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## Key indicators

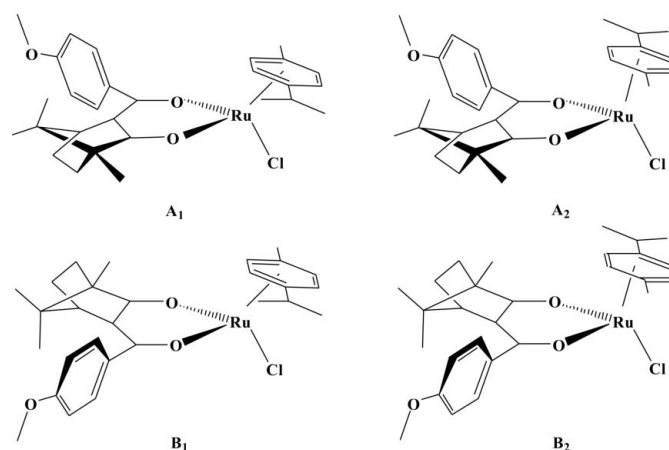
Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$   
 $R$  factor = 0.036  
 $wR$  factor = 0.088  
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Chloro( $\eta^6$ -*p*-cymene)[(1*R*)-(+)-3-(4-methoxybenzoyl)camphor(1-)- $\kappa^2$ O,O']ruthenium(II)In the title compound,  $[\text{Ru}(\text{C}_{18}\text{H}_{21}\text{O}_3)\text{Cl}(\text{C}_{10}\text{H}_{14})]$ , the  $\text{Ru}^{\text{II}}$  atom displays tetrahedral coordination, being linked to the two O atoms of the camphor-derived ligand and the *p*-cymene and Cl ligands.

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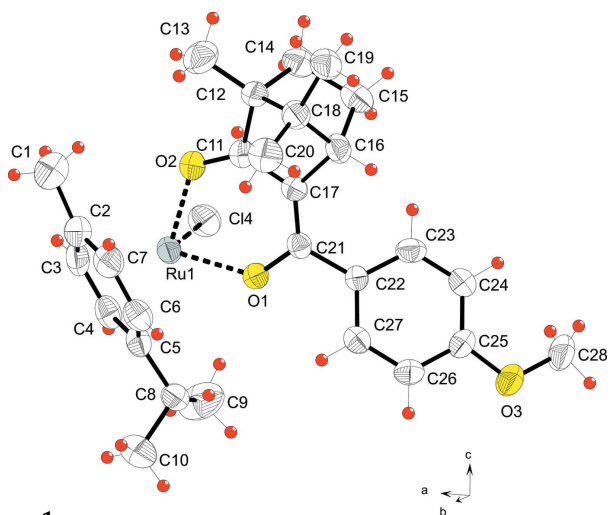
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## Comment

The development of chiral transition metal complexes as catalysts for stereoselective organic transformation is being widely pursued (Noyori, 1994). Several chiral transition metal complexes have been shown to be highly enantioselective catalysts in a variety of synthetic transformations (Wills, 1998; Ghosh *et al.*, 1998). The use of a 1,3-diketone as ligand has found applications in, for example, hydrogenation (Brunner & Wagenhuber, 1996), hydroformylation (Mieczynska *et al.*, 1999) oxidation (Fdil *et al.*, 1996; Mastroirilly *et al.*, 2001) and hetero Diels–Alder reactions (Togni *et al.*, 1993). In most cases, the catalyst is formed *in situ* from suitable precursors and a chiral ligand. Often, and despite its successful activity, reliable information about the nature of the active species and its chemical interaction with the substrate is not available. With this background, we have reported the structure of a monomeric rhodium(I) complex,  $[\text{Rh}(1R)\text{-}(+)\text{-}3\text{-benzoylcamphoryl}][\text{Rh}(\text{cycloocta-1,5-diene})]$  (Spannenberg *et al.*, 2002), as well as a ruthenium(II) complex,  $[(S)\text{-}2\text{-}(\text{anilino-methyl})\text{pyrrolidine-}N,N']\text{-chloro}(p\text{-cymene})\text{Ru}$  (Aitali *et al.*, 2000). The title compound,  $[\text{Ru}(1R)\text{-}(+)\text{-}3\text{-methoxybenzoylcamphoryl-}O,O']\text{-}(p\text{-cymene})$ , a new optically active  $\text{Ru}^{\text{II}}$  complex, has a ligand of each these reported compounds. Among the four discrete stereoisomers possible for the compound (see scheme), the crystal structure is that of form A1.



Four forms of (I)



**Figure 1**  
The molecular structure, with the atom labeling. Displacement ellipsoids are shown at the 50% probability level.

The environment of the Ru<sup>II</sup> atom is made, on one side, of the Cl atoms and of the two O atoms of the methoxybenzoylcamphoryl group and, on the other side, of the six C atoms of the *p*-cymene aromatic ring (Fig. 1). The aromatic ring forms a hexagonal pyramid with an average Ru1–C = 2.179 (4) Å. If *X* is the centroid of the ring, the Ru environment is nearly tetrahedral with Ru1–*X* = 1.655 (2) Å. The Ru–O1 and Ru–O2 bond distances are comparable to those found in the related complex [Ru<sup>II</sup>( $\eta^6$ -*p*-cymene)(acac)Cl] (Fernandez *et al.*, 2004).

The Ru–Cl distance is slightly short compared with the distance [2.4199 (6) Å] found in the reported Rh<sup>I</sup> complex (Aitali *et al.*, 2000). The coordination environment yields a chiral ruthenium center with the *S* configuration (Stanley & Baird, 1975). The only prior example of a chiral ruthenium compound is [Ru<sup>II</sup>( $\eta^6$ -*p*-cymene)(acac)Cl] (Fernandez *et al.*, 2004). Furthermore, to our knowledge, the present structure represents the first case of a ruthenium complex with a chiral 1,3-diketone that acts as a bidentate ligand to form a six-membered chelate ring [the bite angle O1–Ru1–O2 is nearly 90°]. The Ru1/O2/C11/C17/C21/O1 ring is almost planar [maximum deviation of 0.041 (2) Å for O1]. Relative to the Ru–*X* vector, the camphoryl and the isopropenyl groups are *cis*. Within the methoxybenzoylcamphoryl ligand, the free rotation of the methoxyphenyl group must be hampered, as noted from the near perpendicularity to the diketone plane [angle = 85.11 (11)°]. The methoxy group deviates slightly from the aromatic plane; indeed, the angle between the C28/O3/C25 and aromatic planes is 6.3 (7)°. Similarly, for the *p*-cymene ligand, free rotation of the isopropenyl group is also hampered [the dihedral angle between the C8–C10 and C2–C7 planes is 82.4 (4)°].

## Experimental

A solution of [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (214 mg, 0.35 mmol) in 35 ml of THF was added to a suspension of (1*R*)-(+)-3-methoxybenzoylcamphore (183 mg, 0.7 mmol) and NaH (17 mg, 0.96 mmol) in 15 ml of

THF. The mixture was stirred for 1 h at room temperature. It was then evaporated to dryness under reduced pressure. The residue was extracted with ethanol and the solution filtered. Addition of diethyl ether to the filtrate and cooling led to orange crystals suitable for the X-ray analysis. They were separated by filtration, washed with diethyl ether and dried in vacuum. The yield was 50%.

## Crystal data

[Ru(C<sub>18</sub>H<sub>21</sub>O<sub>3</sub>)Cl(C<sub>10</sub>H<sub>14</sub>)]  
*M<sub>r</sub>* = 556.08  
 Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 8.2635 (11) Å  
*b* = 12.5518 (16) Å  
*c* = 25.020 (3) Å  
*V* = 2595.1 (6) Å<sup>3</sup>

*Z* = 4  
*D<sub>x</sub>* = 1.423 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 μ = 0.73 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Parallelepiped, orange  
 0.32 × 0.15 × 0.12 mm

## Data collection

Bruker SMART 1K CCD  
 diffractometer  
 ω scans  
 Absorption correction: Gaussian  
 (*XPRED* in *SHELXTL*;  
 Sheldrick, 1997b)  
*T<sub>min</sub>* = 0.889, *T<sub>max</sub>* = 0.925

17420 measured reflections  
 4540 independent reflections  
 3969 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.051  
 θ<sub>max</sub> = 25.0°

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 0.088  
*S* = 1.02  
 4540 reflections  
 305 parameters  
 H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.052*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δσ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.98 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.36 e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1941 Friedel pairs  
 Flack parameter: -0.07 (4)

**Table 1**

Selected geometric parameters (Å, °).

Ru1–O1	2.067 (3)	Ru1–C5	2.182 (4)
Ru1–O2	2.078 (3)	Ru1–C6	2.197 (5)
Ru1–C3	2.144 (4)	Ru1–C2	2.203 (4)
Ru1–C4	2.174 (5)	Ru1–Cl2	2.4065 (11)
Ru1–C7	2.174 (5)		
O1–Ru1–O2	88.64 (10)	O2–Ru1–C2	169.09 (13)
O1–Ru1–C2	101.14 (14)		

H atoms were positioned geometrically and treated as riding on their parent atom, with C–H = 0.93–0.98 Å and *U*<sub>iso</sub>(H) = *xU*<sub>eq</sub>(C), where *x* = 1.5 for methyl groups and 1.2 for all other H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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