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## Indenyl complexes of ruthenium(II) containing optically active diphosphines. X-ray structures of (*S,S*)-( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)-Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}Cl and of its $\eta^5$ -C<sub>5</sub>H<sub>5</sub> analogue

**Franco Morandini**

*Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, Via Marzolo 1, I-35131 Padova (Italy)*

**Giambattista Consiglio**

*Technisch-Chemisches Laboratorium, ETH-Zentrum, CH-8092 Zürich (Switzerland)*

**Angelo Sironi and Massimo Moret**

*Istituto di Chimica Strutturistica Inorganica, Università di Milano, Via Venezian 21, I-20133 Milano (Italy)*  
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### Abstract

The optically active indenyl complexes ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru(L–L)Cl (where L–L is either (*S,S*)-1,2-dimethyl-1,2-ethanediylbis(diphenylphosphine) (chiraphos) or (*R,R*)-1,2-cyclopentanediyylbis(diphenylphosphine) (cypenphos)) have been synthesized and spectroscopically characterized and compared with the corresponding cyclopentadienyl complexes. Reaction of the new complexes with 2- $\pi$ -donors give cationic adducts in which the pentahaptocoordination of the indenyl ligand is maintained. The crystal structures of (*S,S*)-( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}Cl (**1**) and (*S,S*)-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}Cl (**3**) have been determined.

### Introduction

Study of  $\eta^5$ -cyclopentadienylruthenium complexes containing optically active diphosphine ligands related to diphos (1,2-ethanediylbis(diphenylphosphine)) has allowed us to establish the stereochemical outcome of some simple organometallic reactions which take place at the metal atom [1–3]. Furthermore, we have investigated asymmetric induction phenomena in complexes containing prochiral ligands such as olefins ( $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(L–L)(CH<sub>2</sub>=CHR)]PF<sub>6</sub>) [4,5] or alkylidenecarbenes

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L-L})(=\text{C}=\text{CHR})\text{PF}_6]$  [6]. Particularly for the latter compounds, the difference in population between the two diastereomeric conformers appears to depend mainly on steric factors [6]. Exploitation of these optically active complexes for enantioselective catalysis, although possible in principle, e.g., in hydrogenation [7], appears to be ruled out by the high temperature necessary to achieve reasonable conversions. On the other hand, there is a growing interest in  $\eta^5$ -indenyl complexes. Indenylzirconium compounds, for instance, have been found to be more active as Ziegler–Natta catalysts than the corresponding  $\eta^5$ -cyclopentadienyl [8]. Similarly, the indenyl complex  $[(\eta^5\text{-C}_9\text{H}_7)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2]$  is a much more active catalyst precursor for intermolecular hydroacylation than the analogous cyclopentadienyl complex [9]. The higher reactivity of indenyl complexes than of their cyclopentadienyl counterparts in some substitution reactions has been ascribed to the energetically lesser slippage of the ring from  $\eta^5$  to  $\eta^3$  bonding mode with consequent opening of coordination sites on the metal [10–12]. Indenylruthenium complexes have been reported in patents to be active hydrogenation catalysts even for sterically hindered double bonds embedded in a polymeric chain [13]. We became interested in chiral indenyl complexes of ruthenium because we wished to compare asymmetric discrimination for analogous  $\eta^5$ -cyclopentadienyl and  $\eta^5$ -indenyl complexes and to examine the latter as possible enantio-selective catalysts. We report here the synthesis and the spectroscopic characterization and preliminary observations on a comparison of the reactivity of the enantiomerically pure complexes (*S,S*)- $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{Cl}$  (**1**) and of (*R,R*)- $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_2)_3\text{CHPPh}_2\}\text{Cl}$  (**2**) with that of the analogous cyclopentadienyl complexes (*S,S*)- $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{Cl}$  (**3**) and (*R,R*)- $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_2)_3\text{CHPPh}_2\}\text{Cl}$  (**4**).

## Experimental

All reactions and manipulations were carried out under nitrogen. The solvents were dried and degassed before use.  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Jeol FX 90 Q or on a AM 300 WB Bruker spectrometer. Positive  $\delta$  values in ppm are downfield from internal  $\text{Me}_4\text{Si}$  ( $^1\text{H}$  and  $^{13}\text{C}$ ) or external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). Infrared spectra were recorded with Nujol mulls on a Perkin–Elmer 781 spectrometer. Absorption and CD spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer and a Jasco J600 micrograph, respectively. Indene (99%) was obtained from Aldrich, KH (20–25 wt% dispersion in mineral oil) from Jansen, 1,2-ethanediybis(diphenylphosphine) (dppe) from Fluka, and 1,5-cyclooctadiene (COD) from Jansen, and were used without purification.

(*R,R*)-1,2-Cyclopentanediybis(diphenylphosphine) (cypenphos) [14], (*S,S*)-dimethyl-1,2-ethanediybis(diphenylphosphine) (chiraphos) [15],  $\{\text{RuCl}_2(\text{COD})\}_n$  [16],  $[\text{RuH}(\text{COD})(\text{NH}_2\text{NMe}_2)_3]\text{BPh}_4$  [17] and  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{(\text{S,S})\text{-chiraphos}\}\text{Cl}$  [3] were prepared by published procedures. (*R,R*)- $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_2)_3\text{CHPPh}_2\}\text{Cl}$  was prepared in the same way as the racemic compound [6].

### Preparation of $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{COD})\text{Cl}$

A mixture of 1.3 ml (11.1 mmol) of indene and 1.2 g (30 mmol) of KH (20–25 wt% dispersion in mineral oil) in 15 ml of THF was stirred at room temperature for 4 h. The deep violet suspension was filtered directly into a solution of 7.7 g (10.8

mmol) of  $[\text{RuH}(\text{COD})(\text{NH}_2\text{NMe}_2)_3]\text{BPh}_4$  in 50 ml of THF, and the resulting mixture was kept overnight. Removal of the solvent left a black residue, which was stirred with 25 ml of  $\text{CHCl}_3$  for several hours. The resulting solution was filtered off through neutral  $\text{Al}_2\text{O}_3$  and evaporated, to leave a red powder, which was washed with n-hexane (2 times 20 ml) and dried in vacuo. Yield 2.0 g, 50%.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 7.30 (c.m., 4H); 5.20 (c.m. 3H); 3.68–4.08 (c.m. 4H); 2.01 (c.m., 8H). Anal. Found: C, 56.77; H, 5.27.  $\text{C}_{17}\text{H}_{19}\text{ClRu}$  calcd.: C, 56.74; H, 5.32%.

*Preparation of (S,S)-( $\eta^5\text{-C}_9\text{H}_7$ )Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}Cl (1)*

A solution of 1.85 g (5.1 mmol) of ( $\eta^5\text{-C}_9\text{H}_7$ )Ru(COD)Cl and 2.26 g (5.3 mmol) of chiraphos in 80 ml toluene was refluxed for 8 h. The solvent was then removed under reduced pressure, the residue dissolved in 20 ml  $\text{CH}_2\text{Cl}_2$ , and the solution filtered through neutral  $\text{Al}_2\text{O}_3$ . Addition of n-hexane induced precipitation of a red microcrystalline product, which was recrystallized from  $\text{CH}_2\text{Cl}_2$ /n-hexane. Yield 2.5 g (70%).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 7.24 (c.m., 24 H,  $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$ ); 4.72 (q,  $J$  2.6 Hz, 1 H(ind)); 4.50 (t.,  $J$  2.6 Hz, 1H(ind)); 3.71 (s, 1H(ind)); 2.76(c.m., 1H, CH); 2.06 (c.m., 1H, CH); 0.99 (dq,  $J(\text{HH})$  7.3 Hz,  $J(\text{PH})$  11.7 Hz, 6H,  $\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 91.6, 73.7 (d,  $J(\text{PP})$  39.1 Hz).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 142.4–123.6 (c.m.,  $\text{C}_6\text{H}_5$ ); 113.3 (s, C(ind)); 106.8 s, C(ind)); 87.4 (s, C(ind)); 67.6 (d,  $J$  12.2 Hz, C(ind)); 63.8 (s, C(ind)); 38.1 (c.m., CH); 15.5 (c.m.,  $\text{CH}_3$ ). Anal. Found: C, 62.80; H, 5.08.  $\text{C}_{37}\text{H}_{35}\text{P}_2\text{ClRu}$  calcd.: C, 62.28; H, 4.94%.

*Preparation of (R,R)-( $\eta^5\text{-C}_9\text{H}_7$ )Ru{Ph<sub>2</sub>PCH(CH<sub>2</sub>)<sub>3</sub>CHPPh<sub>2</sub>}Cl (2)*

A mixture of 1.85 g (5.1 mmol) of ( $\eta^5\text{-C}_9\text{H}_7$ )Ru(COD)Cl and a slight excess (5.3 mmol) of (R,R)-cypenphos in 80 ml of toluene was refluxed. The red product was filtered off and washed several times with n-hexane. Yield 2.5 g (70%).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 7.43 (c.m., 24H,  $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$ ); 4.89 (q,  $J$  3 Hz, 1H(ind)); 4.75 (t,  $J$  3 Hz, 1H(ind)); 3.78 (s, 1H(ind)); 3.23, 2.66, 1.84 (c.m., 8H, CH +  $\text{CH}_2$ ).  $^{31}\text{P}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 74.1, 47.7 (d,  $J(\text{PP})$  46.4 Hz).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 137.5–123.8 (c.m.,  $\text{C}_6\text{H}_5$ ); 112.3 (s, C(ind)); 105.1 (s, C(ind)); 85.9 (s, C(ind)); 66.7(d,  $J$  11.6 Hz, C(ind)); 62.8 (s, C(ind)); 48.8, 30.7, 24.3 (c.m., C ring). Anal. Found: C, 65.98; H, 5.15.  $\text{C}_{38}\text{H}_{35}\text{P}_2\text{ClRu}$  calc.: C, 66.13; H, 5.11%.

*Preparation of (S,S)-[( $\eta^5\text{-C}_9\text{H}_7$ ){Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}(C=CHPh)]PF<sub>6</sub>*

A solution of 0.3 g (0.42 mmol) of (S,S)-( $\eta^5\text{-C}_9\text{H}_7$ )Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}Cl, 0.35 g (2.15 mmol) of  $\text{NH}_4\text{PF}_6$ , and 2 ml of phenylacetylene in 20 ml of methanol was stirred at room temperature for 3 h. The solvent was removed under vacuum, the residue was washed 3 times with 15 ml of n-hexane then dissolved in 20 ml of  $\text{CH}_2\text{Cl}_2$ . The solution was filtered, the solvent removed, and the residue washed with two portions (15 ml) of n-hexane. Recrystallization was from  $\text{CH}_2\text{Cl}_2$ /n-hexane. Yield 0.3 g (80%).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 7.39–6.48 (c.m. 29 H,  $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$ ); 5.85 (s, 1H(ind)); 5.69 (s, 1H(ind)); 5.56 (m, 1H, =CH) 4.64 (s, 1H(ind)); 2.74–2.31 (c.m., 2H, CH); 1.01 (dd,  $J(\text{HH})$  6.8 Hz,  $J(\text{PH})$  13.2 Hz, 6H,  $\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 75.4, 73.8 (d,  $J(\text{PP})$  29.3 Hz).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 354.9 (b.s.=C=), 137.0–122.0 (c.m.,  $\text{C}_6\text{H}_5$ ); 117.6 (s, C(ind)); 115.1 (s, C(ind)); 112.2 (s, C(ind)); 99.5 (s, C(ind)); 81.0 (s, C(ind)); 40.0–38.0 (c.m., CH); 15.0 (c.m.  $\text{CH}_3$ ). Anal. Found: C, 60.44; H, 4.92.  $\text{C}_{45}\text{H}_{41}\text{P}_3\text{F}_6\text{Ru}$  calcd.: C, 60.74; H 4.64%.

*Preparation of (S,S)-[( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}(PMe<sub>2</sub>Ph)]Cl*

To a solution of 0.5 g (0.7 mmol) of (S,S)-( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}Cl in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> was added an excess of PMe<sub>2</sub>Ph. The mixture was stirred at room temperature for 48 h. After removal of the solvent, the crude orange-yellow microcrystalline product was washed several times with n-hexane and dried in vacuo. Yield 0.51 g (90%).

The compound behaves as 1/1 electrolyte in methanol ( $\Lambda_M = 111$ ). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 7.14 (c.m., 29H, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>4</sub>); 5.08 (s, 1H(ind)); 4.96 (s, 1H(ind)); 4.58 (s, 1H(ind)); 2.40 (c.m., 2H, CH); 1.05 (c.m., 6H, CH<sub>3</sub>); 1.1, 0.55 (d, *J* 8.1 Hz, 6H, CH<sub>3</sub>). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>) 86.6 (dd *J*(PP) 29.3, 36.6 Hz); 72.3 (dd, *J*(PP) 24.4, 36.6 Hz); 1.55 (dd, *J*(PP) 29.3, 24.4 Hz). <sup>13</sup>C NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 139.0–123.1 (c.m., C<sub>6</sub>H<sub>5</sub>); 114.4 (s, C(ind)); 107.5 (s, C(ind)); 93.8 (s, C(ind)); 73.5 (s, C(ind)); 73.0 (s, C(ind)); 43.8–37.4 (c.m., CH); 20.0–14.1 (c.m., CH<sub>3</sub>) Anal. Found: C, 66.13; H, 5.66. C<sub>45</sub>H<sub>46</sub>P<sub>3</sub>ClRu calcd.: C, 66.21; H, 5.68%.

*Preparation of (S,S)-[( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}(dppe)]PF<sub>6</sub>*

A mixture of 0.5 g (0.7 mmol) of (S,S)-( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}Cl, 0.3 g (0.75 mmol) of dppe, 0.6 g (3.7 mmol) of NH<sub>4</sub>PF<sub>6</sub>, and 20 ml of CH<sub>3</sub>OH was stirred at room temperature for 8 h. The solvent was removed under reduced pressure, the residue dissolved in 10 ml of CH<sub>2</sub>Cl<sub>2</sub>, and the solution filtered. Addition of n-hexane led to the separation of a yellow product. Yield 0.7 g (85%). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 7.22 (c.m., 44H, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>4</sub>); 4.90 (s, 1H(ind)); 4.67 (s, 1H(ind)); 4.39 (s, 1H(ind)); 2.01 (c.m., 6H, CH + CH<sub>2</sub>); 0.66 (c.m., 6H, CH<sub>3</sub>). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>) 83.8 (dd, *J*(PP) 41.5, 26.8 Hz); 67.4 (dd, *J*(PP) 41.5, 26.8 Hz); 34.9 (q., *J*(PP) 26.8 Hz); -12.4 (d, *J*(PP) 26.8 Hz). <sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>) 128.5 (c.m., C<sub>6</sub>H<sub>5</sub>); 114.5 (s, C(ind)); 107.8 (s, C(ind)); 96.2 (s, C(ind)); 73.2 (s, C(ind)); 38.0 (c.m., CH); 25.1 (c.m., CH<sub>2</sub>); 15.0 (c.m., CH<sub>3</sub>).

*General procedure for NMR spectroscopic analysis of reactions of indenyl complexes with CO, PMe<sub>2</sub>Ph, dppe, and CH<sub>3</sub>CN*

A mixture of 30 mg (42  $\mu$ mol) of **1** or **2** and an equimolecular amount of the appropriate ligand was dissolved in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> in a NMR tube under inert atmosphere. CO was bubbled into the solution. The <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra were recorded from time to time at room temperature.

*(S,S)-[( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}(CO)]Cl*

<sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 7.30 (c.m., 24H, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>4</sub>); 5.71 (s, 1H(ind)); 5.65 (s, 1H(ind)); 4.58 (s, 1H(ind)); 2.80 c.m., 1H, CH); 2.24 (c.m., 1H, CH); 1.04 (dd, *J*(HH) 6.2 Hz; *J*(PH) 12.8 Hz, 6H, CH<sub>3</sub>). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>) 77.4, 75.4 (d, *J*(PP) 31.7 Hz). <sup>13</sup>C NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 200.1 (b.s., C $\equiv$ O); 131.4 (c.m., C<sub>6</sub>H<sub>5</sub>); 108.9 (s, C(ind)); 107.0 (s, C(ind)); 101.5 (s, C(ind)); 74.0 (s, C(ind)); 73.4 (s, C(ind)); 43.3, 36.3 (c.m., CH); 14.8 (c.m., CH<sub>3</sub>).  $\nu$ (CO) (1985) cm<sup>-1</sup> (Nujol).

*(S,S)-[( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}(CH<sub>3</sub>CN)]Cl*

<sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 7.53 (c.m., 24 H, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>4</sub>); 4.86 (s, 1H(ind)); 4.78 (s, 1H(ind)); 4.59 (s, 1H(ind)); 2.74–2.28 (c.m., 2H, CH); 1.53 (s, 3H, CH<sub>3</sub>CN); 1.09 (dd, *J*(HH) 6.7 Hz, *J*(PH) 12.4 Hz, 6H, CH<sub>3</sub>). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>) 88.5, 81.1 (d, *J*(PP) 41.5 Hz). <sup>13</sup>C NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 141.9–123.0 (c.m., C<sub>6</sub>H<sub>5</sub>); 108.7 (s, C(ind));

107.1 (s, C(ind)); 94.1 (s, C(ind)); 65.9 (s, C(ind)); 64.8 (s, C(ind)); 36.3 (m., CH); 14.4 (m., CH<sub>3</sub>).

$(R^*, R^*)\text{-}[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}\{\text{Ph}_2\text{P}\overline{\text{C}}\text{H}(\text{CH}_2)_3\text{CHPPh}_2\}\{\text{CO}\}]\text{Cl}$

<sup>1</sup>H NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 7.64 (c.m., 24H, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>4</sub>); 5.51 (s, 2H(ind)); 5.26 (s, 1H(ind)); 3.09–1.33 (c.m., 8H, CH + CH<sub>2</sub>). <sup>31</sup>P NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 60.7, 51.2 (d, *J*(PP) 31.7 Hz). <sup>13</sup>C NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 200.2 (b.s, C≡O); 134.8–123.9 (c.m., C<sub>6</sub>H<sub>5</sub>); 108.9 (s, C(ind)); 108.0 (s, C(ind)); 98.1 (s, C(ind)); 75.3 (s, C(ind)); 73.7 (s, C(ind)); 31.5–23.5 (c.m., C ring).  $\nu$ (CO) 1970 cm<sup>-1</sup> (Nujol).

Table 1

## Crystal analysis parameters

| Compound  | 1   | 3   |
|---|---|---|
| Formula   | C <sub>37</sub> H <sub>35</sub> ClP <sub>2</sub> Ru | C <sub>34</sub> H <sub>35</sub> Cl <sub>3</sub> P <sub>2</sub> Ru |
| Formula weight, uma   | 678.2   | 713.0   |
| Crystal system  | Monoclinic  | Monoclinic  |
| <i>a</i> , Å  | 9.990(3)  | 10.871(4)   |
| <i>b</i> , Å  | 16.558(4)   | 11.205(4)   |
| <i>c</i> , Å  | 10.511(3)   | 13.843(5)   |
| $\beta$ , deg   | 114.10(2)   | 103.07(2)   |
| <i>V</i> , Å <sup>3</sup>   | 1587.1  | 1642.5  |
| <i>Z</i> , $\rho$ (calc) g cm <sup>-3</sup>   | 2, 1.42   | 2, 1.44   |
| Space group   | <i>P</i> 2 <sub>1</sub> (No. 4)                     | <i>P</i> 2 <sub>1</sub> (No. 4)                                   |
| <i>F</i> (000)  | 696   | 728   |
| Radiation (graphite monochr.)   | Mo- <i>K</i> <sub>α</sub>                           | Mo- <i>K</i> <sub>α</sub>   |
| Diffractometer  | CAD-4 Enraf–Nonius                                  | CAD-4 Enraf–Nonius  |
| $\mu$ (Mo- <i>K</i> <sub>α</sub> ), cm <sup>-1</sup>  | 6.92  | 8.32  |
| 2 $\theta$ range, deg   | 6 ≤ 2 $\theta$ ≤ 50                                 | 6 ≤ 2 $\theta$ ≤ 50   |
| Scan method   | $\omega$  | $\omega$  |
| Scan interval, deg  | 0.80 + 0.35 tan( $\theta$ )                         | 1.00 + 0.35 tan( $\theta$ )                                       |
| Prescan speed, deg min <sup>-1</sup>  | 20  | 20  |
| Prescan acceptance $\sigma(I)/I$  | 1.00  | 0.66  |
| Required $\sigma(I)/I$  | 0.01  | 0.03  |
| Max time for one refl. meas., s   | 70  | 60  |
| Collected octants   | ± <i>h, k, l</i>                                    | ± <i>h, k, l</i>  |
| No. of data collected (at RT)   | 2883  | 3028  |
| No. of data used ( <i>I</i> > 3 $\sigma$ ( <i>I</i> ))  | 2195  | 1742  |
| Crystal decay   | no  | no  |
| No. azimuth refl. for abs. corr.  | 3   | 3   |
| Max-min transmission factor   | 1.00–0.96   | 1.00–0.87   |
| Crystal size, mm  | 0.15 × 0.10 × 0.05                                  | 0.38 × 0.14 × 0.05  |
| Weighting fudge <i>p</i> factor   | 0.035   | 0.035   |
| <i>R</i>  | 0.0297  | 0.0415  |
| <i>R</i> <sub>w</sub>   | 0.0341  | 0.0469  |
| ESD   | 1.210   | 1.510   |
| No. variable parameters   | 249   | 235   |
| Max Peak in final diff. Fourier,<br>electron Å <sup>-3</sup>                                    | 0.34  | 0.56  |
| ESD = $(\sum w( F_o  - k F_c )^2 / (N_{\text{obs}} - N_{\text{var}}))^{1/2}$                    |   |   |
| $w = 4F_o^2 / \sigma(F_o^2)^2$ where $\sigma(F_o^2) = (\sigma(I)^2 + (pI)^2)^{1/2} / \text{LP}$ |   |   |
| $R = (\sum( F_o  - k F_c ) / \sum F_o )$  |   |   |
| $R_w = (\sum w( F_o  - k F_c )^2 / \sum wF_o^2)^{1/2}$  |   |   |

Table 2  
Selected geometrical parameters

|                              | Compound 1 | Compound 3 |                           | Compound 1 | Compound 3 |
|------------------------------|------------|------------|---------------------------|------------|------------|
| <b>Bonding distances (Å)</b> |            |            | <b>Bonding angles (°)</b> |            |            |
| Ru–Cl                        | 2.441(2)   | 2.453(2)   | Cl–Ru–P1                  | 86.45(6)   | 85.97(9)   |
| Ru–P1                        | 2.239(2)   | 2.270(2)   | Cl–Ru–P2                  | 97.74(6)   | 96.91(9)   |
| Ru–P2                        | 2.312(2)   | 2.297(3)   | P1–Ru–P2                  | 83.17(6)   | 82.91(9)   |
| Ru–C5                        | 2.369(5)   | 2.246(11)  | Cl–Ru–Cp                  | 119.9      | 120.6      |
| Ru–C6                        | 2.167(6)   | 2.159(10)  | P1–Ru–Cp                  | 128.4      | 129.7      |
| Ru–C7                        | 2.149(6)   | 2.172(10)  | P2–Ru–Cp                  | 129.1      | 128.4      |
| Ru–C8                        | 2.223(7)   | 2.220(11)  | Ru–P1–C1                  | 108.2(2)   | 108.4(3)   |
| Ru–C9                        | 2.362(6)   | 2.245(10)  | Ru–P1–C111                | 119.5(2)   | 118.4(3)   |
| P1–C1                        | 1.849(6)   | 1.853(8)   | Ru–P1–C121                | 117.7(2)   | 115.4(3)   |
| P1–C111                      | 1.838(7)   | 1.831(10)  | C1–P1–C111                | 101.9(3)   | 102.8(4)   |
| P1–C121                      | 1.829(6)   | 1.835(11)  | C1–P1–C121                | 105.8(3)   | 107.4(4)   |
| P2–C2                        | 1.878(6)   | 1.866(10)  | C111–P1–C121              | 101.9(3)   | 103.3(5)   |
| P2–C211                      | 1.845(6)   | 1.872(9)   | Ru–P2–C2                  | 108.7(2)   | 110.2(3)   |
| P2–C221                      | 1.850(6)   | 1.865(11)  | Ru–P2–C211                | 114.1(2)   | 111.5(3)   |
| C1–C2                        | 1.534(8)   | 1.586(13)  | Ru–P2–C221                | 123.7(2)   | 123.9(4)   |
| C1–C3                        | 1.516(8)   | 1.531(12)  | C2–P2–C211                | 104.3(3)   | 104.6(4)   |
| C2–C4                        | 1.545(9)   | 1.532(13)  | C2–P2–C221                | 103.8(3)   | 102.4(5)   |
| C5–C6                        | 1.439(9)   | 1.397(15)  | C211–P2–C221              | 100.3(3)   | 102.3(4)   |
| C6–C7                        | 1.413(10)  | 1.401(15)  | P1–C1–C2                  | 104.6(4)   | 103.7(5)   |
| C7–C8                        | 1.406(10)  | 1.431(15)  | P1–C1–C3                  | 116.8(5)   | 116.4(6)   |
| C8–C9                        | 1.421(10)  | 1.390(20)  | C2–C1–C3                  | 113.1(5)   | 111.1(8)   |
| C9–C5                        | 1.435(9)   | 1.402(15)  | P2–C2–C1                  | 108.0(4)   | 106.7(6)   |
| C9–C10                       | 1.395(11)  |            | P2–C2–C4                  | 115.4(5)   | 115.6(7)   |
| C10–C11                      | 1.358(14)  |            | C1–C2–C4                  | 113.8(5)   | 113.5(8)   |
| C11–C12                      | 1.420(13)  |            | P1–C111–C112              | 119.4(5)   | 120.1(8)   |
| C12–C13                      | 1.355(10)  |            | P1–C111–C116              | 121.7(5)   | 120.6(8)   |
| C13–C5                       | 1.411(11)  |            | P1–C121–C122              | 119.2(5)   | 116.1(8)   |
|                              |            |            | P1–C121–C126              | 121.6(5)   | 123.8(8)   |
|                              |            |            | P2–C211–C212              | 123.4(4)   | 121.4(7)   |
|                              |            |            | P2–C211–C216              | 118.7(4)   | 117.0(7)   |
|                              |            |            | P2–C221–C222              | 122.4(4)   | 122.2(8)   |
|                              |            |            | P2–C221–C226              | 119.0(5)   | 118.0(10)  |
| <b>Torsional angles (°)</b>  |            |            |                           |            |            |
| Ru–P1–C1–C2                  | –54.2      | –53.3      |                           |            |            |
| P1–C1–C2–P2                  | 52.0       | 53.3       |                           |            |            |
| C1–C2–P2–Ru                  | –31.0      | –34.2      |                           |            |            |
| C2–P2–Ru–P1                  | –1.3       | 1.8        |                           |            |            |
| P2–Ru–P1–C1                  | 27.6       | 26.0       |                           |            |            |
| P2–Ru–P1–C111                | –88.2      | –90.4      |                           |            |            |
| P2–Ru–P1–C121                | 147.4      | 146.5      |                           |            |            |
| P1–Ru–P2–C211                | 114.5      | 117.4      |                           |            |            |
| P1–Ru–P2–C221                | –123.2     | –119.8     |                           |            |            |
| Ru–P1–C111–C112              | 16.1       | 23.4       |                           |            |            |
| Ru–P1–C111–C116              | –169.6     | –160.4     |                           |            |            |
| Ru–P1–C121–C122              | 85.9       | 79.2       |                           |            |            |
| Ru–P1–C121–C126              | –90.4      | –93.4      |                           |            |            |
| Ru–P2–C211–C212              | –88.3      | –96.4      |                           |            |            |
| Ru–P2–C211–C216              | 86.9       | 75.2       |                           |            |            |
| Ru–P2–C221–C222              | –163.8     | –141.2     |                           |            |            |
| Ru–P2–C221–C226              | 17.4       | 43.9       |                           |            |            |

$(R^*, R^*)$ - $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}\{\text{Ph}_2\text{P}\overline{\text{C}}\text{H}(\text{CH}_2)_3\text{CHPPh}_2\}\text{(PMe}_2\text{Ph)}]\text{Cl}$

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 7.30–6.41 (c.m., 29H,  $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$ ); 5.21 (s, 1H(ind)); 5.08 (s, 1H(ind)); 4.90 (s, 1H(ind)); 2.85–0.85 (c.m., 14H, CH +  $\text{CH}_2$  +  $\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 67.7 (dd,  $J(\text{PP})$  34.2, 39.1 Hz); 41.0 (dd,  $J(\text{PP})$  29.3, 39.1 Hz); 3.23 (dd,  $J(\text{PP})$  29.3, 34.2 Hz).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 139.0–122.8 (c.m.,  $\text{C}_6\text{H}_5$ );

Table 3

Positional parameters and their estimated standard deviations for  $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}\{(\text{S},\text{S})\text{-Chiraphos}\}\text{Cl}$  (1)

| Atom | <i>x</i>    | <i>y</i>   | <i>z</i>    | <i>B</i> ( $\text{\AA}^2$ ) <sup>a</sup> |
|------|-------------|------------|-------------|--|
| Ru   | −0.24100(4) | 0.000      | −0.23181(4) | 2.585(8)                                 |
| Cl   | −0.0122(2)  | 0.0459(1)  | −0.0466(2)  | 4.43(4)                                  |
| P1   | −0.1023(2)  | −0.0491(1) | −0.3358(2)  | 2.70(3)                                  |
| P2   | −0.2736(2)  | 0.1066(1)  | −0.3837(2)  | 2.50(3)                                  |
| C1   | −0.0288(6)  | 0.0370(4)  | −0.3993(6)  | 2.9(1)                                   |
| C2   | −0.1645(6)  | 0.0863(4)  | −0.4895(5)  | 2.7(1)                                   |
| C3   | 0.0693(6)   | 0.0169(5)  | −0.4733(6)  | 4.3(2)                                   |
| C4   | −0.1291(7)  | 0.1613(5)  | −0.5578(6)  | 4.1(2)                                   |
| C5   | −0.4543(5)  | 0.0051(6)  | −0.1862(5)  | 3.3(1)                                   |
| C6   | −0.4656(6)  | −0.0419(4) | −0.3054(6)  | 3.5(1)                                   |
| C7   | −0.3686(7)  | −0.1081(4) | −0.2576(7)  | 4.1(2)                                   |
| C8   | −0.2862(7)  | −0.0998(5) | −0.1134(7)  | 4.4(2)                                   |
| C9   | −0.3392(7)  | −0.0309(4) | −0.0677(6)  | 4.0(2)                                   |
| C10  | −0.3000(7)  | 0.0037(7)  | 0.0636(6)   | 5.5(2)                                   |
| C11  | −0.3787(9)  | 0.0674(6)  | 0.0771(7)   | 6.8(2)                                   |
| C12  | −0.4968(8)  | 0.1014(5)  | −0.0387(7)  | 5.8(2)                                   |
| C13  | −0.5325(7)  | 0.0721(5)  | −0.1688(7)  | 4.5(2)                                   |
| C111 | −0.1878(6)  | −0.1106(4) | −0.4943(6)  | 2.8(1)*                                  |
| C112 | −0.3402(6)  | −0.1093(4) | −0.5678(6)  | 3.2(1)*                                  |
| C113 | −0.4061(7)  | −0.1481(5) | −0.6960(7)  | 3.8(1)*                                  |
| C114 | −0.3219(8)  | −0.1890(5) | −0.7509(7)  | 4.6(2)*                                  |
| C115 | −0.1734(7)  | −0.1917(5) | −0.6786(7)  | 4.0(1)*                                  |
| C116 | −0.1042(6)  | −0.1531(4) | −0.5502(6)  | 3.5(1)*                                  |
| C121 | 0.0565(6)   | −0.1107(4) | −0.2307(6)  | 3.5(1)*                                  |
| C122 | 0.0379(7)   | −0.1924(4) | −0.2175(6)  | 3.6(1)*                                  |
| C123 | 0.1561(7)   | −0.2400(5) | −0.1349(7)  | 4.4(2)*                                  |
| C124 | 0.2905(8)   | −0.2060(5) | −0.0683(8)  | 5.3(2)*                                  |
| C125 | 0.3113(8)   | −0.1265(5) | −0.0754(8)  | 5.1(2)*                                  |
| C126 | 0.1937(7)   | −0.0766(5) | −0.1575(7)  | 4.2(1)*                                  |
| C211 | −0.4636(6)  | 0.1185(4)  | −0.5147(5)  | 2.6(1)*                                  |
| C212 | −0.5183(7)  | 0.0792(4)  | −0.6433(6)  | 3.4(1)*                                  |
| C213 | −0.6644(7)  | 0.0881(5)  | −0.7330(7)  | 4.4(2)*                                  |
| C214 | −0.7584(7)  | 0.1317(5)  | −0.6981(7)  | 3.8(1)*                                  |
| C215 | −0.7071(7)  | 0.1695(5)  | −0.5698(6)  | 3.8(1)*                                  |
| C216 | −0.5615(6)  | 0.1644(4)  | −0.4804(6)  | 3.1(1)*                                  |
| C221 | −0.2289(6)  | 0.2127(4)  | −0.3270(6)  | 2.9(1)*                                  |
| C222 | −0.2817(7)  | 0.2776(4)  | −0.4186(6)  | 3.7(1)*                                  |
| C223 | −0.2401(7)  | 0.3563(5)  | −0.3716(7)  | 4.3(1)*                                  |
| C224 | −0.1520(8)  | 0.3715(5)  | −0.2385(8)  | 5.2(2)*                                  |
| C225 | −0.1023(8)  | 0.3093(5)  | −0.1477(8)  | 5.1(2)*                                  |
| C226 | −0.1381(7)  | 0.2285(4)  | −0.1897(7)  | 3.8(1)*                                  |

<sup>a</sup> Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:  $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$ .

111.7 (s, C(ind)); 106.8 (s, C(ind)); 93.0 (s, C(ind)); 72.2 (d,  $J$  7.3 Hz, C(ind)); 70.2 (s, C(ind)); 30.7–24.3 (c.m., C ring); 20.8–14.1 (c.m., CH<sub>3</sub>).

### *X-Ray crystal structure of the compounds 1 and 3*

Crystal data and experimental conditions for both compounds are reported in Table 1. The intensity data were collected with an Enraf–Nonius CAD4 automated

Table 4

Positional parameters and their estimated standard deviations for ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru{(*S,S*)-Chiraphos}Cl (3)

| Atom | <i>x</i>   | <i>y</i>   | <i>z</i>   | $B(\text{\AA}^2)^a$ |
|------|------------|------------|------------|---------------------|
| Ru   | 0.11268(7) | 0.000      | 0.29867(6) | 2.95(1)             |
| Cl   | 0.1508(3)  | −0.2041(3) | 0.3625(2)  | 4.31(7)             |
| P1   | 0.2921(2)  | −0.0228(3) | 0.2427(2)  | 3.11(6)             |
| P2   | 0.2467(3)  | 0.0941(3)  | 0.4284(2)  | 3.07(6)             |
| C1   | 0.4284(8)  | −0.0216(9) | 0.3508(7)  | 3.1(2)              |
| C2   | 0.410(1)   | 0.098(1)   | 0.4071(8)  | 3.5(3)              |
| C3   | 0.560(1)   | −0.027(1)  | 0.3279(8)  | 4.8(3)              |
| C4   | 0.516(1)   | 0.121(1)   | 0.4993(9)  | 4.8(3)              |
| Cp1  | −0.050(1)  | −0.034(1)  | 0.1726(9)  | 4.6(3)              |
| Cp2  | −0.0959(9) | −0.036(1)  | 0.2585(9)  | 4.8(3)              |
| Cp3  | −0.076(1)  | 0.075(1)   | 0.3068(8)  | 4.5(3)              |
| Cp4  | −0.015(1)  | 0.147(1)   | 0.2499(9)  | 4.2(3)              |
| Cp5  | −0.000(1)  | 0.083(1)   | 0.1662(8)  | 4.6(3)              |
| C111 | 0.302(1)   | −0.161(1)  | 0.1733(8)  | 3.3(2)*             |
| C112 | 0.358(1)   | −0.264(1)  | 0.2158(8)  | 4.2(3)*             |
| C113 | 0.347(1)   | −0.366(1)  | 0.1594(8)  | 4.6(3)*             |
| C114 | 0.282(1)   | −0.367(1)  | 0.0634(9)  | 5.1(3)*             |
| C115 | 0.226(1)   | −0.264(1)  | 0.0218(9)  | 4.8(3)*             |
| C116 | 0.234(1)   | −0.162(1)  | 0.0736(8)  | 4.5(3)*             |
| C121 | 0.334(1)   | 0.093(1)   | 0.1627(7)  | 3.5(2)*             |
| C122 | 0.288(1)   | 0.207(1)   | 0.1655(9)  | 4.3(3)*             |
| C123 | 0.326(1)   | 0.297(1)   | 0.111(1)   | 6.2(3)*             |
| C124 | 0.405(1)   | 0.271(2)   | 0.051(1)   | 7.6(4)*             |
| C125 | 0.452(1)   | 0.162(1)   | 0.046(1)   | 7.2(4)*             |
| C126 | 0.419(1)   | 0.069(1)   | 0.1021(9)  | 5.5(3)*             |
| C211 | 0.274(1)   | 0.044(1)   | 0.5600(8)  | 4.0(3)*             |
| C212 | 0.288(1)   | 0.125(1)   | 0.6391(9)  | 5.4(3)*             |
| C213 | 0.309(1)   | 0.084(1)   | 0.735(1)   | 5.8(3)*             |
| C214 | 0.325(1)   | −0.034(1)  | 0.754(1)   | 6.8(4)*             |
| C215 | 0.316(2)   | −0.115(2)  | 0.676(1)   | 8.8(5)*             |
| C216 | 0.290(1)   | −0.075(1)  | 0.579(1)   | 6.5(4)*             |
| C221 | 0.2030(9)  | 0.255(1)   | 0.4371(7)  | 3.2(2)*             |
| C222 | 0.100(1)   | 0.278(1)   | 0.4743(8)  | 4.2(3)*             |
| C223 | 0.053(1)   | 0.396(1)   | 0.4710(9)  | 4.3(3)*             |
| C224 | 0.1098(9)  | 0.483(1)   | 0.4297(7)  | 3.9(2)*             |
| C225 | 0.213(1)   | 0.460(1)   | 0.3916(8)  | 4.0(2)*             |
| C226 | 0.261(1)   | 0.343(1)   | 0.3964(8)  | 3.3(2)*             |
| C11  | 0.1151(4)  | 0.1562(4)  | −0.0832(3) | 7.2(1)              |
| C12  | −0.0313(4) | −0.0562(4) | −0.1343(4) | 8.6(1)              |
| CCl  | 0.005(1)   | 0.085(1)   | −0.174(1)  | 6.6(4)*             |

<sup>a</sup> Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:  $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$ .



diffractometer. A least-squares fit of 25 randomly oriented reflections with  $\theta$  ranging from  $10^\circ$  to  $15^\circ$  provided the unit cell parameters. Three standard reflections were measured at regular intervals during the data collections and no decay was observed. The intensities were collected using a variable scan-range with a 25% extension at each end for background determination. Corrections for Lorenz and polarization effects were applied. An empirical absorption correction was performed based on  $\psi$  scans ( $\psi$  0– $360^\circ$ , every  $10^\circ$ ) of three suitable reflections with  $\chi$  values close to  $90^\circ$ . Both structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares using the Enraf–Nonius structure determination package (SDP) [18] on PDP 11/34 computer. After the location of all non-hydrogen atoms, anisotropic thermal factors were assigned to all atoms with the exception of the phenyl carbon atoms. The hydrogen atoms were located in their ideal positions (C–H 0.95 Å) after each cycle but not refined. In both cases the absolute configurations were determined by internal comparison and subsequently confirmed by refining the two possible enantiomers. The final values of the agreement indices for the best enantiomeric choice are reported in Table 1, and the final positional parameters are reported in Tables 3 and 4. The final difference Fourier-map showed only small random residual peaks.

Tables of hydrogen atom coordinates and lists of observed and calculated structure factors are available from the authors.

## Results and discussion

### (a) Preparation and spectroscopical properties

The indenyl complexes **1** and **2** were prepared by treating ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru(COD)Cl (COD = 1,5-cyclooctadiene) with a stoichiometric amount of the appropriate diphosphine in boiling toluene for a few hours. The starting ruthenium compound was obtained by a slight modification of the method reported for the corresponding cyclopentadienyl complexes; **1** and **2** were fully characterized by <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR (cf. ref. 19; see Experimental section). In the <sup>1</sup>H NMR spectra the *ortho* protons of the 5-membered ring of the indenyl ligand are non-equivalent owing to the presence of the chiral diphosphine ligand. The two phosphorus atoms are diastereotopic, giving rise to an AB quartet in the <sup>31</sup>P NMR spectra; their resonances are shifted upfield by 4–10 ppm with respect to those for the corresponding cyclopentadienyl complexes **3** and **4**, possibly reflecting a larger electron donation [20]. A similar shift has been observed for the parent triphenylphosphine complexes [21,22]. The <sup>13</sup>C chemical shifts of the carbon atoms of the 5-membered ring of the indenyl ligand lie between 60 and 120 ppm. According to a previous report [23], this indicates penta-hapto coordination of the indenyl ligands for both complexes **1** and **2**. (See below for the crystal structure of **1**).

The CD spectra of **1** and **2** are shown in Fig. 1, and the spectra of the corresponding cyclopentadienyl complexes **3** and **4** in Fig. 2. The spectra of **3** and **4** are almost the mirror images of each other, as expected from the heterochirality of the ligands ((*S,S*)-chiraphos and (*R,R*)-cypenphos). The spectra of such type of complexes have been assumed [24,25] to be predominantly influenced by the conformation of the chiral diphosphine ligand, which is determined by the requirement that the substituents be equatorially disposed [15]. In the low-energy region of the spectra the first maximum at approximately 420 nm is rather broad; this

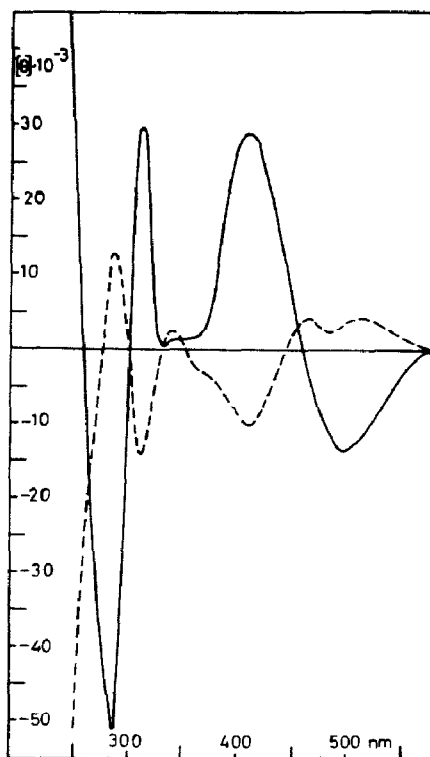


Fig. 1. CD spectra of  $(S,S)$ - $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2)\text{Cl}$  (full line) and of  $(R,R)$ - $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{Ph}_2\text{PCH}(\text{CH}_2)_3\text{CHPPh}_2)\text{Cl}$  (dashed line) in  $\text{CH}_2\text{Cl}_2$ .

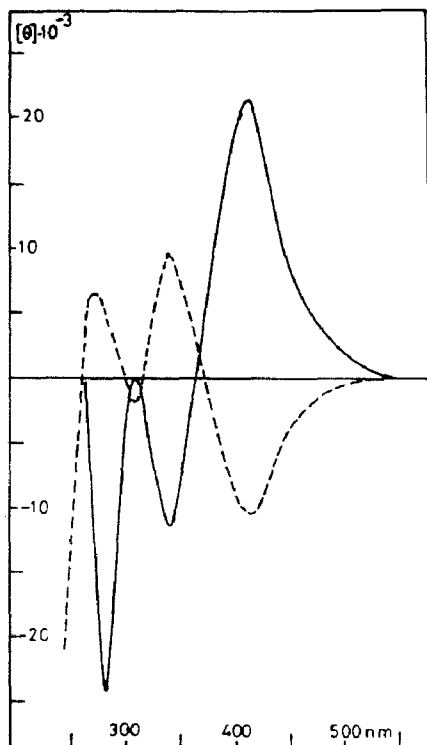


Fig. 2. CD spectra of  $(S,S)$ - $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2)\text{Cl}$  (full line) and of  $(R,R)$ - $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}(\text{CH}_2)_3\text{CHPPh}_2)_3\text{Cl}$  (dashed line) in  $\text{CH}_2\text{Cl}_2$ .

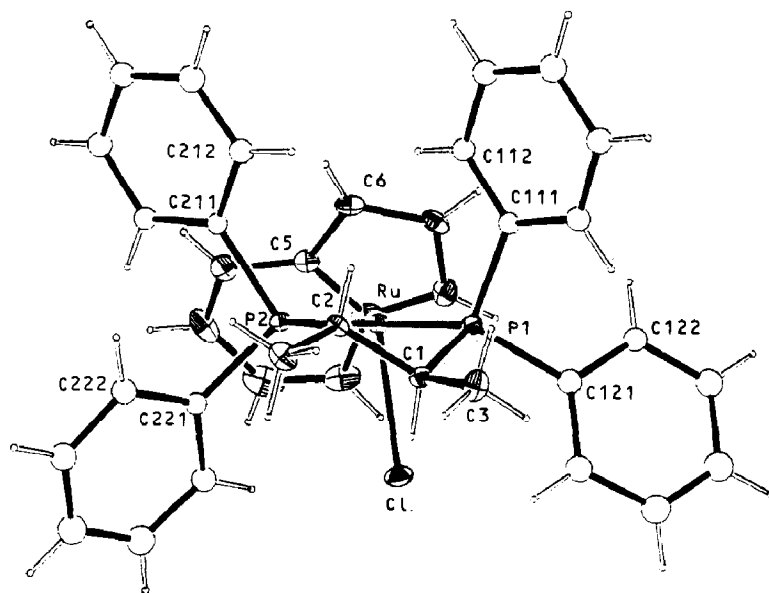


Fig. 3. Molecular structure of  $(S,S)$ - $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{Cl}$  (**1**).

maximum can be assumed to correspond to  $d-d$ -transitions [26]. The broadness is probably caused by the superimposition of (at least two) bands [25]. Two other maxima appear at approximately 340 and 280 nm. The high energy part of the spectrum must be dominated by intraligand electronic transition and is obscured by strong absorption. The lower intensities of the bands for compound **4** compared to those of **3** may be due to the possibility of a different conformation of the cyclopentane ring and/or to a different conformational situation for the phenyl substituent on the phosphorus atoms. In the case of the indenyl complexes the intensities of the bands are lower for **2**, which contains the  $(R,R)$ -cypenphos ligand, than for **1** (with  $(S,S)$ -chiraphos as the ligand). In addition, the spectra again appear more or less enantiomeric to each other. However, in the low-energy region two bands are clearly recognizable in the case of **2**, but only one maximum, at about 500 nm, for **1**. The spectra of the indenyl complexes appear red-shifted compared with those for the complexes containing cyclopentadienyl ligands. No regularity can be recognized in the signs of the bands.

(b) *Crystal structures of  $(S,S)$ - $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{Cl}$  (**1**) and  $(S,S)$ - $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{Cl} \cdot \text{CH}_2\text{Cl}_2$  (**3**)*

The crystal structures of both compounds involve discrete molecules with normal Van der Waals' contacts. In the case of compound **3** a  $\text{CH}_2\text{Cl}_2$  molecule of solvation (1/1 molar ratio) is also present. Figures 3 and 4 report ORTEP views of the two compounds in their absolute configuration. Relevant bond parameters are reported in Table 2. The coordination around the Ru atom may be regarded as octahedral, with one face of the octahedron occupied by the chlorine and the diphosphine ligands and the opposite one by the cyclopentadienyl or the indenyl ligands. The Ru–P (mean 2.276 Å in **1** and 2.284 Å in **3**) and the Ru–Cl (2.441(2) Å in **1** and 2.453(2) Å in **3**) interactions agree well with those found in analogous

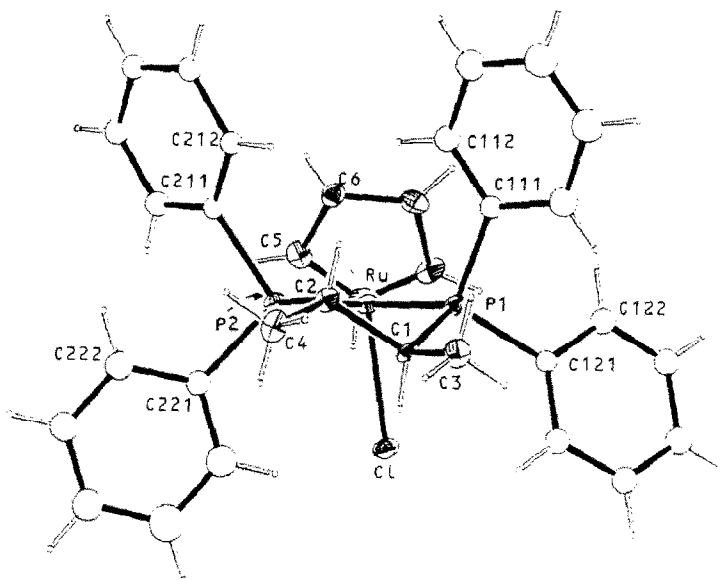


Fig. 4. Molecular structure of  $(S,S)$ - $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2)\text{Cl}$  (**3**).

complexes with chelating diphosphines like  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{prophos})\text{Cl}$  [3,25,27], for which the values of the Ru–P and Ru–Cl bond lengths are 2.277 Å (mean) and 2.444(2) Å, respectively. The P(1)–Ru–P(2) “bite” angle is similar in both compounds ( $83.17(6)^\circ$  in **1** and  $82.91(9)^\circ$  in **3**, and is comparable with that exhibited by all the Ru–prophos complexes (ca.  $88^\circ$ ).

The mean Ru–indenyl is greater than the Ru–cyclopentadienyl distance, 2.254 Å compared with 2.208 Å, mainly because of the presence of two long Ru–C bonds involving the bridgehead carbon atoms C(5) (2.369(5) Å and C(9) (2.362(6) Å). This is a normal feature for the indenyl ligand, and can be associated with an incipient  $\eta^5 \rightarrow \eta^3$  transformation [10], the angle between the least-squares mean planes of the six-membered ring and of the carbon atoms C(6), C(7) and C(8) being  $7.6^\circ$ . The presence of the indenyl group causes an asymmetry of the Ru–P interactions; P(2) which is crowded by the six-membered rings has a longer Ru–P bond length (2.312(2) Å) than P(1) (2.239(2) Å); in the Cp compound the two Ru–P distances are closer together.

For quantitative treatment of the possible conformations for chelating diphosphines a choice of some suitable internal coordinates is necessary. Following the approach suggested by Brunner et al. [28,29], the relevant molecular parameters that can be employed are: (1) the P(1)–Ru–P(2) angle and the torsional angles of the metallacycle that characterize the puckering of the chelated ring; (2) the P–M–P(1)–C<sub>(ipso)</sub> torsional angles describing the axial/equatorial character of the phenyl rings with respect to the P(1)–Ru–P(2) plane; (3) the M–P–C<sub>(ipso)</sub>–C<sub>(ortho)</sub> torsional angles describing the face/edge exposure of the phenyls.

All the pertinent angles are shown in Table 2. From a close analysis of the values it appears that the different steric hindrance by the indenyl and cyclopentadienyl ligands does not influence the metallacycle conformation and the axial/equatorial

arrangement of the phenyl rings. However, it does slightly influence the face/edge exposure of the phenyl groups belonging to P(2).

Both **1** and **3** have a distorted  $\delta$  conformation, with C(1) lying out and C(2) lying on the P(1)–Ru–P(2) plane. The  $\delta$  conformation is preferred because of the (*S,S*) chirality of the C(1) and C(2) atoms; a  $\lambda$  conformation would require the two methyl groups to be in axial positions, rather than in the observed equatorial ones, with greatly increased crowding. While the  $\lambda/\delta$  choice is determined by the axial/equatorial preference of the methyl groups, the observed flap conformation can be accounted for by the octahedral coordination at the Ru center. In particular, the presence of the Cl ligand which is almost orthogonal to the P(1)–Ru–P(2) plane makes the whole Ph<sub>2</sub>CH(Me)P(2) moiety rotate around the P(2)–Ru bond in order to alleviate the steric strain. Thus, while one of the two phenyl groups belonging to P(1) is pseudoaxial and the other pseudoequatorial, those belonging to P(2) are both in an intermediate position. On the other hand the chlorine atom bends towards the P(1) atom (Cl–Ru–P(1) 86.45(6)° and 85.97(9)° in **1** and **3**, respectively) and away from P(2) (Cl–Ru–P(2) 97.74(6)° and 96.91(9)° in **1** and **3**, respectively, to minimize non-bonding interactions with one of the phenyl groups bound to P(2) (Cl...H(35) on C226 2.491 Å in **1**, Cl...H(33) on C226 2.531 Å in **3**). A similar feature was noted in the above mentioned ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(Prophos)Cl and the [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(Norphos)CO]<sup>+</sup> cation [28].

### (c) Preliminary reactivity studies

As a starting point for the possible exploitation of complexes **1** and **2** as catalyst precursors we carried out some preliminary investigations of their reactivity towards donor compounds. We particularly wanted to examine the possible [30] tendency of the  $\eta^5$ -indenyl ligand to reduce its hapticity, thus opening up a free coordination site [12].

The reaction of (*S,S*)-( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}Cl with phenylacetylene is completely analogous to that of the corresponding cyclopentadienyl complex. The benzyliidene carbene complex (*S,S*)-[( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}(C=CHPh)]PF<sub>6</sub> was isolated when NH<sub>4</sub>PF<sub>6</sub> was used as the halogen scavenger [6]. Variable temperature <sup>31</sup>P NMR studies showed the possible diastereomeric conformers, arising from rotation of the benzyliidene carbene ligand, to be present in a 2/1 molar ratio at 80 °C. For the (*S,S*)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}(C=CHPh)]PF<sub>6</sub> equal amounts of the two conformers were found to be present at about the same temperature [6]. The different extents of asymmetric induction may be a consequence of the different face/edge exposure of the phenyl group bound to the phosphorus atoms in the two compounds, as revealed by the X-ray analysis for the precursor chloride complexes **1** and **3** (see above).

Compound **1** was also treated with CH<sub>3</sub>CN, CO, and PMe<sub>2</sub>Ph, and compound **2** with CO and PMe<sub>2</sub>Ph in CH<sub>2</sub>Cl<sub>2</sub>. In all cases, however, <sup>13</sup>C NMR analysis of the indenyl signals [23] showed pentacoordination of the indenyl ligand. The compounds behave as 1/1 electrolytes of the type [( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru(P–P)L]Cl, thus maintaining the 18-e configuration. Attempts to induce  $\eta^3$ -coordination were made in the reaction of **1** with 1,2-ethanediylbis(diphenylphosphine) (dppe) with NH<sub>4</sub>PF<sub>6</sub> as the halide scavenger. Chelation of the dppe ligand was expected to contribute to stabilization of the  $\eta^3$  mode of coordination, but even in this case we isolated (*S,S*)-[( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru{Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>}( $\eta^1$ -dppe)]PF<sub>6</sub>, in which dppe

behaves as a monodentate ligand, as clearly shown by the  $^{31}\text{P}$  NMR spectrum. Therefore the  $\eta^3$ -coordination mode of the indenyl ligand does not appear thermodynamically accessible for this type of complex. However, this does not imply such coordination is not kinetically accessible. In fact, formation of the above complexes takes place quite easily even in toluene as the solvent, in which prior dissociation of the chlorine ligands should not occur.

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