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Rhodium(III) complexes of (*EEE*)-1,5,9-Cyclododecatriene. Syntheses, structures and absolute configurations of derivatives of *catena*-poly-[μ-dichloro-(1,2,12-η)-1,5,8 cyclododecatrienylrhodium] [☆]

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Abstract

The reaction of $RhCl_3 \cdot 3H_2O$ with (*EEE*)-1,5,9-cyclododecatriene in alcohols gives a red polymeric solid compound with chlorine bridges, **1**, in which the hydrocarbon moiety has been reported to be bonded to the metal via an η^3-allylic bond. Re-examination of this reaction has led to the isolation of soluble derivatives obtained by breaking the chlorine bridges with chelating diphosphines and diamines. An X-ray analysis on single crystals of a diphosphino and a diamino derivative, indicates that the cyclo-olefin residue with composition $C_{12}H_{17}$ has undergone isomerization. The two double bonds not involved in the bonding to the metal are 5,8 rather than 5,9.

Keywords: Rhodium; 1,5,9-Cyclododecatriene; Synthesis; X-ray structure η^3-allylic complexes; Olefin isomerization

1. Introduction

Prior work has shown that the reaction between $RhCl_3 \cdot 3H_2O$ and (*EEE*)-1,5,9-cyclododecatriene (CDT) in boiling alcohols leads to a polymeric derivative of Rh^{III}, **1**, tentatively described as $[\{RhCl_2(C_{12}H_{19}\}_n]$, with chlorine bridges [1]. By reaction of **1** with bases such as CO, NH_3, phosphines, etc., monomeric compounds were obtained. A structural analysis on the basis of two-dimensional X-ray data of the monomeric derivative, **2**, obtained by reaction of **1** with 1,2-diaminoethane revealed a distorted η^3-allylic bonding of the hydrocarbon moiety to Rh and the questionable presence of only one free double bond in the hydrocarbon ring [1b].

In order to settle all the unresolved questions, we re-examined the whole problem starting from a revised X-ray analysis of **2** together with a structural determination of the (−) diastereomeric derivative, **3**, obtained by reaction of **1** with (+)-(*S*, *S*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, [(*S*, *S*)-DIOP].

2. Results and discussion

The formation of **1** was strongly affected by the alcohols employed as solvents. In ethanol the overall reaction can be simplified as follows:

$$n\mathrm{RhCl_3} + n\mathrm{CH_3CH_2OH} + 2n\mathrm{C_{12}H_{18}} \longrightarrow \underset{\mathbf{1}}{[\{\mathrm{RhCl_2(C_{12}H_{17})}\}_n]} + n\mathrm{HCl} + n\mathrm{CH_3CHO} + n\mathrm{C_{12}H_{20}}.$$

Actually, it is more intricate because $C_{12}H_{22}$ (but not $C_{12}H_{24}$) is formed, besides $C_{12}H_{20}$. The yields of **1**, and of the dehydrogenation products of the alcohol (acetaldehyde), depend in no simple way upon the starting ratio CDT/Rh. The best conditions to obtain **1** (yield greater than 80%) have been found for ratios CDT/Rh ≥ 1.5. With a ratio close to one the yield drops to ca. 50%.

[☆] Dedicated to Prof. F. Calderazzo in recognition of his important contribution to organometallic chemistry.

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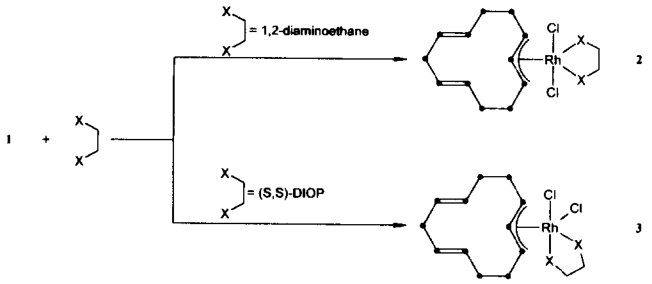


Scheme 1.

In 2-propanol, the reaction course is similar, the product of the dehydrogenation of the alcohol being acetone.

In methanol no metal-olefin product is obtained in a time comparable with that of the other alcohols. Formaldehyde does not form and sometimes a mirror of metallic Rh is produced.

In *t*-butanol, a red, insoluble, polymeric compound is obtained in high yield. It is apparently similar to **1**, but its elemental analysis corresponds roughly to the formula $[\{(RhCl_2)_3(CDT)\}_n]$.

Compound **1** reacts with mono- (B) and bi-dentate (B′) bases, which break the chlorine bridges, forming monomeric compounds $[RhCl_2(C_{12}H_{17})B_2]$ and $[RhCl_2(C_{12}H_{17})B']$ [1b]. The compounds obtained by reaction of **1** with 1,2-diaminoethane, *trans*-$[RhCl_2(C_{12}H_{17})\{(CH_2)_2(NH_2)_2\}](H_2O)$, **2**, and with (*S*, *S*)-DIOP, the diastereomer (-)-*cis*-$[RhCl_2(C_{12}H_{17})\{(S, S)$-DIOP$\}]$, **3**, have been prepared (Scheme 1) and examined by X-ray analysis. Both the structures are consistent with the chemical composition $[\{RhCl_2(C_{12}H_{17})\}_n]$ for **1**, and indicate the presence of two *E* double bonds in positions five and eight in the hydrocarbon ring. The η^3 bonding of the CDT moiety to the metal arises from metallation of the olefin. An isomerization of the olefin is induced with a migration of a double bond from position nine to eight.

The presence of hydrogenated CDT, and of products arising from the dehydrogenation of the alcohols, indicates a transfer of hydrogen from alcohol to the olefin, with formation of a carbonyl product, probably via a metal-hydride species.

We tentatively propose the following reaction mechanism.

(a) Rhodium-hydride species, **4**, containing CDT are first formed by reaction of $RhCl_3$ in alcohol. CDT might behave as a bi- or tri-dentate ligand.

$$RhCl_3 + L + RR'CHOH \longrightarrow \underset{\mathbf{4}}{[HRhCl_2L]} + HCl + RR'CO$$

R = Alkyl, R′ = Alkyl or H, L = 1,5,9 CDT.

Reactions of this type have been extensively described [2].

(b) The hydride induces an intramolecular isomerization of the bonded olefin by shifting a double bond, via hydrogen transfer, from position nine to position eight. The complex **4** is converted into the similar complex **5** in which the bonded olefin can be formulated as 1,5,8-CDT [3].

$$\underset{\mathbf{4}}{[HRhCl_2L]} \longrightarrow \underset{\mathbf{5}}{[HRhCl_2L']} \qquad L' = 1,5,8\ CDT$$

(c) A new CDT unit reacts with the isomerized hydride **5** yielding an intermediate in which it is σ-bonded to Rh [4]. It undergoes hydrolysis through the action of HCl formed in the first step, so producing hydrogenated CDT ($C_{12}H_{20}$) and complex **6**. $C_{12}H_{20}$ can be further reduced to $C_{12}H_{22}$ in an analogous step.

$$\underset{\mathbf{5}}{[HRhCl_2L']} + C_{12}H_{18} \longrightarrow [(C_{12}H_{19})RhCl_2L']$$

$$[(C_{12}H_{19})RhCl_2L'] \xrightarrow{+HCl} \underset{\mathbf{6}}{[RhCl_3L']} + C_{12}H_{20}$$

(d) Complex **6** loses HCl, giving an η^3-allylic bonding with Rh [5] and forming, through polymerization, the final product $[\{RhCl_2(C_{12}H_{17})\}_n]$, **1**.

$$n\underset{\mathbf{6}}{[RhCl_3L']} \longrightarrow nHCl + \underset{\mathbf{1}}{[\{RhCl_2(C_{12}H_{17})\}_n]}$$

The formation of a rhodium-hydride derivative involves dehydrogenation of the alcohol used as solvent. According to our experiments, it forms only in the presence of ethanol or 2-propanol. This can be explained in terms of irreversible oxidation potentials [6] and $\Delta H^{\neq}$ values [7] for the systems (alcohol)/(carbonylic derivative), which are in the order methanol > ethanol > 2-propanol. In the conditions used, methanol exhibits the highest oxidation potential, which probably inhibits the formation of the hydride.

In boiling *t*-butanol, the reaction follows a quite different path. In this case a red insoluble compound, different from **1**, is formed with evolution of HCl. (At present, the reaction and the resulting compound are under investigation.)

The molecular structures of the monomeric derivatives **2** and **3**, obtained by breaking the chlorine bridges of **1** with 1,2-diaminoethane and (*S*, *S*)-DIOP respectively, are shown in Figs. 1 and 2 with the atom labelling scheme. In Table 1 selected geometrical parameters are reported. Both compounds display a distorted octahedral coordination about the Rh (or a distorted trigonal-bipyramidal coordination depending on whether the hydrocarbon is regarded as bi- or mono-dentate ligand. In the case of **3** the asymmetric arrangement of the ligands about Rh is responsible of the different bonding of the C(2)–C(1)–C(12) atom grouping to the metal as compared with **2**. Because of the different environments on the left and on the right

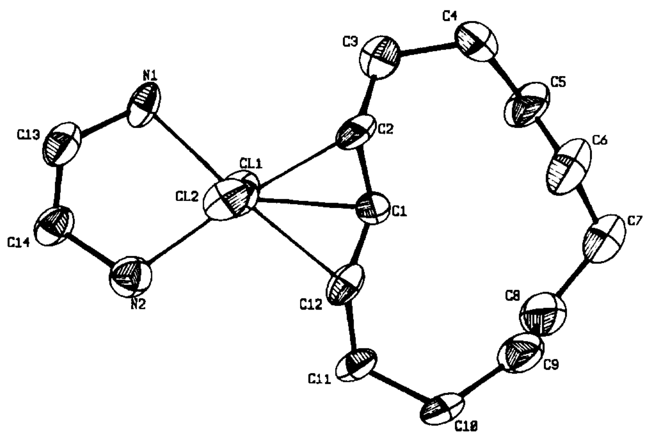


Fig. 1. A perspective view of the molecule of **2**.

side of C(1) in the case of **3**, very different metal–carbon distances are observed: Rh–C(2) (2.206 Å), Rh–C(1) (2.127 Å) and Rh–C(12) (2.382 Å). These can be explained both by *trans* effects and by intramolecular non-bonded interactions. Table 2 reports some short contact distances from C(2), C(3) and C(12), C(11), which seem to be balanced by the larger distance Rh–C(12). Moreover, the bond lengths C(1)–C(2), 1.340 Å, and C(1)–C(12), 1.389 Å, indicate a double and a partial double bond character respectively, in contrast with the values of 1.43 Å and 1.40 Å of the corresponding bonds in the case of **2**. As a consequence, to the bond of Rh with the grouping C(12)–C(1)–C(2), cannot simply be assigned η^3-allylic character, which is the opposite of **2**, where the Rh–C distances range within 2.12–2.16 Å. A σ-bond with C(12) is excluded, owing to the large value of the Rh–C(12) distance (single Rh–C bonds range within 2.03–2.08 Å [8]). The geometrical parameters of **3** can be interpreted better by invoking a substantial contribution of a zwitterion limit form, as shown in Scheme 2. The strict similarity of the conformation of the hydrocarbon ring in the two complexes excludes an sp^3 configuration of C(12) and the location on it of two methylene hydrogen atoms. The large bond angle C(1)–C(12)–

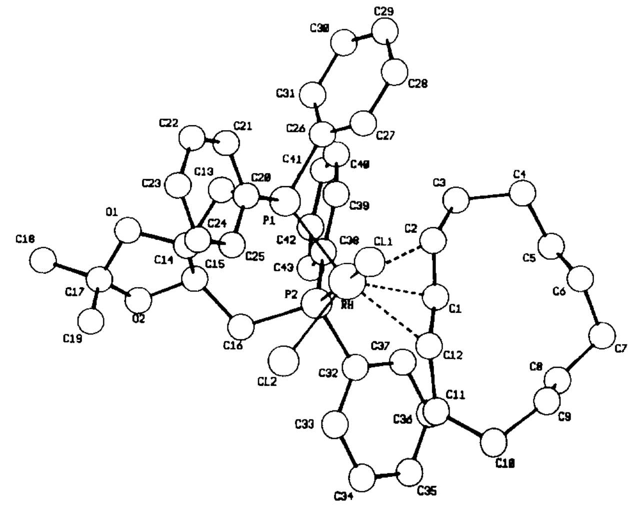


Fig. 2. A perspective view of the molecule of **3**. (The thermal ellipsoids of the atoms are omitted for sake of clarity).

Table 1
Selected geometrical parameters for **2** and **3**

	2	**3**	
Bond distances (Å)			
Rh–Cl(1)	2.341(5)	2.433(6)	
Rh–Cl(2)	2.354(5)	2.466(6)	
Rh–P(1)	–	2.340(6)	
Rh–P(2)	–	2.284(5)	
Rh–N(1)	2.15(1)	–	
Rh–N(2)	2.18(1)	–	
Rh–C(1)	2.12(1)	2.127(3)	
Rh–C(2)	2.16(1)	2.206(2)	
Rh–C(12)	2.164(6)	2.382(2)	
C(1)–C(2)	1.43(1)	1.340(6)	
C(2)–C(3)	1.54(1)	1.551(8)	
C(3)–C(4)	1.55(1)	1.534(8)	
C(4)–C(5)	1.53(1)	1.524(7)	
C(5)–C(6)	1.34(1)	1.342(8)	
C(6)–C(7)	1.52(1)	1.513(8)	
C(7)–C(8)	1.55(1)	1.522(9)	
C(8)–C(9)	1.34(1)	1.334(9)	
C(9)–C(10)	1.54(1)	1.534(9)	
C(10)–C(11)	1.55(1)	1.522(6)	
C(11)–C(12)	1.52(1)	1.506(8)	
C(12)–C(1)	1.40(1)	1.389(9)	
Bond angles (°)			
N(1)–Rh–N(2)	79.6(5)	101.9(3)	P(1)–Rh–Cl(2)
Cl(1)–Rh–N(1)	86.6(6)	81.5(2)	Cl(1)–Rh–P(1)
Cl(1)–Rh–N(2)	87.8(6)	88.8(3)	Cl(1)–Rh–Cl(2)
Cl(1)–Rh–Cl(2)	173.2(4)	173.8(3)	Cl(1)–Rh–P(2)
Cl(2)–Rh–N(1)	87.9(6)	85.7(2)	P(2)–Rh–Cl(2)
Cl(2)–Rh–N(2)	87.4(6)	96.9(2)	P(2)–Rh–P(1)
C(1)–C(2)–C(3)	110.3(8)	115.6(3)	
C(2)–C(3)–C(4)	109.5(4)	109.7(3)	
C(3)–C(4)–C(5)	111.4(6)	106.8(3)	
C(4)–C(5)–C(6)	118.8(7)	111.3(3)	
C(5)–C(6)–C(7)	119.9(6)	112.9(3)	
C(6)–C(7)–C(8)	111.8(5)	104.7(3)	
C(7)–C(8)–C(9)	120.9(7)	129.9(4)	
C(8)–C(9)–C(10)	120.1(7)	120.4(3)	
C(9)–C(10)–C(11)	116.1(3)	111.8(3)	
C(10)–C(11)–C(12)	112.5(5)	118.5(3)	
C(11)–C(12)–C(1)	120.2(9)	132.9(4)	
C(12)–C(1)–C(2)	121.0(9)	132.8(4)	
Torsion angles (°)			
C(1)–C(2)–C(3)–C(4)	−82.3	−86.1	
C(2)–C(3)–C(4)–C(5)	79.0	82.2	
C(3)–C(4)–C(5)–C(6)	−105.3	−115.3	
C(4)–C(5)–C(6)–C(7)	167.2	172.0	
C(5)–C(6)–C(7)–C(8)	−95.7	−100.0	
C(6)–C(7)–C(8)–C(9)	−60.7	−69.0	
C(7)–C(8)–C(9)–C(10)	162.3	172.0	
C(8)–C(9)–C(10)–C(11)	−63.7	−57.4	
C(9)–C(10)–C(11)–C(12)	−47.0	−38.9	
C(10)–C(11)–C(12)–C(1)	89.0	97.6	
C(11)–C(12)–C(1)–C(2)	173.5	187.0	
C(12)–C(1)–C(2)–C(3)	189.7	167.3	

Table 2
Some intramolecular non-bonded distances from C(2), C(3) and C(12), C(11) for **3**

C(2)······C(26)	3.59	C(12)······Cl(2)	3.17
C(2)······C(27)	3.57	C(12)······C(32)	3.54
C(2)······P(1)	3.53	C(11)······C(32)	3.50
C(3)······C(39)	3.25	C(11)······C(33)	3.37

C(11), 132.8°, supports this conclusion, though the hydrogen atom on C(12) was not detected from difference Fourier synthesis. However, all the hydrogen atoms of the allylic group were located in the case of **2**, which confirms the composition of the coordinated ring in both the structures as $C_{12}H_{17}$.

Thus, C(12) is chiral in **3**. Once the (*S*, *S*) absolute configuration of the employed DIOP has been confirmed, we could assign to C(12) an (*R*) configuration [9] and an (*S*) configuration to both the well localized double bonds C(5)–C(6) (1.342 Å) and C(8)–C(9) (1.334 Å) (the assignment is based on a comparison with (+)-(*S*)-*trans*-cyclooctene [10]).

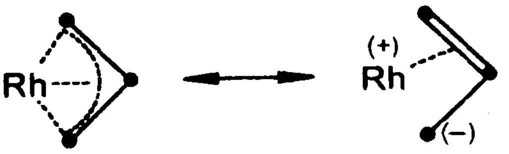
If the partial double-bond character of C(1)–C(2) is accepted, and it is assigned (*S*) configuration [9], it follows that the migration of a double bond occurring in the course of the reaction takes place from the bond C(9)–C(10) to the bond C(8)–C(9). Unless quite intricate conformational rearrangements are invoked, it is legitimate to presume that the migration occurs from an (*R*) configuration of the original double bond in C(9)–C(10) to an (*S*) configuration of the newly formed adjacent double bond C(8)–C(9). Similar arguments can be adopted for **2**, though in this case origins of the two free double bonds cannot be ascertained. Therefore the configuration of CDT before the reaction is probably (*SSR*). This result is consistent with our previous data [11] which showed predominance of the configurations (*SSR*) or (*RRS*) compared to (*SSS*) or (*RRR*) in pure CDT.

The ^1H NMR spectra of **2** and **3** are very complex, and it was impossible to distinguish separate signals assignable to particular hydrogen nuclei.

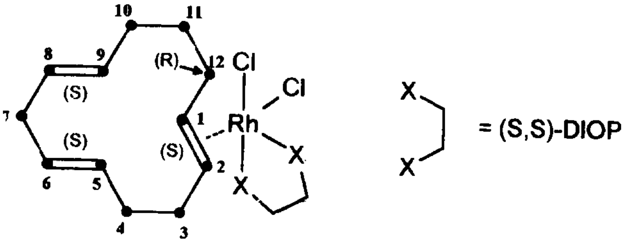
3. Conclusion

In contrast with a previous formulation , the presence of two free double bonds in the coordinated CDT has been proved both for **2** and **3**, at positions five and eight, which proves that an isomerization has been induced by rhodium-hydride species in the course of the reaction. The hydride is formed in the first step of the reaction through the action of alcohols in a complex reduction process in which HCl is evolved, a carbonyl compound is formed, and the excess of olefin is reduced. A mechanistic picture of the overall process has been proposed.

In the case of **3**, the two uncoordinated double bonds of the ring display an (*S*) configuration and the asymmetric carbon atom C(12), forming a partial zwitterion with the metal, assumes an (*R*) configuration. The conformational assignments are schematically shown in Scheme 3.



Scheme 2.



Scheme 3.

4. Experimental section

All reactions and manipulations, if not stated otherwise, were carried out under dry argon with standard Schlenk, vacuum line or septum/cannula techniques. Solvents were purified, dried and distilled before use. (+)-(*S*, *S*)-DIOP, (*EEE*)-1,5,9-cyclododecatriene and $RhCl_3 \cdot 3H_2O$ were purchased from Aldrich, 1,2-diaminoethane from Carlo Erba and used without further purification.

IR spectra were obtained on a Perkin Elmer 597 spectrophotometer. Optical activities were measured on a Perkin Elmer 171 polarimeter. GC/MS determinations were carried out on a Carlo Erba QMD 1000 instrument equipped with a capillary column PS 264, 30 m, carrier gas He 1 ml min^{-1}, temperature from 100 to 250°C, 10°C min^{-1}. Elemental analyses were provided by the Microanalysis Laboratory of the CIMA Department of the University of Padova.

4.1. Synthesis

4.1.1. Synthesis of $[\{RhCl_2(C_{12}H_{17})\}_n]$, 1

Compound **1** was prepared as previously described [1]. In a series of experiments, the alcohol used as solvent and the ratio olefin/Rh were changed. A typical reaction is reported here.

$RhCl_3 \cdot 3H_2O$ (0.745 g, 2.83 mmol) was dissolved in 40 ml of ethanol and CDT (0.688 g, 4.25 mmol) was added. The solution was sealed in a vial which was maintained at 80°C. After 1 h a red solid began to form and precipitation was complete after 8 h. The vial was opened and the solid was filtered off, washed with ethanol and dried under vacuum. Yield: 0.775 g, 82%.

1: M.p. 218–220°C (dec.). Anal. Found: C, 42.72; H, 5.31. $C_{12}H_{17}Cl_2Rh$ Calc.: C, 43.01; H, 5.11%.

The mother liquors were concentrated to ca. 2 ml, filtered to eliminate a little solid which precipitated, and passed through a SiO_2 column which retains all Rh-containing compounds (hexane as eluant). The solution was concentrated and showed the presence of $C_{12}H_{20}$, $C_{12}H_{22}$, and unreacted $C_{12}H_{18}$ (GC/MS determination).

A separate experiment was performed with the same procedure. At the end of the reaction the mixture was distilled until dryness, and the condensed solution revealed the presence of HCl, determined by titration (73%) and of acetaldehyde (84%) determined by GC/MS and formation, identification and weighing of its 2,4-dinitrophenylhydrazone [12].

Similar results were obtained by performing the reaction in 2-propanol, with acetone as carbonyl product.

A lower ratio olefin/Rh gave a decreased yield of **1** and of carbonyl compounds. As an example a ratio olefin/Rh = 1 lowered the yield of **1** to ca. 50%.

4.1.2. Reaction of $RhCl_3 \cdot 3H_2O$ with CDT in t-butanol

$RhCl_3 \cdot 3H_2O$ (0.320 g, 1.22 mmol) was dissolved in 50 ml of *t*-butanol and CDT (0.290 g, 1.80 mmol) was added. The solution was sealed in a vial which was maintained at 85°C. After 1 h a red solid began to form and precipitation was complete after 3 h. The solid was filtered off, washed with *t*-butanol and hexane, and dried under vacuum. Yield: 0.220 g, Anal. Found: C, 21.25; H, 2.99%.

4.1.3. Attempted reaction of $RhCl_3 \cdot 3H_2O$ with CDT in methanol

Attempts to perform the reaction of $RhCl_3 \cdot 3H_2O$ with CDT in methanol never led to solid compounds. Sometime a metallic Rh mirror formed.

Table 3
Summary of the crystal data and intensity data collection for **2** and **3**

	2	**3**
Formula	$RhCl_2N_2C_{14}H_{25} \cdot H_2O$	$RhCl_2P_2O_2C_{43}H_{49}$
M	406.77	883.82
Crystal (mm)	0.20 × 0.30 × 0.35	0.25 × 0.25 × 0.20
T (K)	298	
Radiation	graphite monochromated Mo–Kα (λ = 0.7107 Å)	
Space group	$P\bar{1}$	$C2$
a (Å)	10.041(4)	24.492(8)
b (Å)	11.562(4)	15.651(5)
c (Å)	9.142(4)	13.556(5)
α (°)	109.8(1)	–
β (°)	112.2(1)	90.5(1)
γ (°)	77.1(2)	–
V (Å^3)	914.02	5196.15
Z	2	4
D_c (g cm^{-3})	1.49	1.07
F(000)	424	1728
μ (cm^{-1})	11.07	4.62
Scan speed (° min^{-1})	2.0 in the 2θ scan mode	
Scan width (°)	1.2	
Take-off angle (°)	3	
2θ range (°)	$3.0 \le 2\theta \le 45$	
Total reflections	4424	4750
Reflections used for refinement [a]	1786	2278
Solution method	Patterson	
Refined parameters	181	451
R [b] (on F_0)	0.080	0.061
R_w [c]	0.086	0.066
Goodness of fit [d]	0.78	1.01
Highest map residuals (e Å^{-3})	1.30	0.65

[a] $F_0^2 \ge 2\sigma(F_0^2)$
[b] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$
[c] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$
[d] G.O.F = $[\Sigma w(|F_0| - |F_c|)^2/(ND - NV)^2]^{1/2}$

4.1.4. Reaction of 1 with 1,2-diaminoethane. Synthesis of trans-*$[RhCl_2(C_{12}H_{17})\{(CH_2)_2(NH_2)_2\}]H_2O$, 2*

Compound **2** was synthesized as previously reported [1] and was crystallized by slow evaporation in air of a saturated solution in acetone. Well formed crystals suitable for X-ray analysis resulted. These contain one molecule of crystallization water per molecule of complex, probably from the atmosphere.

2: M.p. 197–200°C (dec.). Anal. Found: C, 41.60; H, 6.82; N, 6.77. $C_{14}H_{25}Cl_2N_2Rh \cdot H_2O$ Calc.: C, 41.34; H, 6.69; N, 6.89%.

*4.1.5. Reaction of 1 with (+)-(S, S)-DIOP. Synthesis of (-)-*cis-*$[RhCl_2(C_{12}H_{17})\{(S,S)\text{-}DIOP\}]$, 3*

To a suspension of **1** (0.675 g, 2.01 mmol) in 40 ml of toluene, a solution of (+)-(*S*, *S*)-DIOP (1.00 g, 2.01 mmol) in 20 ml of toluene was slowly added. After 3 h stirring, the slightly cloudy solution was filtered, concentrated to 10 ml, and 10 ml of cyclohexane were added under stirring at room temperature. A yellow solid (0.150 g) was obtained. A second crop of solid was obtained by adding further cyclohexane and cooling at −20°C (0.200 g). Repeated recrystallizations from toluene/cyclohexane finally gave solids of constant α.

3: M.p. 198–201°C (dec). $[\alpha]_{578}{}^{25} = -268$ (0.1, CH_2Cl_2) Anal. Found: C, 58.60; H, 5.73. $C_{43}H_{49}Cl_2O_2P_2Rh$ Calc.: C, 58.44; H, 5.59%.

4.2. Collection of X-ray diffraction data

X-ray-quality crystals of **2** and **3** were obtained by recrystallization from acetone and toluene/cyclohexane solutions, respectively. Single crystals were mounted on a Philips PW-100 computer-controlled four-circle diffractometer with graphite monochromator. Standard centring and auto-indexing procedures indicated a triclinic lattice for **3** (the space group $P\bar{1}$ was initially assigned and later confirmed by a well-behaved refinement process) and a centred monoclinic lattice, space group $C2$, for **2**. The orientation matrix and accurate unit cell dimensions were determined from angular settings of 25 high-angle reflections. The intensities were corrected for Lorentz and polarization effects, but not for absorption owing to the relatively low value of μ. Crystallographic data are collected in Table 3.

Table 4
Fractional coordinates of non-hydrogen atoms of **2**

Rh	−0.8112(1)	−0.11727(9)	−0.2517(1)
Cl(1)	−0.5629(4)	−0.1402(3)	−0.2094(5)
Cl(2)	−1.0580(4)	−0.0694(3)	−0.2771(5)
N(1)	−0.764(1)	0.0153(9)	−0.012(1)
N(2)	−0.828(1)	0.051(1)	−0.317(1)
C(1)	−0.787(2)	−0.311(1)	−0.356(2)
C(2)	−0.826(1)	−0.287(1)	−0.213(1)
C(3)	−0.703(1)	−0.340(1)	−0.083(2)
C(4)	−0.713(1)	−0.479(1)	−0.121(1)
C(5)	−0.651(1)	−0.557(1)	−0.257(1)
C(6)	−0.743(1)	−0.604(1)	−0.408(2)
C(7)	−0.688(1)	−0.658(1)	−0.553(2)
C(8)	−0.714(1)	−0.562(1)	−0.649(1)
C(9)	−0.848(1)	−0.513(1)	−0.720(1)
C(10)	−0.871(1)	−0.394(1)	−0.770(2)
C(11)	−0.821(1)	−0.276(1)	−0.627(1)
C(12)	−0.872(1)	−0.259(1)	−0.484(1)
C(13)	−0.807(2)	0.142(1)	−0.031(2)
C(14)	−0.765(2)	0.151(1)	−0.167(2)
O(1)W	−0.450(1)	0.104(1)	−0.340(1)

Table 5
Fractional coordinates of non-hydrogen atoms of **3**

Rh	−0.20150(6)	0.100000	−0.6535(1)
Cl(1)	−0.1807(3)	0.2136(4)	−0.5365(5)
Cl(2)	−0.1070(2)	0.1095(5)	−0.7138(4)
P(1)	−0.1906(2)	0.0162(3)	−0.5117(4)
P(2)	−0.2113(2)	−0.0101(3)	−0.7628(4)
O(1)	−0.0952(5)	−0.1772(9)	−0.558(1)
O(2)	−0.0987(6)	−0.199(1)	−0.721(1)
C(2)	−0.2857(8)	0.1476(9)	−0.6370(9)
C(3)	−0.3420(7)	0.1017(9)	−0.6357(9)
C(4)	−0.3880(8)	0.1681(9)	−0.6403(9)
C(5)	−0.3956(9)	0.1920(8)	−0.7485(8)
C(6)	−0.3830(7)	0.2743(9)	−0.7643(8)
C(7)	−0.3824(8)	0.2975(9)	−0.8726(9)
C(8)	−0.3223(7)	0.2970(8)	−0.9001(9)
C(9)	−0.2822(9)	0.3500(9)	−0.873(1)
C(10)	−0.2228(8)	0.3300(9)	−0.8997(9)
C(11)	−0.2047(8)	0.2436(9)	−0.8595(9)
C(12)	−0.2237(7)	0.2172(8)	−0.7586(8)
C(1)	−0.2662(7)	0.1657(8)	−0.7267(9)
C(13)	−0.1733(9)	−0.097(1)	−0.521(2)
C(14)	−0.1266(8)	−0.110(1)	−0.593(2)
C(15)	−0.1425(8)	−0.145(1)	−0.698(1)
C(16)	−0.1518(9)	−0.077(1)	−0.779(1)
C(17)	−0.0641(9)	−0.207(2)	−0.643(2)
C(18)	−0.0481(9)	−0.300(2)	−0.628(2)
C(19)	−0.020(1)	−0.152(2)	−0.658(2)
C(20)	−0.1368(5)	0.043(1)	−0.429(1)
C(21)	−0.1404(5)	0.016(1)	−0.331(1)
C(22)	−0.0972(5)	0.030(1)	−0.265(1)
C(23)	−0.0503(5)	0.072(1)	−0.298(1)
C(24)	−0.0467(5)	0.099(1)	−0.395(1)
C(25)	−0.0899(5)	0.085(1)	−0.461(1)
C(26)	−0.2484(4)	0.0188(8)	−0.4295(8)
C(27)	−0.2622(4)	0.0961(8)	−0.3849(8)
C(28)	−0.3080(4)	0.1009(8)	−0.3246(8)
C(29)	−0.3399(4)	0.0284(8)	−0.3089(8)
C(30)	−0.3261(4)	−0.0488(8)	−0.3536(8)
C(31)	−0.2803(4)	−0.0536(8)	−0.4139(8)
C(32)	−0.2230(6)	0.0250(9)	−0.8934(8)
C(33)	−0.1771(6)	0.0482(9)	−0.9474(8)
C(34)	−0.1829(6)	0.0757(9)	−1.0448(8)
C(35)	−0.2347(6)	0.0801(9)	−1.0882(8)
C(36)	−0.2806(6)	0.0570(9)	−1.0341(8)
C(37)	−0.2747(6)	0.0295(9)	−0.9368(8)
C(38)	−0.2669(6)	−0.0885(7)	−0.751(1)
C(39)	−0.2970(6)	−0.0908(7)	−0.664(1)
C(40)	−0.3361(6)	−0.1544(7)	−0.650(1)
C(41)	−0.3452(6)	−0.2156(7)	−0.723(1)
C(42)	−0.3151(6)	−0.2132(7)	−0.810(1)
C(43)	−0.2760(6)	−0.1497(7)	−0.824(1)

In both cases the structures were solved from Patterson syntheses and completed from difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. Some of the hydrogen atoms were located from difference Fourier syntheses. Nevertheless they were geometrically recalculated together with the remaining H atoms, assigned isotropic thermal parameters (with $U(H) = 1.2U(C)$) and included in the final calculation, but not refined. The hydrogen atoms of the water present in **2** were omitted. Blocked cascade least-square refinements were used. They converged to the conventional R indices of 0.080 and 0.061 for **2** and **3** respectively. An unitary weighting scheme was used. Scattering factors for the atoms were taken from Cromer and Waber [13], the scattering factors for Rh, Cl, and P were corrected for the real and imaginary parts of anomalous dispersion using Cromer's values [14]. All computations were carried out using the SHELX-76 program [15]. The final positional parameters of the non-hydrogen atoms are listed in Table 4 and 5.

The anisotropic thermal parameters of the non-hydrogen atoms, the positional parameters of the hydrogen atoms, and full lists of bond lengths and angles and lists of calculated and observed structure factors for **2** and **3** are available from the Cambridge Crystallographic Data Centre.

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