Preparation and resolution of chiral areneruthenium(II) complexes

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Abstract

The synthesis of the chiral complexes [{RuCl$_2$(η^6-C$_6$H$_5$CHMeR)}$_2$], (R = Et, 1, ^{t}Bu, 2), is reported. 1 was prepared from RuCl$_3 \cdot$3H$_2$O and 1-(2-butyl)-1,4-cyclohexadiene, whereas 2 was obtained starting from [Ru(η^6-naphthalene)(η^4-COD)] (COD = 1,5-cyclooctadiene) and 2,2-dimethyl-3-phenylbutane, which gives [Ru(η^6-C$_6$H$_5$CHMe^{t}Bu)(η^4-COD)] and subsequent reaction with HCl. Complexes 1 and 2 react with (+)-neomenthyldiphenylphosphine (NMDPP) to give monomeric diastereomers [RuCl$_2$(η^6-C$_6$H$_5$CHMeEt)(NMDPP)] (3a, 3b), and [RuCl$_2$(η^6-C$_6$H$_5$CHMe^{t}Bu)(NMDPP)], (4a, 4b), which were separated by HPLC. The structure of compound 3a was solved by Patterson and Fourier techniques and refined by full-matrix least-squares analysis to R = 0.053, R_w = 0.061. The arene is η^6-bonded to the ruthenium with the phosphorus and the two chlorine atoms arranged as a three legs piano stool. The absolute configuration of the chiral centre of the aromatic ligand in 3a is R. The monomeric diastereomers 3a, 3b, 4a and 4b, were reconverted into their dimeric precursors (R,R)-1a, (S,S)-1b, (R,R)-2a and (S,S)-2b as pure enantiomers. The CD spectra of (R,R)-1a and (S,S)-2b are also reported.

Key words: Ruthenium; Chirality; Arene

1. Introduction

The preparation of chiral transition metal complexes is a very active research area, having as one main goal the enantioselective synthesis of organic compounds [1,2]. Much of the success achieved in recent years has been obtained using metals of Groups 8, 9 and 10, especially ruthenium and rhodium, and optically active diphosphines [1,2]. Areneruthenium(II) complexes containing BINAP (BINAP = bis(diphenylphosphino)-1,1'-binaphthyl) are particularly efficient catalysts for the asymmetric hydrogenation of α-acylaminoacrylic acids [2]. Recently, chiral complexes which do not contain bulky and often expensive tertiary phosphines have been employed in asymmetric catalysis. For example, titanium and zirconium compounds containing optically active cyclopentadienyls have been

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shown to be good catalytic precursors in the hydrogenation of olefines and in the hydro-oligomerization of propene [3].

In view of the interesting catalytic properties shown by areneruthenium complexes [4] and of the particular stability of the arene–metal bond in these compounds [5], we studied the resolution of chiral [{RuCl$_2$(η^6-arene)}$_2$] complexes that are very useful precursors to a wide range of other areneruthenium compounds [4]. Recently [6] we reported the resolution of the methyl-*ortho*-toluate complex [{RuCl$_2$(η^6-*o*-MeC$_6$H$_4$CO$_2$-Me)}$_2$], a chiral molecule in which the arene ring has two different substituents in the 1 and 2 positions and gives rise to "planar chirality". The key step of the resolution was the separation by fractional crystallization of its diastereomeric adducts [RuCl$_2$(η^6-*o*-MeC$_6$H$_4$CO$_2$Me)(NMDPP)], (NMDPP = (+)-neo-menthyldiphenylphosphine), obtained by reaction of [{RuCl$_2$(η^6-*o*-MeC$_6$H$_4$CO$_2$Me)}$_2$] with NMDPP. In this paper we describe the synthesis of the new

areneruthenium dichloride complexes [{RuCl$_2$(η^6-C$_6$H$_5$CHMeR)}$_2$], (R = Et, 1; R = ^{t}Bu, 2), in which the arene contains an asymmetric alkyl group. We report the resolution of these complexes by an efficient HPLC separation of the corresponding diastereomeric derivatives [RuCl$_2$(η^6-C$_6$H$_5$CHMeR)(NMDPP)] and subsequent removal of the phosphine. The X-ray structural analysis of one of the diastereomers, which allowed the assignment of the absolute configuration at the chiral centre, and the chirooptical properties of the enantiomers are also discussed.

2. Results and discussion

2.1. Preparation of complexes [{RuCl$_2$(η^6-C$_6$H$_5$-CHMeR}$_2$] (R = Et, 1; ^{t}Bu, 2)

A general method for the synthesis of [{RuCl$_2$(η^6-arene)}$_2$] is the reaction between RuCl$_3 \cdot$ 3H$_2$O and the corresponding 1,3- and 1,4-dihydroarene [7]. Birch reduction of 2-phenylbutane gave 1-(2-butyl)-1,4-cyclohexadiene, which reacts with ethanolic RuCl$_3 \cdot$ nH$_2$O to give the 2-phenylbutane complex [{RuCl$_2$(η^6-C$_6$H$_5$CHMeEt}$_2$] (1) in 70% yield (Scheme 1).

A different procedure was employed to synthesize [{RuCl$_2$(η^6-C$_6$H$_5$CHMe^{t}Bu)}$_2$] (2) because 1-(2,2-dimethyl-3-butyl)-1,4-cyclohexadiene is not easily obtained by Birch reduction of 2,2-dimethyl-3-phenylbutane. Complex 2 was prepared in good yield by arene exchange between [Ru(η^6-C$_{10}$H$_8$)(η^4-COD)] (C$_{10}$H$_8$ = naphthalene; COD = 1,5-cyclooctadiene), and 2,2-dimethyl-3-phenylbutane in the presence of acetonitrile, and subsequent treatment of [Ru(η^6-C$_6$H$_5$CHMe^{t}Bu)(η^4-COD)] with HCl (Scheme 2).

The starting complex [Ru(η^6-C$_{10}$H$_8$)(η^4-COD)] is easily available in high quantity, as recently reported [8], by treatment of [Ru(acac)$_2$(η^4-COD)] (acac = acetylacetonate) with sodium naphthalene. The method of Scheme 2 provides an alternative synthesis of complex 1, that is the exchange reaction of [Ru(η^6-C$_{10}$H$_8$)(η^4-COD)] with 2-phenylbutane. Complexes 1 and 2 are red-brown solids that are insoluble in hydrocarbons, poorly soluble in methanol or acetone, and soluble in acetonitrile or dimethyl sulfoxide. Their far IR spectra show two strong bands for each complex at about 295 and 250 cm^{-1}, assignable to ν(Ru-Cl) modes of terminal and bridging chlorine atoms, suggesting that these complexes are dinuclear [7]; at least in the solid state, they can exist in the two enantiomeric forms (R,R) and (S,S) and in the meso-form (R,S) (Scheme 3).

Solvents such as acetonitrile or dimethylsulfoxide break the chlorine bridges of 1 and 2 forming the monomeric adducts [RuCl$_2$(η^6-C$_6$H$_5$CHMeR)(solvent)] as a racemic mixture (Scheme 4) [7].

Consistent with the ^{1}H NMR spectra, 1 and 2 in CD$_3$CN (Table 1) show resonances assignable to only one species, [RuCl$_2$(η^6-arene)(CD$_3$CN)]. Complex 1 exhibits a triplet at δ 0.94 ppm and a doublet at δ 1.31 ppm, assigned to the methyl protons CH_3-CH$_2$ and CH_3-CH, respectively; two multiplets at δ 1.51 and 1.74 ppm, assigned to the diastereotopic methylene protons C$H$$H$-C*, and a multiplet at δ 2.69 ppm due to the methyne proton. In the same area complex 2 shows a singlet at δ 0.9 ppm, a doublet at δ 1.39 ppm and a quartet at δ 2.55 ppm, assigned to the ^{t}Bu, CH$_3$ and CH protons, respectively. The aromatic protons of
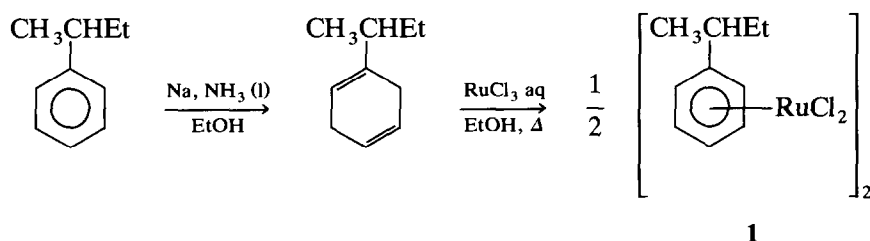
Scheme 1.
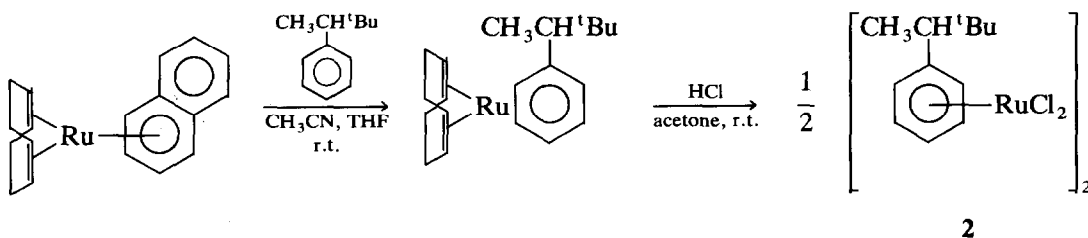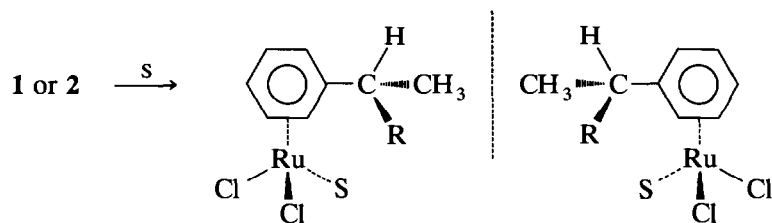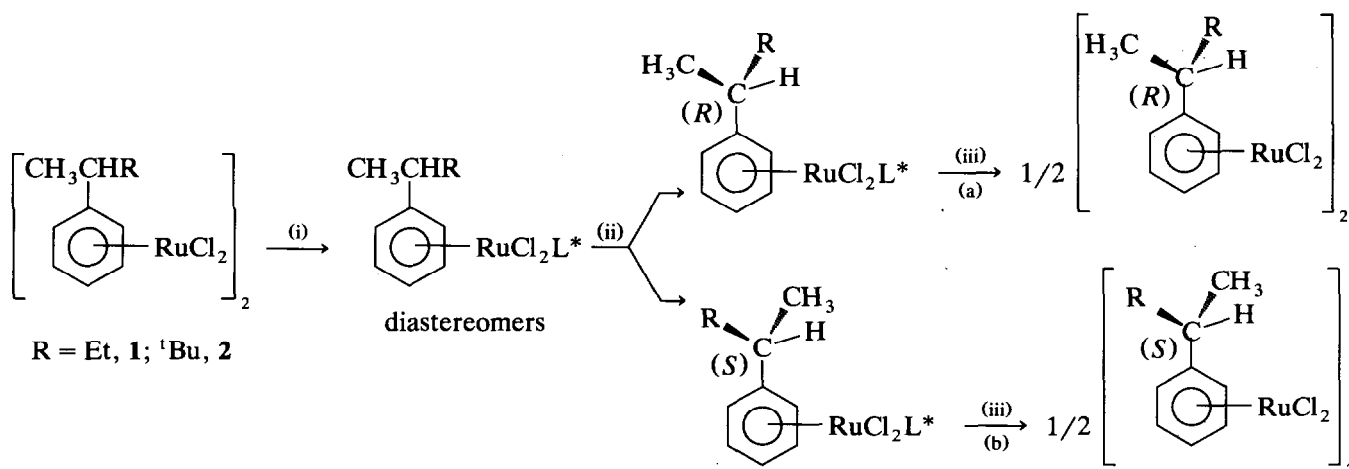
Scheme 2.
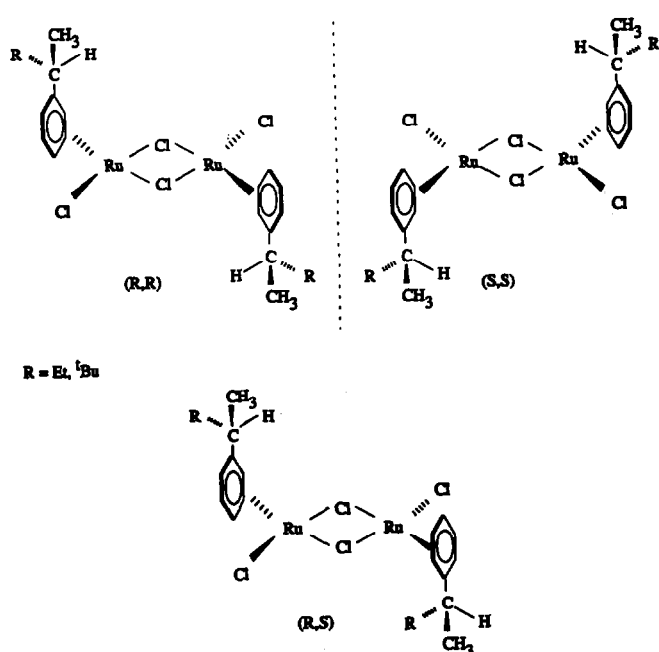
Scheme 3.

1 and 2 exhibit a broad resonance in the region of δ 5.4–5.8 ppm, the upfield shift being similar to that observed in other [{RuCl₂(η⁶-arene)}₂] complexes [7].

2.2. Resolution of the complexes 1 and 2

Complexes 1 and 2 have been resolved as outlined in Scheme 5 (i) by the formation of diastereomers by reaction with an auxiliary optically active compound, (ii) by separation of the diastereomers by HPLC, and (iii) by the removal of the resolving agent to obtain the pure enantiomers.

By treating the complexes 1 and 2 with a stoichiometric amount of NMDPP, the monomeric complexes [RuCl₂(η⁶-C₆H₅CHMeR)(NMDPP)] (R = Et, 3; ᵗBu, 4), have been obtained almost quantitatively as diastereomeric mixtures. In the ¹H NMR spectrum of 3 (Table 1 and Fig. 1) two doublets of the same intensity at δ 1.283 and 1.384 ppm are observed. They have been attributed by double resonance experiments to the methyl protons of the alkyl substituent of the η⁶-arene, C₆H₅CHMeEt, and they arise from the diastereomers 3a and 3b present in equal amounts. Similarly the ¹H NMR spectrum of 4 (Table 1, Fig. 2) exhibits two singlets of the same intensity at δ 0.861 and 0.891 ppm due to the ᵗBu protons arising from the diastereomers 4a and 4b present in the same amount. In contrast, no difference between the diastereomers 3a, 3b and 4a, 4b, respectively, was observable by ³¹P{¹H} NMR spectroscopy. Their spectra show only one resonance at δ(P) (relative to external triphenyl

1 or 2 ——S——→

S = MeCN or DMSO

Scheme 4.

R = Et, 1; ᵗBu, 2

diastereomers

Scheme 5. (i) (+)-neomenthyldiphenylphosphine, L*, 2-propanol, Δ; (ii) HPLC, LiChrosorbNH₂; (iii) (a) 1,5-cyclooctadiene, Na₂CO₃, 2-propanol, Δ; (b) conc. HCl, acetone, r.t.

TABLE 1. Analytical and spectroscopic data for [(RuCl₂(η⁶-arene))₂] and [RuCl₂(η⁶-arene)(NMDPP)]

Compound [a]	Analysis [b] (%)				¹H NMR data [c]			
					NMDPP		Aromatic ligand	
	C	H	Cl	P	Arene protons	Others	Arene protons	Others
(1) [(RuCl₂ (η⁶-C₆H₅CH(CH₃)Et))₂]	38.95 (39.21)	4.93 (4.57)	23.01 (23.20)				5.72–5.50 (m, 5H)	2.69 (m, 1H, CH); 1.74 (m, 1H, CHH-CH₃); 1.51 (m, 1H, CHH-CH₃); 1.31 (d, 3H, CH-CH₃); 0.94 (t, 3H, CH₂-CH₃)
(2) [(RuCl₂{η⁶-C₆H₅CH(CH₃)ᵗBu})₂]	42.76 (43.11)	5.18 (5.39)	21.59 (21.26)				5.82–5.43 (m, 5H)	2.55 (m, 1H, CH); 1.39 (d, 3H, CH₃); 0.90 (s, 9H, ᵗBu)
(3a) (R)-[RuCl₂{η⁶-C₆H₅CH(CH₃)Et}-(NMDPP)]	60.73 [d] (60.95)	7.01 (6.83)	11.65 (11.27)	4.68 (4.92)	8.30–8.07 (m, 2H), 7.90–7.72 (m, 2H), 7.63–7.40 (m, 6H)	2.47 (m, 1H, CH-P); 2.17–1.1 (br m, CH and CHH); 0.95 (d, 3H, CH₃-CH); 0.72 (d, 3H, CHCH₃(CH₃)); 0.26 (d, 3H, CH(CH₃)CH₃)	5.27 (d, 1H), 5.12 (d, 1H), 4.68, (t, 1H)	2.88 (m, 1H, CH); 1.9–1.5 (CH₂) [e]; 1.28 (d, 3H, CH₃-CH); 0.93 (t, 3H, CH₃-CH₂)
(3b) (S)-[RuCl₂{η⁶-C₆H₅CH(CH₃)Et}-(NMDPP)]					8.30–8.07 (m, 2H), 7.90–7.72 (m, 2H), 7.63–7.40 (m, 6H)	2.47 (m, 1H, CH-P); 2.17–1.1 (br m, CH and CHH); 0.95 (d, 3H, CH₃-CH); 0.72 (d, 3H, CHCH₃(CH₃)); 0.26 (d, 3H, CH(CH₃)CH₃)	5.5 (d, 1H), 5.2 (t, 1H), 4.98 (d, 1H), 4.42 (m, 1H), 4.08 (m, 1H)	2.88 (m, 1H, CH); 1.9–1.5 (CH₂); 1.38 (d, CH₃-CH); 0.91 (t, 3H, CH₂-CH₃)
(4a) (R)-[RuCl₂{η⁶-C₆H₅CH(CH₃)ᵗBu}-(NMDPP)]	61.87 [d] (62.01)	7.04 (7.14)	10.54 (10.79)	4.95 (4.71)	8.25–8.15 (m, 2H), 7.85–7.70 (m, 2H), 7.60–7.40 (m, 6H)	2.45 (m, 1H, CH-P); 2.20–1.1 (br m, -CH₂ and CH₂); 1.0 (d, 3H, CH₃-CH); 0.72 (d, 3H, CHCH₃(CH₃)); 0.27 (d, 3H, CH(CH₃)CH₃)	5.58 (d, 1H), 5.10 (d, 1H), 4.95–4.7 (m, 2H), 3.7 (m, 1H)	2.68 (q, 1H, CH); 2.51 (d, 3H, CH₃); 0.86 (s, 9H, ᵗBu)
(4b) (S)-[RuCl₂{η⁶-C₆H₅CH(CH₃)ᵗBu}-(NMDPP)]					8.25–8.15 (m, 2H), 7.85–7.70 (m, 2H), 7.60–7.40 (m, 6H)	2.45 (m, 1H, CH-P); 2.20–1.1 (br m, -CH₂ and CH₂); 1.0 (d, 3H, CH₃-CH); 0.72 (d, 3H, CHCH₃(CH₃)); 0.27 (d, 3H, CH(CH₃)CH₃)	5.78 (d, 1H), 5.17 (t, 1H), 4.95–4.84 (m, 2H), 3.77 (m, 1H)	2.68 (q, 1H, CH); 2.58 (d, 3H, CH₃); 0.89 (s, 9H, ᵗBu)

[a] NMDPP = (+)-neo-menthyldiphenylphosphine.

[b] Calculated values are given in parentheses.

[c] Spectra were measured at 200 MHz using Me₄Si as internal standard, in [²H₃] acetonitrile for compound 1 and 2, in [²H₁] chloroform for compound 3a, 3b and 4a, 4b; δ scale; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

[d] Microanalyses have been performed on the diastereomeric mixtures of 3a/3b = 1 and 4a/4b = 1.
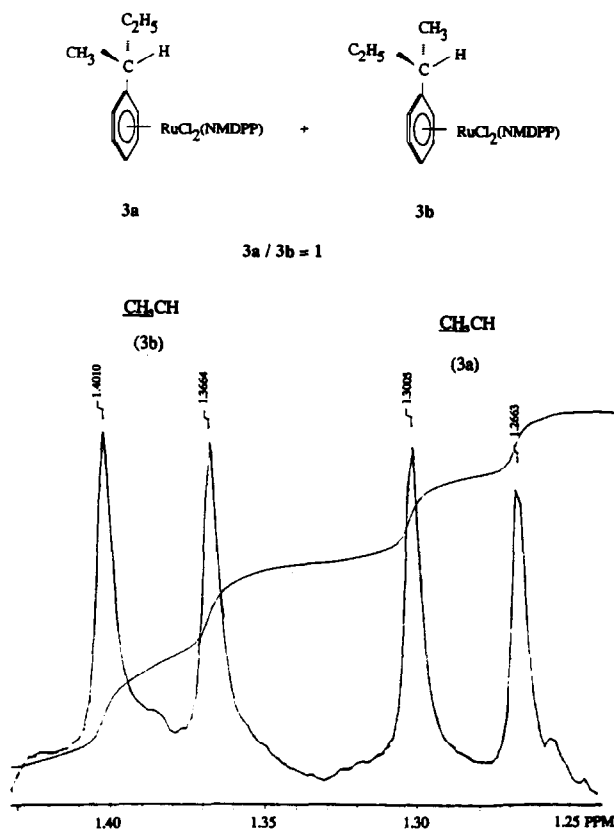
[e] Observed by double resonance.

Fig. 1. ¹H NMR spectrum (methyl protons of sec-butyl group) of the diastereomers 3a and 3b, present in equal amounts.

phosphate) 23.33 for **3** and 26.2 for **4**, indicating that the chemical environment around the phosphorus atom is similar for each pair of diastereomers.

The diastereomers **3a, 3b** and **4a, 4b** have been separated by HPLC on LiChrosorb-NH₂ using hexane/2-propanol (Fig. 3). The separation has been carried out on a semi-preparative scale to give the pure diastereomers in 90% yield, based on amount of starting mixture (see Experimental section). The diastereomers have been characterized by ¹H NMR spectroscopy (Table 1). Attempts to separate the diastereomers by fractional crystallization from mixtures of dichloromethane/pentane or ethanol/pentane failed. In the case of the diastereomers **3a, 3b**, a solid containing 75% (calculated from ¹H NMR data) of the more insoluble diastereomer was obtained after three consecutive crystallizations from methanol/diethyl ether. The mother liquor furnished a solid containing 65% of the more soluble diastereomer. No separation was possible for the diastereomers **4a, 4b**.

The X-ray molecular structure of diastereomer **3a** with atomic numbering and a view of the coordination around ruthenium along the vector joining the ruthenium atom to the ring centroid are shown in Fig. 4 and

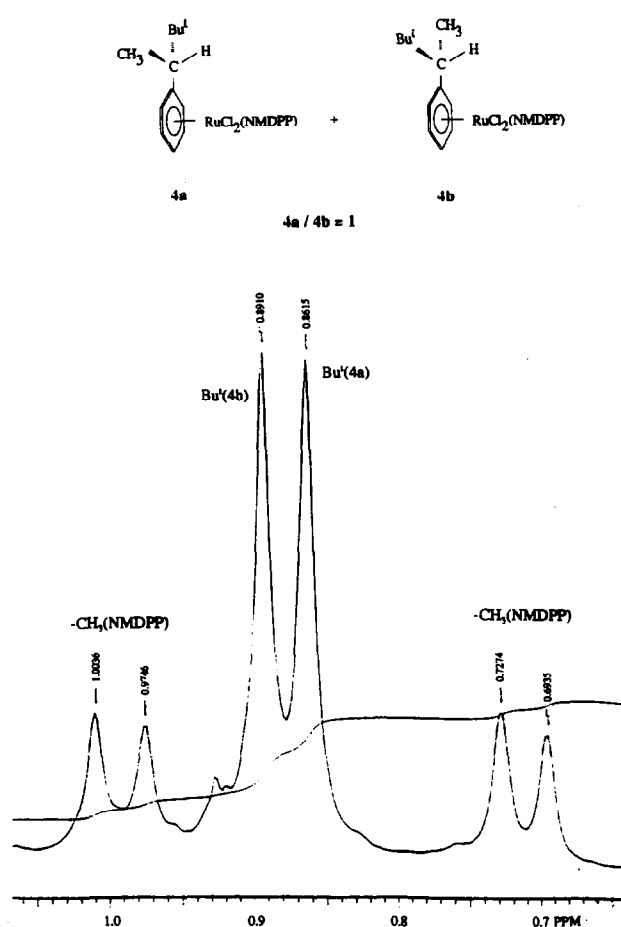Fig. 2. ¹H NMR spectrum (methyl protons of the tert-butyl group) of the diastereomers **4a** and **4b**, present in equal amounts.

Fig. 5, respectively. A list of bond distances and angles is in Table 2. The X-ray analysis shows that the absolute configuration of the chiral carbon atom of the 2-phenylbutane is *R*.
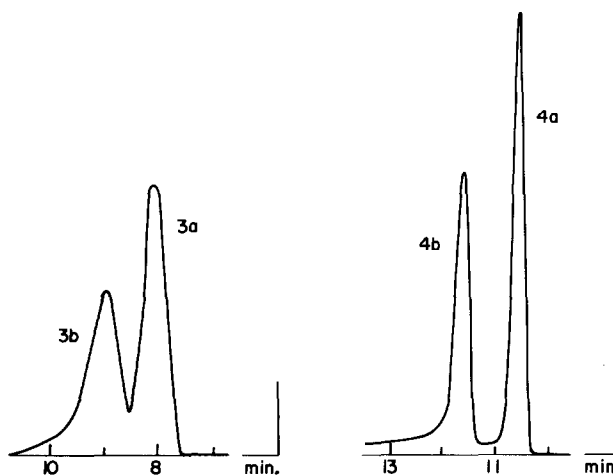

Fig. 3. HPLC chromatogram (LiChrosorbNH₂; hexane/2-propanol 98/2) of diastereomers **3a, 3b** and **4a, 4b**.
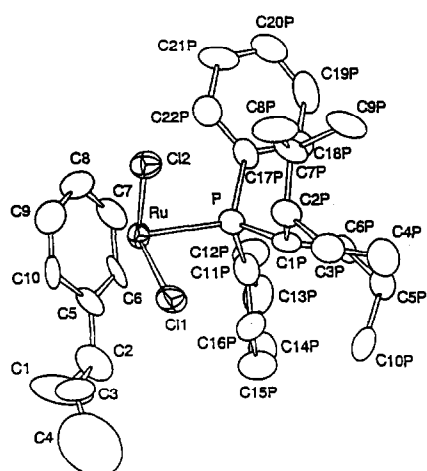
Fig. 4. ORTEP view of the molecule with the atom numbering. The thermal ellipsoids are represented at 50% probability.

As displayed in Fig. 4, the usual "three-legged pi-ano-stool" coordination typical for these organometallic complexes [6,9] is observed. The coordination geometry and the metal–ligand distances are almost the same as in $[RuCl_2(\eta^6\text{-}o\text{-}MeC_6H_4CO_2Me)(NMDPP)]$ [6], but the orientations of the arene in the two cases are different. As is evident from the projection in Fig. 5, the arene carbon atom bearing the aliphatic substituent points between chlorine atom Cl1 and the phosphine, whereas in $[RuCl_2(\eta^6\text{-}o\text{-}MeC_6H_4CO_2Me)$-(NMDPP)] the arene carbon atoms carrying the methyl and ester substituents point between the two chlorine atoms and are located opposite the phosphine. The van der Waals potential energy profile (Fig. 6) calculated for 3a upon rotation of 2-phenylbutane about the Ru-ring centroid axis (Φ_1) shows that a large distribution of conformations is accessible to the free molecule. Energy barriers lower than 7 kJ mol^{-1} are calculated for values of Φ_1 between -30 and $60°$ with respect to
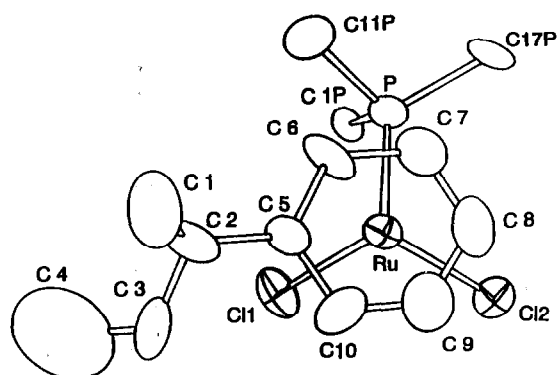

Fig. 5. Projection of the molecule along the Ru-centroid axis of the arene group, showing the relative dispositions of 2-phenylbutane and NMDPP.

TABLE 2. Structural parameters in the complex 3a. Distances are in Å, angles in degrees. E.s.d.'s are in parentheses

Ru–Cl1	2.410(6)	C1P–C2P	1.53(3)
Ru–Cl2	2.407(6)	C1P–C6P	1.56(3)
Ru–P	2.372(6)	C2P–C3P	1.60(4)
Ru–C5	2.24(2)	C2P–C7P	1.55(3)
Ru–C6	2.20(2)	C3P–C4P	1.52(4)
Ru–C7	2.15(2)	C4P–C5P	1.51(4)
Ru–C8	2.18(2)	C5P–C6P	1.54(3)
Ru–C9	2.19(3)	C5P–C10P	1.56(3)
Ru–C10	2.27(2)	C7P–C8P	1.52(4)
Ru–Cph *	1.70(2)	C7P–C9P	1.53(3)
P–C1P	1.89(2)	C11P–C12P	1.41(3)
P–C11P	1.80(2)	C11P–C16P	1.44(3)
P–C17P	1.83(2)	C12P–C13P	1.41(4)
C1–C2	1.68(4)	C13P–C14P	1.37(4)
C2–C3	1.55(4)	C14P–C15P	1.36(4)
C2–C5	1.50(3)	C15P–C16P	1.38(4)
C3–C4	1.42(6)	C17P–C18P	1.41(3)
C5–C6	1.37(3)	C17P–C22P	1.40(3)
C5–C10	1.47(3)	C18P–C19P	1.39(3)
C6–C7	1.42(3)	C19P–C20P	1.37(4)
C7–C8	1.43(3)	C20P–C21P	1.41(4)
C8–C9	1.38(4)	C21P–C22P	1.39(3)
C9–C10	1.35(4)		

P–Ru–Cph	128.0(7)	C1P–C2P–C3P	105.(2)
Cl2–Ru–Cph	124.6(8)	C3P–C2P–C7P	115.(2)
Cl2–Ru–P	89.5(2)	C2P–C3P–C4P	114.(2)
Cl1–Ru–Cph	126.8(9)	C3P–C4P–C5P	115.(2)
Cl1–Ru–P	87.7(2)	C4P–C5P–C10P	115.(3)
Cl1–Ru–Cl2	87.5(2)	C4P–C5P–C6P	108.(2)
Ru–P–C17P	115.2(7)	C6P–C5P–C10P	110.(2)
Ru–P–C11P	106.7(7)	C1P–C6P–C5P	112.(2)
Ru–P–C1P	118.6(6)	C2P–C7P–C9P	118.(2)
11P–P–C17P	106.(1)	C2P–C7P–C8P	111.(2)
C1P–P–C17P	108.7(9)	C8P–C7P–C9P	107.(2)
C1P–P–C11P	100.0(9)	P–C11P–C16P	119.(2)
C1–C2–C5	110.(2)	P–C11P–C12P	124.(2)
C1–C2–C3	111.(2)	C12P–C11P–C16P	117.(2)
C3–C2–C5	115.(2)	C11P–C12P–C13P	119.(2)
C2–C3–C4	117.(3)	C12P–C13P–C14P	123.(3)
C2–C5–C10	121.(2)	C13P–C14P–C15P	119.(2)
C2–C5–C6	121.(2)	C14P–C15P–C16P	121.(2)
C6–C5–C10	118.(2)	C11P–C16P–C15P	121.(2)
C5–C6–C7	121.(2)	P–C17P–C22P	120.(2)
C6–C7–C8	121.(2)	P–C17P–C18P	119.(2)
C7–C8–C9	116.(2)	C18P–C17P–C22P	121.(2)
C8–C9–C10	126.(3)	C17P–C18P–C19P	116.(2)
C5–C10–C9	119.(2)	C18P–C19P–C20P	125.(3)
P–C1P–C6P	115.(1)	C19P–C20P–C21P	117.(2)
P–C1P–C2P	118.(1)	C20P–C21P–C22P	120.(2)
C2P–C1P–C6P	114.(2)	C17P–C22P–C21P	121.(2)
C1P–C2P–C7P	121.(2)		

* Cph is the centroid of the 2-phenylbutane phenyl ring.

the position observed in the crystal. In the liquid phase the arene presumably oscillates freely between these two values, whereas rotation between 230° and 320° is hindered by the interaction between sec-butyl group and the phosphine.
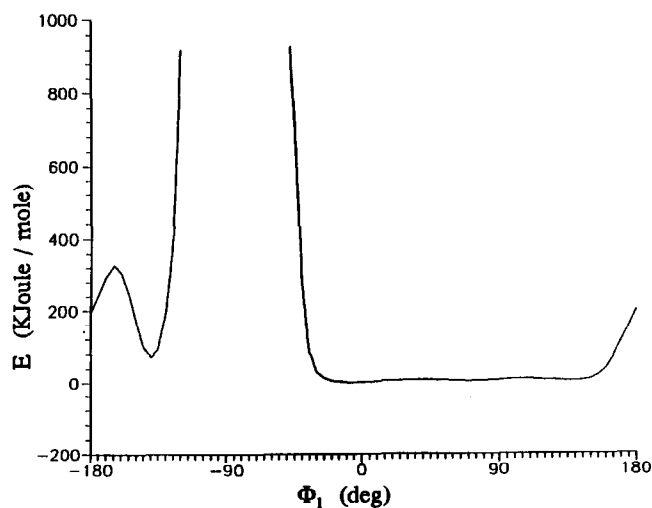
Fig. 6. Calculated difference potential energy profile for the rotation of 2-phenylbutane about the Ru–arene bond in the free molecule of 3a. The conformation found in the crystal is assumed to have zero energy. Positive values of Φ_1 correspond to counterclockwise rotations.

The angle between the normal to the mean plane of the arene ring and the vector joining the ruthenium atom ring centroid is 166.8(8)°. This deviation from 180° can be ascribed to the unsymmetrical substitution on the arene with groups of very different bulk. In this case, however, in contrast to [RuCl$_2$(η^6-o-MeC$_6$H$_4$-CO$_2$Me)(NMDPP)], the *trans* effect of the phosphine and the steric hindrance of the sec-butyl group do not act in the same direction. So the longest Ru–C distance is observed for Ru–C10 (2.27(2) Å) *i.e.* to an unsubstituted arene carbon atom which is *trans* to the phosphine.

2.2.1. 2-Phenylbutane

As can be seen in Fig. 4, the chain C1–C2–C3–C4 makes a bow that crosses the plane containing the phenyl ring. The torsion angles C1–C2–C3–C4 and C5–C2–C3–C4 are 68(3)° and 166(3)°, respectively; the phenyl ring is planar within the estimated standard deviations. The atom C1 is at one side of this plane, the atom C2 is on the plane whereas C3 and C4 atoms are on the other side, the same side as the ruthenium atom. The carbon–carbon distances appear to be normal, except for C1–C2 and C3–C4, which are affected by the high thermal motion of the C1 and C4 atoms.

2.2.2. Neo-menthyldiphenylphosphine

The phosphorus atom is tetrahedrally coordinated and the *neo*-menthyl group is a little further from the phosphorus than the phenyl group: 1.89(2) Å (mean value). Observing the compound 3a in the Ru–P direction, the *neo*-menthyl group faces the chlorine atoms,

being closer to Cl1. The dihedral angles Cl1–RuP–C1P and Cl2–RuP–C1P are 19.2(7)° and 68.3(7)°, respectively. The *neo*-menthyl group has a chair conformation, with the methyl and isopropyl groups in axial positions and the phosphorus atom in equatorial position; the phenyl groups point toward the arene and are mainly responsible for the inaccessible energy barrier (calculated value greater than 1000 kJ mol^{-1}) to the complete rotation of the arene. In the liquid phase the barrier may be considerably lowered by simultaneous rotation of the η^6-arene and rotation about the Ru–P bond.

NMDPP can be removed from the diastereomers 3a, 3b and 4a, 4b following our previously reported procedures [6,10]. Each diastereomer was heated with 1,5-cyclooctadiene, in the presence of 2-propanol and anhydrous sodium carbonate, to form the corresponding compounds [Ru(η^6-arene)(η^4-COD)]. They were extracted from the reaction mixture with hexane and the solution was treated *in situ* with concentrated HCl in acetone to give the enantiomers (R,R)-1a, (S,S)-1b and (R,R)-2a, (S,S)-2b as dimeric chlorobridged complexes (Scheme 3).

The reactions employed to remove the resolving agent do not involve the chiral centre on the arene. In fact, the reaction of one enantiomer with NMDPP gives the corresponding adduct with the same optical purity. Since the absolute configuration of diastereomer 3a, containing C$_6$H$_5$CHMeEt bound to ruthenium, is known by X-ray crystallography to be R, the absolute configuration of 1a and 1b can be assigned. The absolute configuration of the arene in enantiomers 2a and 2b can be determined by comparison of their CD spectra with those of 1a and 1b. Figure 7 illustrates the absorption and CD spectra of (R)-[RuCl$_2$(MeCN)(η^6-C$_6$H$_5$CHMeEt)] (1a) and (S)-[RuCl$_2$(MeCN)(η^6-C$_6$H$_5$CHMe^{t}Bu)] (2b). The UV spectra show bands at 420 (ϵ_{max} = 796) and 337 nm (ϵ_{max} = 1355) in 1a, at 410 (ϵ_{max} = 669) and an absorption between 350 and 300 nm (ϵ_{335} = 602) in 2b, which from the intensity values can be assigned to d-d transitions [11]. Correspondingly, the CD spectra are dominated by a Cotton effect at 400 nm that is positive ($\Delta\epsilon \approx$ +0.075) for complex 1a, having the chiral ligand with (R) absolute configuration, and negative ($\Delta\epsilon \approx$ −0.15) for complex 2b. The more intense $\Delta\epsilon$ value for 2b can be related to a major configurational homogeneity of the chiral arene present in this compound. As the complexes have a similar chemical structure, the opposite sign of the Cotton effect indicates that the absolute configuration of the asymmetric carbon atom in 2b is (S). This has been confirmed by heating acetonitrile solutions of complex 2b for a week in order to remove the arene from the ruthenium and recording
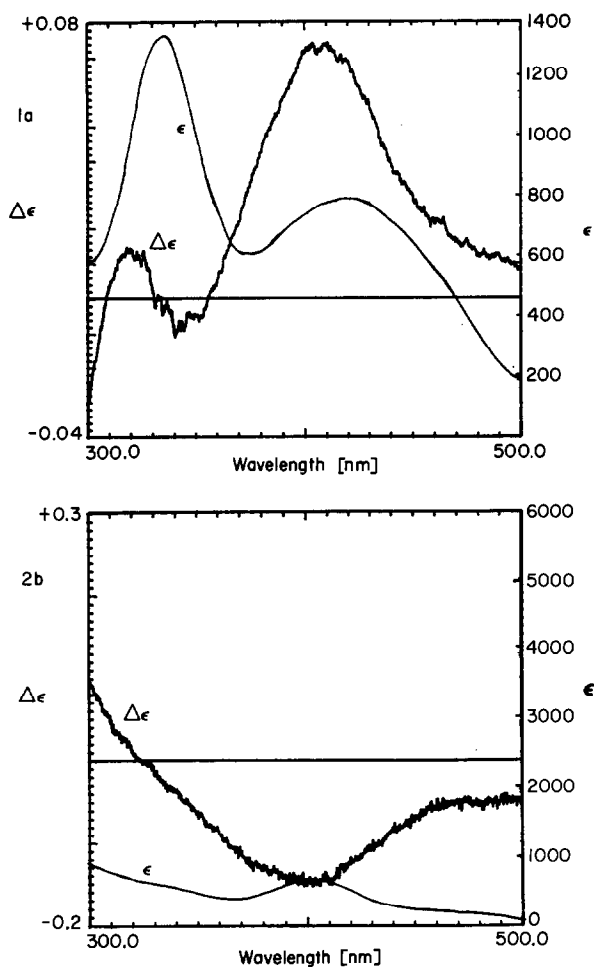
Fig. 7. UV and CD spectra of the pure enantiomers: $(-)(R)$-[RuCl$_2$(η^6-C$_6$H$_5$CHMeEt)(NCMe)], 1a ($c = 1.35 \times 10^{-3}$ mol dm^{-3}, MeCN). $(+)(S)$-[RuCl$_2$(η^6-C$_6$H$_5$CHMe^{t}Bu)(NCMe)], 2b ($c = 2.99 \times 10^{-4}$ mol dm^{-3}, MeCN).

the CD spectrum of the solution containing the free optically active arene. The CD spectrum shows a positive Cotton effect at *ca.* 260 nm showing that the configuration of the asymmetric carbon atom of C$_6$H$_5$CHMe^{t}Bu is *S*, as reported in literature [12].

3. Conclusion

The areneruthenium dichloride complexes 1 and 2, in which the arene contains different chiral groups, have been synthesized in good yields by two procedures. The synthesis from [Ru(η^6-C$_{10}$H$_8$)(η^4-COD)] (see Scheme 2) is of particular interest because it employs the aromatic compound directly and thus provides an alternative preparation of arene-Ru^0 and Ru^{II} complexes when the 1,3- or 1,4-cyclodiene is not easily accessible.

The diastereomeric adducts 3a, 3b and 4a, 4b, obtained by the reaction of 1 and 2 with NMDPP, respec-

tively, have very similar properties, *e.g.* ^{1}H and ^{31}P NMR spectra, and they cannot be cleanly separated by fractional crystallization. However, very efficient separation has been achieved using HPLC techniques; this method seems very promising for the separation of other complexes of this kind.

The diastereomers 3a, 3b and 4a, 4b have been easily reconverted into their optically active dimeric precursors 1a, 1b and 2a, 2b with full retention of the configuration at the chiral centre. They appear to be configurationally very stable in acetonitrile: the UV and CD spectra do not change when the solutions are heated for 24 h at 50°C or left at room temperature for a week; as mentioned earlier, the aromatic ligand is removed from the ruthenium atom only by prolonged heating at 70°C.

4. Experimental details

All reactions were carried out under a dry oxygen-free atmosphere, using conventional Schlenk-tube techniques. The areneruthenium complexes are air-stable in the solid state. Solvents were dried and degassed before use. 1-(2-butyl)-1,4-cyclohexadiene was prepared from 2-phenylbutane (Fluka product, distilled before use) by sodium-ammonia reduction. 2,2-Dimethyl-3-phenylbutane was prepared according to the literature methods starting from acetophenone and t-butyl magnesium chloride [13]. A commercial sample of (+)-neomenthyldiphenylphosphine (NMDPP) was used as received. [Ru(η^6-C$_{10}$H$_8$)(η^4-COD)] was synthesized according to the literature [8].

^{1}H NMR spectra were recorded on a Gemini 200 instrument at 200 MHz and on a Varian VXR-300 one at 300 MHz and ^{31}P NMR spectra were recorded on a Varian VXR-300 instrument at 121 MHz. Proton chemical shifts were determined relative to internal (CH$_3$)$_4$Si (δ 0 ppm) and ^{31}P chemical shifts (δ(P)) relative to triphenyl phosphate. Coupling constants *J* are in Hz. Circular dichroism spectra were recorded for acetonitrile solutions on a Jasco J-600 C dichograph. Ultraviolet and visible spectra in the same solvent were recorded on a Jasco UVIDEC 710 spectrometer. Chromatography was conducted on a 2 X 250 mm Merck LiChrosorbNH$_2$ column.

Microanalyses were carried out by the Facoltá di Farmacia, Universitá di Pisa, Italy.

4.1. Preparation of di-µ-chloro-bis[chloro(η^6-(RS)-2-phenylbutane)ruthenium(II)]/{RuCl$_2$(η^6-(RS)-C$_6$H$_5$CH-MeEt)}$_2$] (1)

RuCl$_3 \cdot$ 3H$_2$O (3 g, 12 mmol) and 1-(2-butyl)-1,4-cyclohexadiene (6.5 g, 48 mmol) were dissolved in methanol (100 ml) and the mixture heated under reflux

with magnetic stirring for 8 h. On standing overnight at −20°C, red-brown microcrystals of **1** separated out. They were collected, washed several times with methanol and dried *in vacuo* (2.65 g, 4 mmol).

4.2. Preparation of di-μ-chloro-bis[chloro(η⁶-(RS)-2,2-dimethyl-3-phenylbutane)ruthenium(II)][{RuCl₂(η⁶-(RS)-C₆H₅CHMe'Bu)}₂] (2)

4.2.1. Synthesis of [η⁴-1,5-cyclooctadiene][η⁶-(RS)-2,2-dimethyl-3-phenylbutane]ruthenium(0), [Ru(η⁶-(RS)-C₆H₅CHMe'Bu)(η⁴-COD)]

[Ru(η⁶-C₁₀H₈)(η⁴-COD)] (1 g, 2.956 mmol) and 2,2-dimethyl-3-phenylbutane (0.479 g, 2.956 mmol) were treated with THF (5 ml) and acetonitrile (1.52 ml, 29 mmol). The mixture was stirred at room temperature for six days and then evaporated to dryness. Naphthalene was removed by sublimation (10⁻⁴ mmHg). The solid was dissolved in pentane and chromatographed on alumina (20 cm, activity grade III). Hexane eluted a yellow fraction that, on removal of solvent under reduced pressure, gave 0.887 g (2.4 mmol) of [Ru(η⁶-(RS)-2,2-dimethyl-3-phenylbutane)(η⁴-COD)] as a yellow solid. ¹H NMR (200 MHz, C₆D₆): 5.55–3.85 (m, 5H, C₆H₅); 3.65 (m, 2H, =CH–); 3.45 (m, 2H, =CH–); 2.45 (m, 4H, CH₂); 2.30 (m, 4H, CH₂); 1.98 (q, 1H, CH); 1.52 (d, 3H, CH₃); 0.90 (s, 9H, 'Bu) [14].

4.2.2. Reaction of [Ru(η⁶-C₆H₅CHMe'Bu)(η⁴-COD)] with HCl

[Ru(η⁶-(RS)-2,2-dimethyl-3-phenylbutane)(η⁴-COD)] (200 mg, 0.54 mmol) was dissolved in acetone (5 ml) and the solution was treated with 5 ml of a 1:3 mixture of concentrated HCl and acetone. The resulting dark red solution was stirred for 1 h at room temperature and was evaporated to dryness and the residue was washed with ether and dried under reduced pressure to give **2** (0.162 mg, 24 mmol) as a red-brown solid.

4.3. Preparation of dichloro[η⁶-(RS)-2-phenylbutane)((+)-neomenthyldiphenylphosphine)]ruthenium(II) [RuCl₂{η⁶-(RS)-C₆H₅CH(Me)Et}(NMDPP)] (3a and 3b)

A stirred suspension of **1** (0.303 g, 0.5 mmol) and (+)-*neo*-menthyldiphenylphosphine (0.326 g, 1 mmol) in 2-propanol (45 ml) was heated under reflux for 2 h. The red-brown solution was filtered and the solvent was removed *in vacuo*. The residue was washed several times with ether and vacuum dried to give **3** (0.420 g, 0.8 mmol) as a 1/1 mixture of diastereomers **3a** and **3b** as estimated from the intensity ratio of the doublets due to the methyl protons (*CH₃*CH) of the arene

moiety. Three crystallizations from methanol/diethyl ether 1/2 gave the less soluble diastereomer **3a** of *ca.* 75% purity (60 mg, 20%) as an orange-red solid. From the mother-liquor of the reaction, after four steps in which the solution was concentrated and diethyl ether was added, a solid containing 65% of the more soluble diastereomer **3b** was obtained (30 mg, 10%).

The diastereomers **3a** and **3b** were separated by HPLC, using a semipreparative column LiChrosorb NH₂, with a mixture of hexane/isopropanol 98/2 as eluent. From 200 mg of the 1/1 mixture, **3a** (75 mg) and **3b** (70 mg) were obtained as pure compounds.

4.4. Preparation of dichloro[η⁶-(RS)-3,3-dimethyl-2-phenylbutane)((+)-neomenthyldiphenylphosphine)]ruthenium(II)[RuCl₂(η⁶-(RS)-C₆H₅CHMe'Bu)(NMDPP)] (4a and 4b)

These diastereomers were prepared and separated as described for **3a** and **3b**. By reaction of **2** (0.150 g, 22 mmol) and NMDPP (0.142 g, 44 mmol) in 2-propanol (30 ml) under reflux, the diastereomers **4a** and **4b** (0.260 g, 39 mmol) as a 1/1 mixture were obtained. By HPLC on the semipreparative column LiChrosorb NH₂, starting from 180 mg of the mixture 1/1, (*R*)-**4a** (85 mg) and (*S*)-**4b** (80 mg) were obtained.

4.5. Conversion of (R) and (S)-[RuCl₂(η⁶-2-phenylbutane)(+)-NMDPP] (3a, 3b) into (R,R) and (S,S)-[{RuCl₂(η⁶-C₆H₅CHMeEt)}₂]

Only the preparation of (*R,R*)-**1a** is described in detail, the experimental procedure being the same for all the other compounds.

A suspension of **3a** (75 mg, 0.12 mmol) and anhydrous Na₂CO₃ (60 mg, 0.57 mmol) in 1,5-cyclooctadiene (0.45 ml, 3.7 mmol) and 2-propanol (10 ml) was heated under reflux for 3 h. The yellow-brown solution was evaporated to dryness under reduced pressure and the residue was extracted with hexane (4 × 10 ml). The solution was concentrated to 6 ml and chromatographed on an alumina column (10 cm, activity grade III). Hexane eluted a yellow fraction, which on evaporation under reduced pressure gave 25 mg (0.07 mmol, 55%) of [Ru(η⁶-(*R*)-C₆H₅CHMeEt)(η⁴-COD)] as a yellow solid. ¹H NMR (200 MHz, C₆D₆): 5.18–4.04 (m, 5H, C₆H₅); 3.5 (m, 4H, =CH–); 2.36 (m, 8H, CH₂); 2.3 (1H, CH); 1.45 (m, 2H, CH₂); 1.25 (d, 3H, CH–*CH₃*); 0.86 (t, 3H, CH₂–*CH₃*) [15].

The solid was dissolved in acetone (5 ml) and a solution of concentrated HCl in acetone was added dropwise with stirring. A red solid precipitated, which was filtered off, washed with acetone and dried under reduced pressure to give (*R,R*)-[{RuCl₂(η⁶-2-phenyl-butane)}₂] (20 mg, 0.03 mmol) as a red-brown solid.

TABLE 3. Experimental data for the crystallographic analysis of 3a

Formula	$C_{32}H_{43}Cl_2PRu$
Molecular weight	630.6
Space group	$P2_12_12_1$
a /Å	9.892(2)
b /Å	13.880(3)
c /Å	22.223(3)
U /Å^3	3051(1)
Z	4
d_{calc} /Mg m^{-3}	1.373
Reflections for ⎫ number	17
Lattice parameters ⎭ θ range/°	8.4–12.0
Radiation	MoKα
λ /Å	0.70930
$F(000)$	1312
T /K	294
Crystal size/mm	0.20×0.27×0.50
Diffractometer	Ital Structures
μ /mm^{-1}	6.54
Absorption corrections (min., max.)	0.30, 1.85
Scan speed/°s^{-1}	0.06
Scan width/°	0.80
θ-range/°	3.0-25
h-range	0-10
k-range	0-14
l-range	0-23
Standard reflection	0 3 3
Intensity variation	$< 3\sigma(I_{s.r.})$ [a]
Scan mode	$\theta/2\theta$
Condition for observed reflections	$I > 3\sigma(I)$
No. of unique measured reflections	2133
No. of reflections used in the refinement	1349
Anisotropic least-squares on F	full-matrix
Max. least-squares shift-to-error ratio	0.41
Min., Max. height in final Fourier map, ρ/eÅ^{-3}	− 0.51, 0.56
No. of refined parameters	325
$R = \Sigma \Delta F / \Sigma |F_o|$	0.053
$R' = [\Sigma w(\Delta F)^2 / \Sigma w F_o^2]^{1/2}$	0.061
$S = [\Sigma w(\Delta F)^2 / (N - P)]^{1/2b}$	3.76
Weighting scheme	unit weights

[a] $I_{s.r.}$ = Intensity of the standard reflection.
[b] P = number of parameters, N = number of observations.

4.6. Crystal structure analysis

Prismatic crystals of **3a**, obtained from ether-methanol, were sealed at the end of glass fibres and their Weissenberg diffraction patterns were examined. The lattice showed orthorombic symmetry and the systematic absences suggested $P2_12_12_1$ as the only possible space group. The crystal producing the sharpest spots on the film was used to collect intensity data on a single-crystal four-circle diffractometer under the experimental condition summarized in Table 3. The absence of any measurable decay of the specimen was checked by periodically scanning the reflection 0 3 3, used as a standard. After correction of the collected data for Lorentz and polarization effects, the intensity

of equivalent reflections were merged, giving a total of 2133 intensity data. The absorption correction was applied by use of the method of Walker and Stuart [16].

The position of the ruthenium atom was determined by the Patterson method with use of the SHELX 86 program [17] and the atom search was completed by the standard Fourier synthesis in the SHELX 76 program [18]. Selection of the enantiomer of the arene-metal group was made by imposing the correct configuration on the *neo*-menthyl group. The atomic positions were refined by full-matrix least-squares methods. In the final cycles the non-hydrogen atoms were refined with anisotropic thermal parameters and the 43 hydrogen atoms were introduced in calculated positions and allowed to ride on the connected carbon atoms. The thermal factors of the hydrogen atoms were set to the values of the corresponding carbon atoms and not

TABLE 4. Atomic coordinates of non-hydrogen atoms of the complex 3a

Atom	x	y	z	B_{eq}
Ru	0.3686(2)	0.3656(1)	0.1898(7)	2.77(4)
Cl1	0.4778(7)	0.3105(4)	0.0992(3)	4.1(2)
Cl2	0.5542(6)	0.4760(4)	0.2023(3)	4.1(2)
P	0.2554(6)	0.4819(4)	0.1300(3)	3.0(2)
C1	0.133(3)	0.063(2)	0.193(2)	10.(1)
C2	0.249(3)	0.137(2)	0.163(1)	5.5(7)
C3	0.376(4)	0.080(2)	0.143(1)	6.1(8)
C4	0.360(6)	0.016(3)	0.093(2)	17.(2)
C5	0.276(2)	0.220(1)	0.204(1)	3.4(7)
C6	0.181(2)	0.290(1)	0.2137(9)	3.8(7)
C7	0.207(2)	0.367(2)	0.254(1)	4.5(6)
C8	0.331(3)	0.374(2)	0.2865(8)	4.8(8)
C9	0.422(3)	0.300(2)	0.276(1)	6.(1)
C10	0.402(3)	0.225(2)	0.239(1)	4.8(8)
C1P	0.327(2)	0.513(1)	0.0537(9)	2.4(5)
C2P	0.471(3)	0.554(1)	0.052(1)	4.1(7)
C3P	0.515(3)	0.549(2)	−0.018(1)	5.4(9)
C4P	0.414(3)	0.594(2)	−0.061(1)	5.7(9)
C5P	0.272(4)	0.554(2)	−0.056(1)	5.4(9)
C6P	0.227(3)	0.563(1)	0.0098(9)	4.1(7)
C7P	0.507(2)	0.650(1)	0.084(1)	4.1(6)
C8P	0.659(3)	0.663(2)	0.089(1)	7.(1)
C9P	0.449(4)	0.743(2)	0.059(1)	9.(1)
C10P	0.257(3)	0.447(2)	−0.0774(9)	4.7(8)
C11P	0.097(2)	0.429(2)	0.108(1)	3.9(7)
C12P	−0.028(2)	0.454(2)	0.133(1)	4.0(8)
C13P	−0.145(3)	0.402(2)	0.117(1)	5.6(8)
C14P	−0.141(3)	0.329(2)	0.075(1)	5.2(8)
C15P	−0.020(3)	0.303(2)	0.050(1)	5.2(9)
C16P	0.097(2)	0.352(2)	0.0649(9)	4.1(7)
C17P	0.212(2)	0.594(1)	0.169(1)	3.2(7)
C18P	0.123(3)	0.660(1)	0.1407(9)	5.3(8)
C19P	0.096(4)	0.744(2)	0.173(1)	8.(1)
C20P	0.150(4)	0.768(2)	0.227(1)	5.7(9)
C21P	0.239(2)	0.701(2)	0.254(1)	4.4(7)
C22P	0.269(2)	0.615(1)	0.225(1)	3.4(7)

refined. The final reliability factor R was 0.053, refining 325 parameters on 1349 observed independent reflections with unit weights.

Atomic scattering factors and anomalous scattering coefficients were taken from the literature [19], ORTEP II [20] and PARST [21] programs were also used. The calculations were carried out on an IBM 3081 computer of the "Centro Nazionale Universitario di Calcolo Elettronico, C.N.U.C.E." (Pisa). A list of the final atomic coordinates with isotropic equivalent thermal factors (B_{eq}) is shown in Table 4. Full lists including anisotropic thermal parameters and coordinates of hydrogen atoms are available from the Cambridge Crystallographic Data Centre.

The atom-atom non-bonded potential energy calculations were made by means of the program ROTENER [22], which is a computer routine using a function of the type $E_{ij} = B_{ij} \exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6}$. The coulombic energy was neglected and the H atoms were assumed to be in calculated positions (C–H 1.07 Å).

Acknowledgment

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