressure to give  $[(\text{dppoo})\text{Rh}][\text{ClO}_4]$  (**4**) in which  $\text{dppoo}$  adopts the same mode of bonding, as deduced from spectroscopic data. The formation of **4** involves the transient formation of unstable  $[(\text{dppoo})\text{Rh}(\text{H})_2][\text{ClO}_4]$  which has been detected by nuclear magnetic resonance (NMR) spectroscopy. Under carbon monoxide,  $[(\text{dppoo})\text{Rh}(\text{CO})_2][\text{ClO}_4]$  (**6**) is formed, and is readily decarbonylated to  $[(\text{dppoo})\text{Rh}(\text{CO})][\text{ClO}_4]$  (**7**) under vacuum. In **6**,  $\text{dppoo}$  is *trans* bidentate. In **7**, low temperature NMR experiments imply an equilibrium between  $\eta^3$  and  $\eta^4$  bonding for  $\text{dppoo}$ . **2** is a poor catalyst for the hydrogenation of alkynes and ketones and shows a low activity towards the hydroformylation of 1-hexene.

**Key words:** Rhodium; Hydrogenation; Hydroformylation; Phosphine ether

## 1. Introduction

Coordination chemistry and catalysis with complexes containing hemilabile \* oxygen–phosphorus ligands is an active field of interest because the weak metal–oxygen bonds may create reversibly empty coordination sites favourable for catalytic activity [1].

In this family of ligands, the  $\alpha,\omega$ -bis(diphenylphosphino)polyethers play a special role since complexation of alkali cations by the polyether chain close to the transition metal can be expected, promoting acyl formation or stabilizing the acyl species [2]. The polyethers can also encapsulate solvent molecules [3].

Curiously, little information is available concerning

the application of such ligands in catalysis. Pursuing our investigations of functionalized phosphines in catalysis [4], we have selected the easily available 1,8-bis(diphenylphosphino)-3,6-dioxaoctane ( $\text{dppoo}$ ) [5], which has been demonstrated to act as a *cis* or *trans* bidentate ligand through phosphorus [5–7] and as a tetradentate ligand [6]. This great flexibility seemed to be propitious for catalysis. Moreover, this study led us to reconsider its complexing properties towards cationic rhodium salts because we have found only an X-ray structure determination for  $[(\text{dppoo})\text{Rh}(\text{CO})(\text{C}_2\text{H}_5\text{OH})][\text{PF}_6]$  (**1**) without other spectroscopic characterization [3b] and a partial spectroscopic study of  $[(\text{dppoo})\text{Rh}(\text{COD})][\text{ClO}_4]$  (**2**) [8].

In this paper, we report a full characterization of **2**, a study of its reactivity towards chloroform, hydrogen and carbon monoxide, and some data on the catalytic activity of **2** for the hydrogenation of alkynes and for the hydroformylation of 1-hexene.

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\* Hemilabile refers to a polydentate ligand, one or more donor atoms of which can become free during reaction.

## 2. Results and discussion

### 2.1. Synthesis and reactivity of $[(dppoo)Rh(COD)]^+$ towards chloroform

This cation has been previously synthesized by Thewissen *et al.* [8] as the perchlorate salt and characterized by chemical analysis and  $^{31}P$  nuclear magnetic resonance (NMR) spectroscopy. The NMR spectrum showed the expected resonance at 12.27 ppm ( $J_{RhP} = 144.3$  Hz) and several other resonances which were presumed to be due to dimeric or polymeric species or the result of cyclooctadiene elimination.

In our hands the synthesis of  $[(dppoo)Rh(COD)]-[ClO_4]$  (**2**) using the published procedure, *i.e.* the addition of an equivalent of dppoo in tetrahydrofuran (THF) solution to a mixture of  $[Rh(COD)acac]$  and perchloric acid in THF, led to the isolation of a pure compound whose  $^{31}P$  NMR spectrum exhibited only one doublet at 11.42 ppm ( $J_{RhP} = 144.3$  Hz) in dichloromethane solution. The  $^1H$  NMR spectrum in the same solvent showed the expected resonances (see Section 3) for complexed 1,5-cyclooctadiene and dppoo. The cation salt with  $[PF_6]^-$  (**2'**) was obtained starting from  $[(RhCl(COD))_2]$  and two equivalents of dppoo in dichloromethane–methanol with a slight excess of  $[NH_4][PF_6]$ .

We discovered fortuitously the origin of one of the other products observed by Thewissen *et al.* [8] by running the  $^{31}P$  NMR spectrum in chloroform: a new doublet appeared rapidly at 45.3 ppm ( $J_{RhP} = 125.7$  Hz), which compared well with one of the unknown products [8] ( $\delta = 45.44$  ppm,  $J_{RhP} = 125.4$  Hz). After 1 h, no starting material remained. The reaction on a preparative scale gave the new complex **3**. The  $^1H$  NMR spectrum of this compound showed it to be free of 1,5-cyclooctadiene, and only the resonances of the complexed dppoo were observed. The nature of **3** ( $[Rh(dppoo)Cl_2][PF_6]$ ) has been obtained by X-ray structural determination.

A perspective view of the cationic part of the molecule is given in Fig. 1 with the labelling scheme. Bond lengths and angles of interest are gathered in Table 1. The cationic part of the molecule consists of a rhodium atom surrounded by dppoo  $\eta^4$  bonded in a plane and two *trans* chlorine atoms, the molecule having a distorted octahedral geometry. To our knowledge, this is the first structural characterization of  $\eta^4$  bonding for dppoo, although it has been proposed on the basis of IR spectroscopic data for nickel(II) complexes [6].

The Rh(1), P(1), P(2), O(1) and O(2) atoms are approximately in a plane but, due to the steric strains imposed by the tetradentate ligand, there are important distortions from an octahedral geometry in this

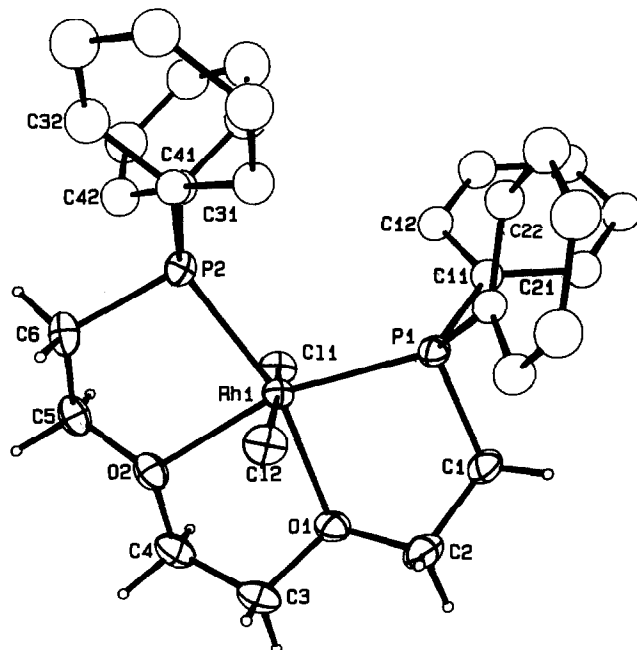


Fig. 1. Perspective view of the complex  $[Rh(Ph_2PCH_2CH_2OCH_2)_2Cl_2][PF_6]$  (**3**). Thermal ellipsoids are shown at the 30% probability level.

plane:  $111.0^\circ(1)$  for the P(1)–Rh(1)–P(2) angle and  $79.1^\circ(3)$  for O(1)–Rh(1)–O(2). The rhodium–oxygen bond distances are similar to those found in  $[Rh(CO)-[P(Ph_2CH_2CH_2)_2O]][PF_6]$  ( $2.112(7)$  Å) [3a], but the Rh–P distances are longer than in this complex ( $2.307(3)$ ,  $2.294(3)$  Å [3a]). This is certainly due to the *trans* phosphorus and oxygen atoms. The Cl(1), Rh(1) and Cl(2) atoms are not linearly arranged and the two Rh–Cl bonds are slightly bent towards the oxygen atoms.

To summarize, the reaction of chloroform with **2** has induced the loss of 1,5-cyclooctadiene and the oxidation of rhodium(I) to rhodium(III). Even though chloroform is a well-known chlorinating agent for organometallic complexes, to our knowledge this is the first case where smooth oxidation has been observed for a complex  $[Rh(COD)L_2]^+$ .

To gain an insight into the mechanism of this reaction, it was monitored by  $^1H$  NMR spectroscopy. At the end of the reaction, there are resonances only of free 1,5-cyclooctadiene, **3** and 1,1,2,2-tetrachloroethane. The latter compound suggests a radical mechanism for the action of chloroform, and the ease of this reaction may be due to assistance by coordination of the ether chain of dppoo.

The use of **2** as a catalyst for hydrogenation and hydroformylation reactions led us to test its reactivity towards dihydrogen and carbon monoxide.

TABLE 1. Selected bond lengths (Å) and angles (°) for [Rh(1)Cl<sub>2</sub>][PF<sub>6</sub>] (3)

Bond lengths			
Rh(1)–O(1)	2.135(7)	P(2)–C(31)	1.811(7)
Rh(1)–O(2)	2.133(7)	P(2)–C(41)	1.799(7)
Rh(1)–P(1)	2.257(3)	O(1)–C(2)	1.44(1)
Rh(1)–P(2)	2.248(3)	O(1)–C(3)	1.45(1)
Rh(1)–Cl(1)	2.318(3)	O(2)–C(4)	1.44(1)
Rh(1)–Cl(2)	2.328(3)	O(2)–C(5)	1.44(1)
P(1)–C(1)	1.85(1)	C(1)–C(2)	1.51(2)
P(1)–C(11)	1.814(7)	C(3)–C(4)	1.50(2)
P(1)–C(21)	1.806(7)	C(5)–C(6)	1.51(1)
P(2)–C(6)	1.85(1)		
Bond angles			
O(2)–Rh(1)–O(1)	79.1(3)	P(2)–Rh(1)–Cl(1)	91.4(1)
O(2)–Rh(1)–P(2)	85.2(2)	P(2)–Rh(1)–Cl(2)	91.4(1)
O(2)–Rh(1)–P(1)	163.6(2)	P(1)–Rh(1)–Cl(1)	93.2(1)
O(2)–Rh(1)–Cl(1)	88.9(2)	P(1)–Rh(1)–Cl(2)	92.7(1)
O(2)–Rh(1)–Cl(2)	84.0(2)	Cl(1)–Rh(1)–Cl(2)	172.1(1)
O(1)–Rh(1)–P(2)	164.0(2)	C(21)–P(1)–C(11)	102.3(3)
O(1)–Rh(1)–P(1)	84.9(2)	C(21)–P(1)–C(1)	108.4(4)
O(1)–Rh(1)–Cl(1)	85.6(2)	C(21)–P(1)–Rh(1)	118.4(2)
O(1)–Rh(1)–Cl(2)	89.7(2)	C(11)–P(1)–C(1)	103.8(4)
P(2)–Rh(1)–P(1)	111.0(1)	C(11)–P(1)–Rh(1)	124.4(2)
C(1)–P(1)–Rh(1)	97.8(3)	C(4)–O(2)–C(5)	117.4(7)
C(41)–P(2)–C(31)	103.4(3)	C(4)–O(2)–Rh(1)	108.2(8)
C(41)–P(2)–C(6)	106.7(4)	C(5)–O(2)–Rh(1)	113.7(6)
C(41)–P(2)–Rh(1)	117.8(3)	C(2)–C(1)–P(1)	114.3(8)
C(31)–P(2)–C(6)	106.2(4)	O(1)–C(2)–C(1)	104.8(9)
C(31)–P(2)–Rh(1)	123.2(2)	O(1)–C(3)–C(4)	106.2(9)
C(6)–P(2)–Rh(1)	97.8(3)	O(2)–C(4)–C(3)	106.9(8)
C(2)–O(1)–C(3)	116.0(8)	O(2)–C(5)–C(6)	104.9(8)
C(2)–O(1)–Rh(1)	113.6(6)	C(5)–C(6)–P(2)	112.5(8)
C(3)–O(1)–Rh(1)	109.3(6)		

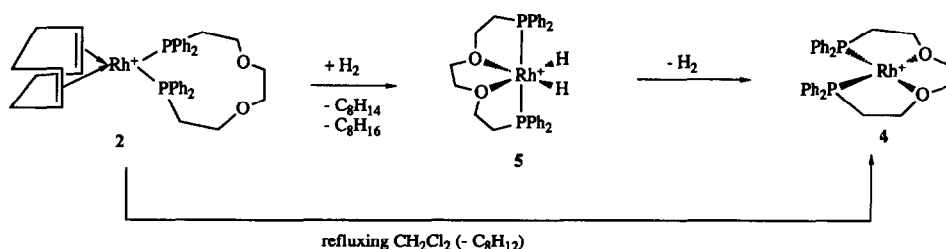
resonances of the complexed dppoo are observed. This suggests the formation of [(dppoo)Rh][ClO<sub>4</sub>] in which dppoo is tetradentate as in **3**. This is supported by the <sup>31</sup>P NMR data: the high value of *J*<sub>RhP</sub> is consistent with phosphorus atoms *trans* to atoms of low *trans* influence, such as oxygen [9]. Similar values have been observed for complexes [RhL<sub>2</sub>]<sup>+</sup> where L is an ether-phosphine [10,11] (190 < *J* < 200 Hz) or for compounds [Rh(PR<sub>3</sub>)<sub>2</sub>(ROH)<sub>2</sub>]<sup>+</sup> (190 < *J* < 210 Hz) [9,12]. Formation of **4** certainly involves the transient formation of a hydride intermediate since dihydride complexes [H<sub>2</sub>RhL<sub>2</sub>]<sup>+</sup> (L = ether-phosphine) are unstable [10,11]. To detect this intermediate we have carried out NMR experiments at low temperature under 10 atm pressure of dihydrogen. Under these conditions, a doublet of triplets is observed in the <sup>1</sup>H NMR spectrum at –21.26 ppm (*J*<sub>P–H</sub> = 15.9 Hz, *J*<sub>Rh–H</sub> = 30 Hz) consistent with the formation of [H<sub>2</sub>Rh(dppoo)][ClO<sub>4</sub>] (**5**). In the low field region, signals from cyclooctene and cyclooctane are observed, together with signals due to the complexed dppoo. In the <sup>31</sup>P NMR spectrum a doublet is found at 44.7 ppm (*J*<sub>RhP</sub> = 115.8 Hz). These data are similar to those of [H<sub>2</sub>RhL<sub>2</sub>]<sup>+</sup> (L = (tetrahydrofurfuryl)phosphine [10] or <sup>1</sup>Pr<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OMe [11]) for which *cis* hydride ligands and *trans* phosphorus atoms have been proposed. Thus in **5** dppoo should be non-planar tetradentate. If the NMR tube is depressurized, complex **4** rapidly appears at room temperature at the expense of complex **5**. Complex **4** is also observed by <sup>31</sup>P NMR spectroscopy on heating **2** under reflux in dichloromethane, but its low thermal stability prevents its preparation in good yield. All these observations are summarized in Scheme 1.

## 2.2. Reactivity of [(dppoo)Rh(COD)][ClO<sub>4</sub>] towards dihydrogen

**2** reacts quickly with dihydrogen at atmospheric pressure and room temperature to give a new complex **4**, whose <sup>31</sup>P NMR spectrum exhibits a doublet at δ = 59.3 ppm (*J*<sub>RhP</sub> = 203.2 Hz). In the <sup>1</sup>H NMR spectrum no hydride resonances are detected and only

## 2.3. Reactivity of [(dppoo)Rh(COD)][ClO<sub>4</sub>] towards carbon monoxide

**2** in solution in dichloromethane reacts readily with carbon monoxide with the loss of 1,5-cyclooctadiene to give **6**, which can be handled only under carbon



Scheme 1.

monoxide. In the IR spectrum, a  $\nu_{\text{CO}}$  absorption band is observed at  $2010\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the solution shows free 1,5-cyclooctadiene and complexed dppoo, while in the  $^{31}\text{P}$  NMR spectrum at room temperature a doublet is observed at 19.8 ppm with  $J_{\text{RhP}} = 105.1\text{ Hz}$ . At 190 K under carbon monoxide the main resonance is a doublet at 25.2 ppm ( $J_{\text{RhP}} = 101.8\text{ Hz}$ ) which can be attributed to **6**, but a small doublet is also observed at 28.3 ppm ( $J_{\text{RhP}} = 73.3\text{ Hz}$ ).

When the solution of **6** is evaporated to dryness and left under vacuum for 2 h a new complex, **7**, is formed which shows  $\nu_{\text{CO}}$  at  $1990\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum shows only the resonances of dppoo, slightly modified compared with complex **6**. A doublet is observed at 30.6 ppm with  $J_{\text{RhP}} = 123.8\text{ Hz}$  in the room temperature  $^{31}\text{P}$  NMR spectrum. Bubbling carbon monoxide into a solution of **7** immediately regenerates the complex **6**.

Examination of literature data concerning similar cationic carbonyl complexes of rhodium containing hemilabile oxygen–phosphorus ligands suggests that we are observing an equilibrium between monocarbonyl (**7**) and dicarbonyl (**6**) species, the tricarbonyl species only being observed at low temperature under carbon monoxide. Rhodium–phosphorus complexes have coupling constants in the range 70–80 Hz ( $[\text{Rh}(\text{CO})_3\text{L}_2]^+$ ) [13] and 116 Hz ( $[\text{Rh}(\text{CO})_2\text{L}_2]^+$ ) [14]. In the case of monocarbonyl complexes, with the rhodium atom bonded to two *trans* phosphorus atoms and to an oxygen atom of one of the ether-phosphines *trans* to the carbonyl, the coupling constants are in the range 120–130 Hz [10,13,14].

If our hypothesis is correct, **7** should be fluxional. To check this, we have carried out  $^1\text{H}$  and  $^{31}\text{P}$  NMR experiments at low temperature. Actually, the situation is more complex: the doublet observed at room temperature changes to two broad peaks centred at 31.3 and 23.1 ppm at 213 K. At 178 K, the broad peak at 31.3 ppm transforms into a broad doublet at 33.1 ppm ( $J_{\text{RhP}} = 128.2\text{ Hz}$ ) and the broad peak at 23.1 ppm into two sharp doublets at 23.2 ppm ( $J_{\text{RhP}} = 123.6\text{ Hz}$ ) and 22.6 ppm ( $J_{\text{RhP}} = 125.4\text{ Hz}$ ). The approximate intensity

ratio of these three signals is 1 : 1 : 0.5. The similarity of the coupling constants of the three signals indicates that the phosphorus atoms are *trans* in the three products. Comparison with the results observed by Lindner and coworkers [1,10,13] suggests that the two signals at 23.2 and 22.6 ppm should be due to a pair of diastereoisomers in which dppoo is bonded by the two phosphorus atoms and one of the oxygens of the ether chain. We attribute the other resonance to a complex with a trigonal bipyramidal structure in which dppoo is  $\eta^4$  bonded, the two phosphorus atoms are axial and the two oxygen atoms and the carbonyl group are equatorial. These results are summarized in Scheme 2. In Lindner's phosphines, an equilibrium between monocarbonyl and tricarbonyl species was observed, with no evidence of an intermediate dicarbonyl complex.

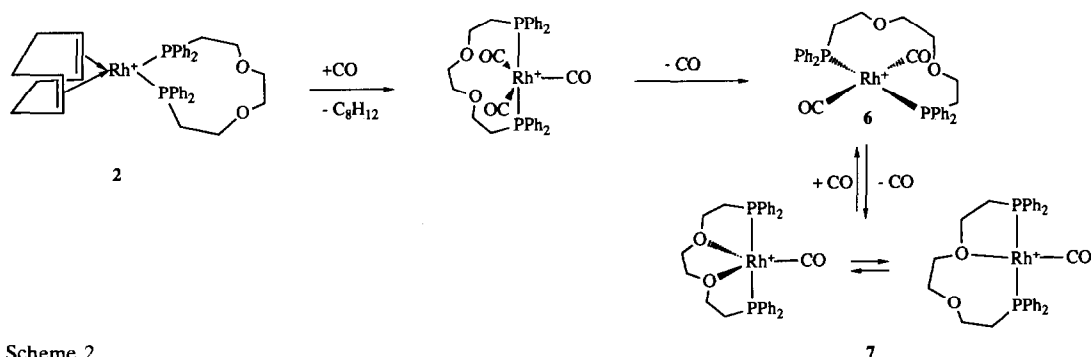
#### 2.4. Catalytic properties of $[(\text{dppoo})\text{Rh}(\text{COD})][\text{ClO}_4]$

The complexes  $[(\text{PR}_3)_2\text{Rh}(\text{COD})]^+$  are good precursors for catalytically active species for the hydrogenation of alkynes, alkenes and ketones, the active species being generated by the hydrogenation of 1,5-cyclooctadiene and stabilized by the coordination of two solvent molecules [15–20]. The ligand dppoo can play the role of the solvent through the oxygen atoms of its ether chain, and we have checked the catalytic activity of **2** for the hydrogenation of alkynes or ketones.

Using the conditions of Schrock and Osborn [17] (THF as solvent; catalyst concentration, 5.3 mM; alkyne/catalyst = 170;  $30^\circ\text{C}$ ; 1 atm  $\text{H}_2$ ), we observed a very low activity for the hydrogenation of phenylacetylene. Increasing the dihydrogen pressure to 10 atm led to 100% conversion in 3 h with 66% selectivity in styrene and 12% in ethylbenzene, the remaining product being a yellow organic polymer not fully characterized.

In the case of 3-hexanone no hydrogenation was observed under the Schrock–Osborn conditions [19] even with a pressure of hydrogen of 10 atm.

Complex **2** has disappointing catalytic activity com-



Scheme 2.

pared with similar complexes with tertiary phosphines. This may be due to the multidentate chelating behaviour of dppoo, which prevents the access of reactants to the coordination sphere of rhodium.

A weak activity has also been observed for the hydroformylation of 1-hexene: at 50°C under 20 atm of a 1:1 mixture of CO + H<sub>2</sub>, 67% conversion to aldehydes has been observed after 6 h with an *n*/iso ratio of 2.4.

### 3. Experimental section

All reactions were performed under dinitrogen using standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer 225 spectrometer. NMR spectra were recorded on Bruker AC 80 (<sup>31</sup>P), AC 200 (<sup>1</sup>H) and AM 250 (variable temperature experiments) instruments. Elemental analyses (C and H) were performed in our laboratory. [(COD)Rh(acac)] [21] and (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>)<sub>2</sub> [6] (dppoo) have been prepared according to published procedures.

#### 3.1. Synthesis of [(COD)Rh(dppoo)][ClO<sub>4</sub>] (2)

To [(COD)Rh(acac)] (0.3 g, 1 mmol) in 3.5 ml of THF was added 0.99 mmol of HClO<sub>4</sub>. After 15 min stirring, dppoo (0.94 mmol, 0.45 g) in 6 ml of THF was added and the solution was stirred for 2 h. The solution was then evaporated to dryness and the residue was dissolved in acetone. Diethyl ether induced the precipitation of **2** (0.6 g) as yellow crystals (yield, 80%) which were purified by crystallization in methanol. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub> sol.): 4.65 (4H, COD), 4.44 (dt, *J*<sub>HH</sub> = 7 Hz, *J*<sub>PH</sub> = 11.2 Hz; 4H, CH<sub>2</sub>CH<sub>2</sub>P), 3.97 (s, 4H, OCH<sub>2</sub>), 2.60 (dt, *J*<sub>HH</sub> = 7 Hz, *J*<sub>PH</sub> = 8.6 Hz; 4H, CH<sub>2</sub>CH<sub>2</sub>P), 2.22 (m, 8H, COD). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub> sol.): 11.42 ppm (d, *J*<sub>RhP</sub> = 144.3 Hz). Anal. Calc. for C<sub>40</sub>H<sub>52</sub>ClO<sub>8</sub>P<sub>2</sub>Rh (**3**, 2CH<sub>3</sub>OH): C, 55.79; H, 6.09. Found: C, 55.75; H, 5.84%.

#### 3.2. Synthesis of [(COD)Rh(dppoo)][PF<sub>6</sub>] (2')

To [(COD)RhCl]<sub>2</sub> (0.2 g, 0.4 mmol) in 10 ml of a 1:1 mixture of dichloromethane-methanol was added dppoo (0.9 mmol, 0.45 g) and [NH<sub>4</sub>][PF<sub>6</sub>] (0.3 g). The solution was stirred for 2 h. It was then evaporated to dryness and the residue was dissolved in methanol. Cooling to -20°C induced the formation of 0.4 g of **2'** as yellow crystals (yield, 57%). Anal. Calc. for C<sub>38</sub>H<sub>44</sub>F<sub>6</sub>O<sub>2</sub>P<sub>3</sub>Rh: C, 54.15; H, 5.22. Found: C, 53.75; H, 5.54%.

#### 3.3. Synthesis of [(dppoo)RhCl<sub>2</sub>][PF<sub>6</sub>] (3)

[(COD)Rh(dppoo)][PF<sub>6</sub>] (0.2 g) was dissolved in 5 ml of chloroform and the solution was stirred at room temperature for 2 h. After evaporation of the solvent

in vacuum, crystallization in methanol afforded **3** as pale orange crystals (0.15 g, 79% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub> sol.): 4.59 (s, 4H, OCH<sub>2</sub>), 4.48 (dt, *J*<sub>HH</sub> = 6.1 Hz, *J*<sub>PH</sub> = 24.9 Hz; 4H, CH<sub>2</sub>CH<sub>2</sub>P), 3.36 (dt, *J*<sub>HH</sub> = 6.1 Hz, *J*<sub>PH</sub> = 11.1 Hz; 4H, CH<sub>2</sub>CH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub> sol.): 45.3 (d, *J*<sub>RhP</sub> = 125.4 Hz), 144.5 (PF<sub>6</sub>, *J*<sub>PF</sub> = 710 Hz) ppm. Anal. Calc. for C<sub>30</sub>H<sub>32</sub>Cl<sub>2</sub>F<sub>6</sub>O<sub>2</sub>P<sub>3</sub>Rh: C, 44.74; H, 4.01. Found: C, 44.52; H, 4.25%.

#### 3.4. Reaction of [(COD)Rh(dppoo)][ClO<sub>4</sub>] with hydrogen

##### 3.4.1. Synthesis of 4

Dihydrogen was bubbled through a solution of **2** (0.2 g) in dichloromethane for 1 h. The solution turned rapidly pale yellow. It was then evaporated to dryness and the residue was dissolved in a small amount of acetone. The product was reprecipitated by adding diethyl ether to the acetone solution, affording **4** (0.12 g, 69% yield) as a pale yellow powder which was unstable on prolonged contact with the solution. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub> sol.): 4.40 (s, 4H, OCH<sub>2</sub>), 4.02 (dt, *J*<sub>HH</sub> = 6 Hz, *J*<sub>PH</sub> = 22 Hz; 4H, CH<sub>2</sub>CH<sub>2</sub>P), 2.70 (dt, *J*<sub>HH</sub> = 6 Hz, *J*<sub>PH</sub> = 9.1 Hz; 4H, CH<sub>2</sub>CH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub> sol.): 59.3 ppm (d, *J*<sub>RhP</sub> = 203.2 Hz). Anal. Calc. for C<sub>30</sub>H<sub>32</sub>ClO<sub>6</sub>P<sub>2</sub>Rh: C, 52.31; H, 4.68. Found: C, 52.71; H, 4.84%.

##### 3.4.2. Synthesis of 5

**2** (0.05 g) was dissolved in CD<sub>2</sub>Cl<sub>2</sub> in a heavy wall NMR tube equipped with a pressure valve. Dihydrogen was admitted (10 atm) and the NMR experiments were run at 193 K. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub> sol.): 4.55 (s, 4H, OCH<sub>2</sub>), 4.31 (b, 4H, CH<sub>2</sub>CH<sub>2</sub>P), 2.88 (b, 4H, CH<sub>2</sub>CH<sub>2</sub>P), -21.26 (dt, *J*<sub>PH</sub> = 15.9 Hz, *J*<sub>RhH</sub> = 30 Hz, 2H, RhH). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub> sol.): 44.7 ppm (d, *J*<sub>RhP</sub> = 115.8 Hz).

#### 3.5. Reaction of [(COD)Rh(dppoo)][ClO<sub>4</sub>] with carbon monoxide

##### 3.5.1. Synthesis of 6

Carbon monoxide was bubbled through a solution of **2** (0.2 g) in dichloromethane for 1 h. The solution turned rapidly pale yellow. It was then evaporated to dryness to remove 1,5-cyclooctadiene. The residue was dissolved in a small amount of dichloromethane and the solution was saturated with carbon monoxide. Diethyl ether saturated with carbon monoxide was added to the solution and **6** precipitated as a yellow powder (0.15 g, 75% yield). ν(CO) (CH<sub>2</sub>Cl<sub>2</sub> sol.): 2010 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub> sol.): 3.78 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>P), 3.69 (s, 4H, OCH<sub>2</sub>), 2.98 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>P) (293 K). <sup>31</sup>P

$\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$  sol.): 19.8 ppm (d,  $J_{\text{RhP}} = 105.1$  Hz) (293 K). Anal. Calc. for  $\text{C}_{32}\text{H}_{32}\text{ClO}_8\text{P}_2\text{Rh}$ : C, 51.60; H, 4.33. Found: C, 51.72; H, 4.55%.

### 3.5.2. Synthesis of 7

**2** (0.2 g) was treated as for the synthesis of **6** but decarbonylation was achieved by refluxing in THF or by prolonged vacuum treatment. The complex was purified by crystallization from methanol, affording **7** (0.110 g, 61% yield) as yellow crystals.  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$  sol.):  $1990\text{ cm}^{-1}$ .  $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$  sol., 293 K): 4.00 (m, 4H,  $\text{CH}_2\text{CH}_2\text{P}$ ), 3.80 (s, 4H,  $\text{OCH}_2$ ), 3.12 (m, 4H,  $\text{CH}_2\text{CH}_2\text{P}$ ).  $\{^{31}\text{P}\{^1\text{H}\}\}$  NMR ( $\text{CD}_2\text{Cl}_2$  sol.): (293 K) 30.6 ppm (d,  $J_{\text{RhP}} = 123.8$  Hz). Anal. Calc. for  $\text{C}_{31}\text{H}_{32}\text{ClO}_7\text{P}_2\text{Rh}$ : C, 51.94; H, 4.50. Found: C, 52.21; H, 4.64%.

### 3.6. Catalytic experiments

All catalytic runs were performed in a 100 ml home-built stainless steel autoclave equipped with gas and liquid inlets, a heating device and magnetic stirring. Gas chromatography (GC) analyses were performed on an Intersmat IGC 120 FL flame ionization detector gas chromatograph, fitted with a  $3\text{ m} \times \frac{1}{8}$  in

column (10% Carbowax 20M on Chromosorb W 80/100 mesh) using  $\text{N}_2$  as carrier gas. *o*-Xylene was used as internal standard for the hydrogenation of phenylacetylene and 3-hexanone and mesitylene for the hydroformylation of 1-hexene.

The experimental conditions were as follows: (i) hydrogenation of phenylacetylene: phenylacetylene (17 mmol), **2** (0.1 mmol), THF (16 ml), *o*-xylene (2 ml),  $\text{H}_2$  (10 bar),  $30^\circ\text{C}$ ; (ii) hydrogenation of 3-hexanone: 3-hexanone (17 mmol), **2** (0.1 mmol), THF (16.5 ml),  $\text{H}_2\text{O}$  (0.02 ml), *o*-xylene (2 ml),  $\text{H}_2$  (10 bar),  $30^\circ\text{C}$ ; (iii) hydroformylation of 1-hexene: 1-hexene (20 mmol), **2** (0.1 mmol),  $\text{CH}_2\text{Cl}_2$  (16 ml), mesitylene (1.5 ml),  $\text{NEt}_3$  (0.04 ml),  $\text{H}_2$  (10 bar),  $\text{CO}$  (10 bar),  $50^\circ\text{C}$ .

### 3.7. Crystallographic studies

Crystals of **3** suitable for X-ray diffraction were obtained by recrystallization from a dichloromethane-methanol mixture at  $-20^\circ\text{C}$ . Data were collected on an Enraf-Nonius CAD4 diffractometer at  $22^\circ\text{C}$ . Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range  $24^\circ < 2\theta(\text{Mo K}\alpha_1) < 28^\circ$ . The space group was determined

TABLE 2. Experimental data for X-ray study of compound  $[\text{Rh}(\text{dppoo})\text{Cl}_2][\text{PF}_6] \cdot \text{H}_2\text{O}$

Compound	$[\text{RhCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{PPh}_2)][\text{PF}_6] \cdot \text{H}_2\text{O}$
Formula	$\text{C}_{30}\text{H}_{34}\text{Cl}_2\text{F}_6\text{O}_3\text{P}_3\text{Rh}$
$F_w$ (a.m.u.)	823.32
$a$ (Å)	10.573(1)
$b$ (Å)	24.685(2)
$c$ (Å)	12.985(1)
$\beta$ ( $^\circ$ )	93.49(1)
$V$ (Å <sup>3</sup> )	3383.6(6)
$Z$	4
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.617
Space group	$P2_1/c$
$T$ ( $^\circ\text{C}$ )	22
Radiation	Graphite monochromated, $\text{Mo K}\alpha$ , $\lambda(\text{Mo K}\alpha_1) = 0.7093$ Å
Linear absorption coefficient (cm <sup>-1</sup> )	8.58
Transmission factors <sup>a</sup>	0.93–1
Receiving aperture (mm)	$4.0 \times 4.0$
Take off angle ( $^\circ$ )	3.5
Scan speed (deg min <sup>-1</sup> )	2
Scan mode	$\omega/2\theta$
Scan range ( $^\circ$ )	0.80 below $\text{K}\alpha_1$ to 0.80 above $\text{K}\alpha_2$
$2\theta$ limit ( $^\circ$ )	2–46
Unique data used in final refinement, $F_o^2 > 3\sigma(F_o^2)$	3637
Final number of variables	233
$R$ (on $F_o$ , $F_o^2 > 3\sigma(F_o^2)$ ) <sup>b</sup>	0.056
$R_w$ (on $F_o$ , $F_o^2 > 3\sigma(F_o^2)$ ) <sup>c</sup>	0.068
Goodness of fit	4.06

<sup>a</sup>  $\Psi$ -scan method. <sup>b</sup>  $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ . <sup>c</sup>  $R_w = [\sum w(|F_o\| - |F_c|)^2 / (\sum w |F_o|^2)]^{1/2}$ , unit weights.

TABLE 3. Fractional atomic coordinates and isotropic or equivalent temperature factors ( $\text{\AA}^2 \times 100$ ) with estimated standard deviations in parentheses ( $U_{\text{eq}} = 1/3$  trace  $U$ )

Atom	x	y	z	$U_{\text{eq}} / U_{\text{iso}}$
Rh(1)	0.86112(7)	0.35785(3)	0.13684(5)	2.95(4)
Cl(1)	0.7978(3)	0.4233(1)	0.0165(2)	4.4(2)
Cl(2)	0.9206(3)	0.2836(1)	0.2392(2)	4.4(2)
P(1)	1.0176(2)	0.4101(1)	0.2092(2)	3.4(1)
P(2)	0.6814(2)	0.3680(1)	0.2190(2)	3.5(1)
O(1)	0.9978(6)	0.3353(3)	0.0302(5)	4.1(4)
O(2)	0.7569(7)	0.2992(3)	0.0457(5)	4.3(4)
C(1)	1.143(1)	0.3909(5)	0.1227(8)	4.8(7)
C(2)	1.126(1)	0.3355(5)	0.0740(9)	5.4(7)
C(3)	0.957(1)	0.2860(5)	-0.0225(8)	5.1(7)
C(4)	0.817(1)	0.2928(5)	-0.0498(8)	4.9(7)
C(5)	0.622(1)	0.3082(5)	0.0397(8)	4.6(7)
C(6)	0.588(1)	0.3146(5)	0.1502(8)	4.6(7)
C(11)	1.0182(5)	0.4836(3)	0.2059(5)	3.8(2)
C(12)	0.9095(5)	0.5141(3)	0.1810(5)	4.8(3)
C(13)	0.9141(5)	0.5705(3)	0.1869(5)	6.1(3)
C(14)	1.0274(5)	0.5964(3)	0.2176(5)	6.2(3)
C(15)	1.1362(5)	0.5659(3)	0.2424(5)	5.9(3)
C(16)	1.1315(5)	0.5095(3)	0.2365(5)	4.9(3)
C(21)	1.0742(6)	0.3961(2)	0.3406(5)	3.5(2)
C(22)	1.0343(6)	0.4297(2)	0.4186(5)	4.5(3)
C(23)	1.0683(6)	0.4179(2)	0.5216(5)	5.7(3)
C(24)	1.1422(6)	0.3724(2)	0.5466(5)	6.1(3)
C(25)	1.1822(6)	0.3388(2)	0.4686(5)	5.8(3)
C(26)	1.1481(6)	0.3506(2)	0.3655(5)	4.9(3)
C(31)	0.6709(5)	0.3546(3)	0.3553(5)	3.6(2)
C(32)	0.5505(5)	0.3489(3)	0.3925(5)	6.0(3)
C(33)	0.5374(5)	0.3404(3)	0.4975(5)	6.4(3)
C(34)	0.6447(5)	0.3374(3)	0.5653(5)	5.7(3)
C(35)	0.7650(5)	0.3431(3)	0.5281(5)	5.8(3)
C(36)	0.7781(5)	0.3517(3)	0.4231(5)	4.7(3)
C(41)	0.5947(7)	0.4303(3)	0.1996(5)	4.4(3)
C(42)	0.4971(7)	0.4354(3)	0.1230(5)	6.0(3)
C(43)	0.4354(7)	0.4850(3)	0.1078(5)	7.7(4)
C(44)	0.4713(7)	0.5294(3)	0.1692(5)	7.6(4)
C(45)	0.5690(7)	0.5243(3)	0.2458(5)	8.3(4)
C(46)	0.6307(7)	0.4747(3)	0.2610(5)	6.4(3)
P(3)	0.3797(3)	0.2019(1)	0.3045(2)	5.0(2)
F(1)	0.5088(6)	0.2078(4)	0.3065(6)	8.1(5)
F(2)	0.3629(9)	0.1627(5)	0.2124(8)	14.5(9)
F(3)	0.2108(7)	0.1962(4)	0.3037(7)	9.2(6)
F(4)	0.358(1)	0.2369(5)	0.4058(9)	13.5(9)
F(5)	0.3753(8)	0.1523(4)	0.3817(8)	11.2(7)
F(6)	0.3423(9)	0.2514(5)	0.235(1)	17.(1)
O(w)	0.3771(9)	0.0025(4)	-0.0339(7)	8.2(3)

by careful examination of systematic extinctions in the listing of the measured reflections. All calculations were performed on a Micro Vax 3400. Data reductions were carried out using the SDP crystallographic computing package [22]. The intensities were corrected from absorption using the empirical  $\Psi$ -scan method [23]. Table 2 presents further crystallographic information.

The structure was solved using the SHELXS-86 program [24] and refined using the SHELX-76 program [25].

The position of Rh, Cl and P atoms was determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses. At a final stage of the refinement, a difference Fourier map revealed a strong peak situated at non-bonding distances from any atoms of the molecule: this peak has been attributed to the oxygen atom of a water molecule. Atomic scattering factors were taken from the usual tabulations [26]. Anomalous dispersion terms for Rh, Cl and P atoms were included in  $F_c$  [27]. All non-hydrogen atoms were allowed to vibrate anisotropically, except the carbon atoms of the phenyl rings which were refined as isotropic rigid groups ( $C_6H_5$  ring: imposed  $D_{6h}$  symmetry,  $C-C = 1.395 \text{ \AA}$ ,  $C-H = 0.97 \text{ \AA}$ ) and the oxygen atom of the water molecule. Hydrogen atoms were entered in idealized positions ( $C-H = 0.97 \text{ \AA}$ ) and held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart *et al.* [28].

Final atomic coordinates and  $U_{\text{eq}} \times 100$  (or  $U_{\text{iso}} \times 100$ ) for non-hydrogen atoms are given in Table 3. Tables of thermal parameters and complete lists of bond lengths and angles are available from the Cambridge Crystallographic Data Centre or from the authors and a list of structure factors is available from the authors.

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