Synthesis of the Arene Complex [{$RuCl_2(\eta^6$-*o*-$MeC_6H_4CO_2Me)\}_2$] and Separation of its Diastereomeric (−)(*S*)-1-Phenylethylamine Adducts

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The synthesis of [{$RuCl_2(\eta^6$-*o*-$MeC_6H_4CO_2Me)\}_2$], (*o*-$MeC_6H_4CO_2Me$ = methyl *o*-toluate), from $RuCl_3{\cdot}3H_2O$ and methyl 1,4-dihydro-*o*-toluate is reported. This is the first example of an arene–ruthenium complex having planar chirality with respect to the face of the co-ordinated arene. Its reactions with tertiary phosphines and primary amines have been examined. Using optically active amines, the complexes [$RuCl_2(\eta^6$-*o*-$MeC_6H_4CO_2Me)L'$] [L' = (−)(*S*)-1-phenylethylamine or (+)-dehydroabietylamine], and [$RuCl(\eta^6$-*o*-$MeC_6H_4CO_2Me)$(N–N)]PF_6 [N–N = (−)(*R*,*R*)-1,2-diphenyl-1,2-diaminoethane], have been obtained as diastereomeric mixtures. The diastereomers of [$RuCl_2(\eta^6$-*o*-$MeC_6H_4CO_2Me)$\{(−)(*S*)-MeCH(Ph)NH_2\}] have been partially separated by fractional crystallisation, the less soluble one being obtained with >90% enrichment. Their circular dichroism spectra have been compared with those of complexes containing achiral arene–ruthenium moieties.

The synthesis and resolution of chiral organometallic complexes is one of the more interesting recent aspects of organo-transition metal chemistry, especially in the context of asymmetric synthesis. In some of these complexes optically active ligands such as phosphines, amines, *etc.* are present,[1] in others the metal is the centre of chirality.[2] Chiral organometallic molecules having a planar chirality have also been reported. Square-planar platinum(II) compounds with η^2-prochiral olefins,[3] ferrocenes,[4] cymantrenes, [$Mn(CO)_3(\eta^5$-$C_5H_5)$],[4] or arene complexes,[5] in which the cyclopentadienyl or arene ring has two different substitutents in 1,2- or 1,3-positions relative to each other, are examples of these molecules.

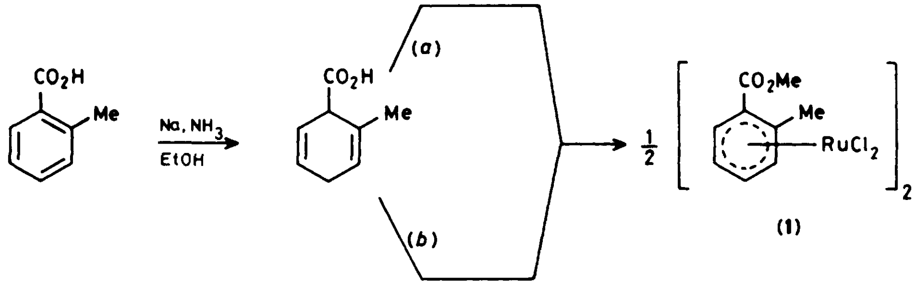
Arene–transition metal compounds,[6] particularly those containing ruthenium,[7] have been employed as catalysts in reactions of industrial relevance, and in optically active form they could be of interest as catalytic precursors in asymmetric synthesis, provided that the planar chirality influences the stereochemical pathway of the reaction.

We now report the synthesis of the first chiral arene–ruthenium complex [{$RuCl_2(\eta^6$-*o*-$MeC_6H_4CO_2Me)\}_2$], in which the presence of two different substituents in positions 1 and 2 in the arene ring generates a planar chirality in the co-ordination to the metal with respect to the face of the co-ordinated arene. The reactions of this complex with tertiary phosphines and primary amines and the separation of the diastereomeric adducts with (−)(*S*)-1-phenylethylamine are also described.

Results and Discussion

Preparation of [{$RuCl_2(\eta^6$-*o*-$MeC_6H_4CO_2Me)\}_2$], (**1**).—Arene–di-μ-chloro-ruthenium complexes, [$(RuCl_2R)_2$], can be made by dehydrogenation of the appropriate cyclohexa-1,3-, or 1,4-, diene with alcoholic ruthenium trichloride.[8] Following this procedure the complex [{$RuCl_2(\eta^6$-*o*-$MeC_6H_4CO_2Me)\}_2$], (**1**), has been obtained by heating a methanolic solution of ruthenium trichloride with methyl 1,4-dihydro-*o*-toluate, which is readily accessible from *o*-toluic acid by metal–ammonia reduction [Scheme 1(*a*)]. The overall yield of the reactions is *ca.* 80%. Complex (**1**) can also be obtained by direct reaction of 1,4-dihydro-*o*-toluic acid with methanolic ruthenium trichloride, although the yield in this case is only 30% [Scheme 1(*b*)].

Complex (**1**) is a red-brown, diamagnetic solid which is fairly soluble in dimethyl sulphoxide or acetonitrile, poorly soluble in methanol, and almost insoluble in acetone. The far-i.r. spectrum of (**1**) shows two strong bands at 300 and 255 cm^{-1} assignable to ν(Ru–Cl) modes of terminal and bridging chlorine atoms.[8] These data suggest that (**1**) has a dimeric chloro-bridged structure in which the co-ordinated arenes are mutually *trans*, as found by *X*-ray crystallography for the osmium(II) complex



Scheme 1. Reaction conditions: (*a*) (*i*) CH_3I, K_2CO_3; (*ii*) $RuCl_3{\cdot}3H_2O$, MeOH, heat; (*b*) $RuCl_3{\cdot}3H_2O$, MeOH, heat

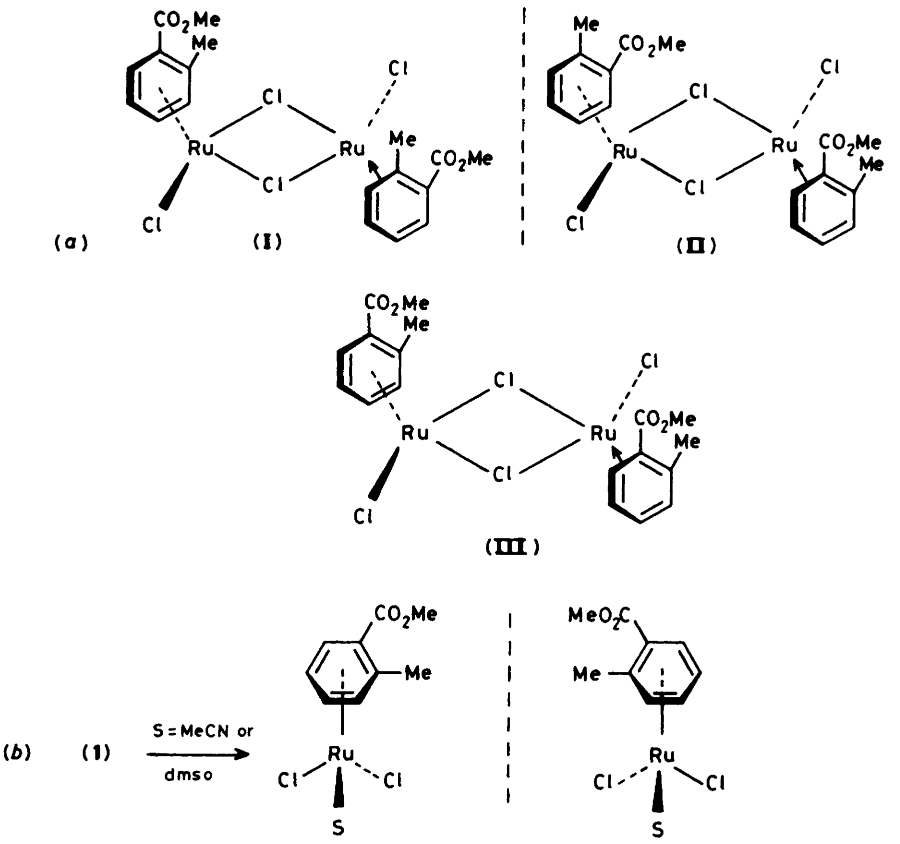
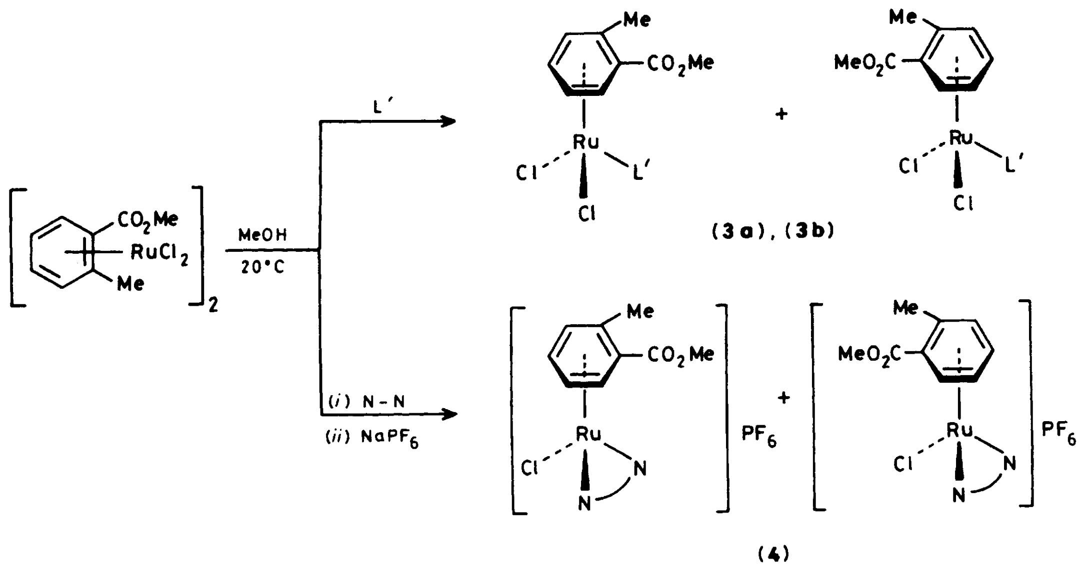


Figure 1. (*a*) Possible stereoisomers of complex (**1**): (**I**) and (**II**) are enantiomers, (**III**) is the *meso* form. (*b*) Enantiomers resulting from the reaction of (**1**) with co-ordinating solvents



Scheme 2. L′ = (−)(*S*)-1-Phenylethylamine, (**3a**); or (+)-dehydroabietylamine, (**3b**). N–N = (−)(*R*,*R*)-1,2-diphenyl-1,2-diaminoethane. (**4**)

$[\{OsCl_2(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2]$.[9] In addition, because a dissymmetrically disubstituted η^6-arene generates a planar chirality with respect to the face of the co-ordinated arene,[2a,4,10] (**1**) could, in principle, be present as a mixture of the three species shown in Figure 1(*a*), in which (**I**) and (**II**) are enantiomers (*rac* form) and (**III**) is the *meso* form. The solid state i.r. spectra in the ν(RuCl) region would probably not be sensitive enough to distinguish between the *rac* and *meso* forms, if both were present.

The co-ordinating solvents acetonitrile or dimethyl sulphoxide probably break the chloro bridges of (**1**) forming monomeric adducts as a racemic mixture [Figure 1(*b*)]. Accordingly, the ^{1}H n.m.r. spectrum of (**1**) in CD_3CN (see Experimental section) exhibits only two singlets at δ 2.47 and

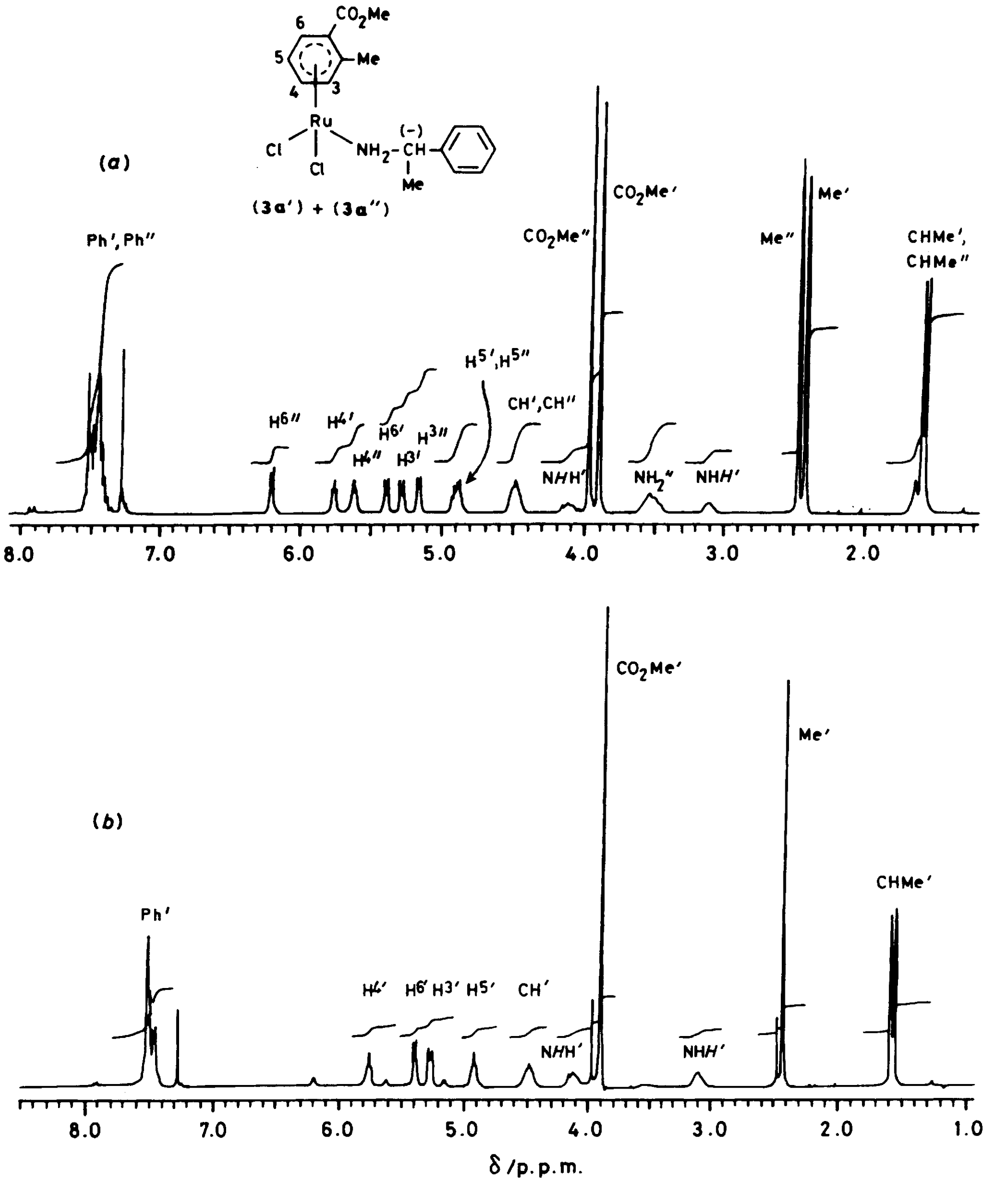


Figure 2. ^1H N.m.r. spectra (300 MHz, $CDCl_3$) of the two diastereomeric mixtures of the complex (**3a**); (*a*) (**3a**'):(**3a**'') = 50:50; (*b*) (**3a**'):(**3a**'') = 90:10

3.87 assigned to the Me and CO_2Me, respectively. The aromatic protons appear as four signals in the region of δ 5.4—6.5, the upfield shifts relative to free methyl *o*-toluate being similar to those observed for $[Cr(CO)_3(o\text{-}MeC_6H_4CO_2Me)]$.[11] The low field doublet at δ 6.44 is assigned to the proton, H^6, *ortho* to the deshielding group CO_2Me.

Reactions of (**1**) *with Tertiary Phosphines and Optically Active Amines.*—Complex (**1**) reacts, as expected,[8] with tertiary phosphines such as triphenylphosphine or dimethylphenylphosphine to give the corresponding monomeric complexes $[RuCl_2(\eta^6\text{-}o\text{-}MeC_6H_4CO_2Me)L]$, (**2**) [L = PPh_3 (**2a**) or PMe_2Ph (**2b**)], which, in contrast to (**1**), are soluble in weakly co-ordinating solvents such as dichloromethane, chloroform, or acetone. The ^1H n.m.r. spectrum of (**2b**) shows two sets of doublets for the diastereotopic methyl groups of PMe_2Ph at δ 1.81 and 1.90 [*J*(MeP) = 12 and 11.8 Hz], consistent with the presence of a chiral arene–ruthenium moiety.

Thus, if (**1**) is treated with an optically active ligand two diastereomeric adducts will be formed which should be separable by the usual chemical and physical methods.* We have investigated chiral amines for this purpose because they are easily available and because we expect them to be removable from the metal after the diastereomers have been separated. Although the reactions of $[(RuCl_2R)_2]$ (R = arene) complexes with ligands such as tertiary phosphines, phosphites, pyridines, and ammonia have been widely investigated,[12] surprisingly little is known about their reaction with primary amines.

As illustrated in Scheme 2, (**1**) reacts with (–)(*S*)1-

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* Attempts to resolve the acid derived from (**1**) by fractional crystallisation of its salts with brucine (2,4a,5,5a,7,8,15,15a,15b,15c-decahydro-10,11-dimethoxy-4,6-methano-6*H*,14*H*-indolo[3,2,1-*ij*]oxepino[2,3,4-*de*]pyrrolo[2,3-*h*]quinolin-14-one) and (–)(*S*)-1-phenylethylamine have failed (M. A. Bennett and L. A. P. Kane-Maguire, unpublished work).

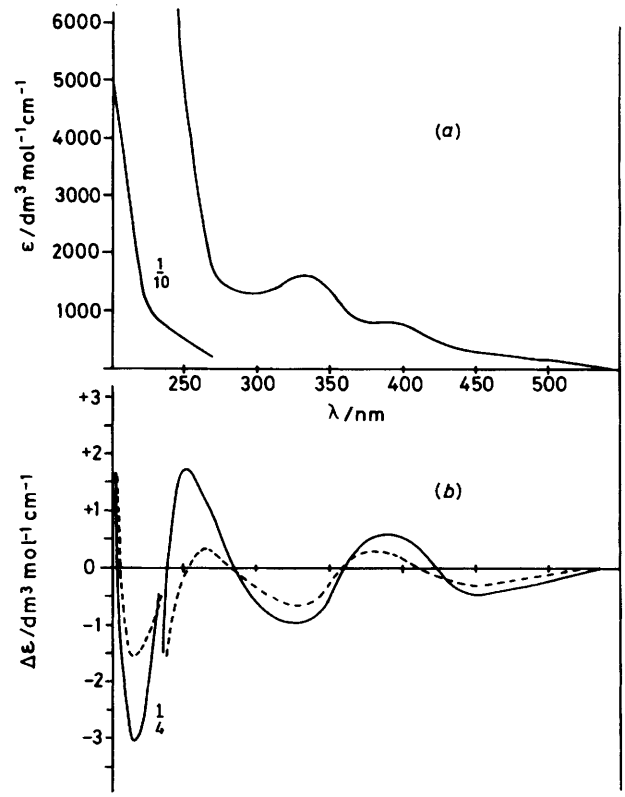

Figure 3. (*a*) U.v. and (*b*) c.d. spectra ($c = 2 \times 10^{-3}$ mol dm^{-3}, MeCN) of diastereomeric mixtures of complex (**3a**) of different composition; (——) 90:10, (– – –) 50:50

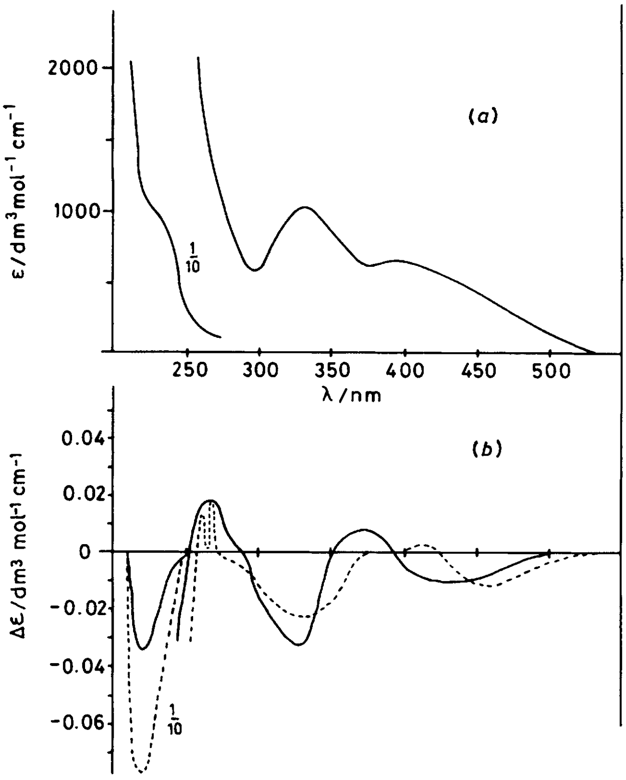

Figure 4. (*a*) U.v. and (*b*) c.d. spectra ($c = 2 \times 10^{-3}$ mol dm^{-3}, MeCN) of complexes (**3c**) (——) and (**3d**) (– – –)

phenylethylamine or with (+)dehydroabietylamine(1,2,3,4,4a,-9,10,10a-octahydro-1,4a-dimethyl-7-isopropyl-1-phenanthrene-methylamine), containing a bulky chiral group, to give the new complexes [RuCl$_2$(η^6-*o*-MeC$_6$H$_4$CO$_2$Me)L′], (**3a**) and (**3b**), respectively, as diastereomeric mixtures. With the bidentate amine (−)(*R,R*)-1,2-diphenyl-1,2-diaminoethane (N–N) the ionic complex [RuCl(η^6-*o*-MeC$_6$H$_4$CO$_2$Me)(N–N)]PF$_6$, (**4**), is isolated, also as a diastereomeric mixture, after adding NaPF$_6$.

Of the three complexes (**3a**), (**3b**), and (**4**), only (**3a**) proved to be useful for the resolution of (**1**). Its ^{1}H n.m.r. spectrum [Figure 2(*a*)] clearly shows pairs of singlets due to the CO$_2$Me and Me protons of the two diastereomers that are present in equal amounts. Fractional crystallisation of (**3a**) from methanol–diethyl ether gave a crystalline solid containing 90% of the more insoluble diastereomer [Figure 2(*b*)]. From the mother-liquor a mixture containing 75% of the more soluble diastereomer was obtained.

U.v. and c.d. spectra of different mixtures of (**3a**), having the diastereomeric composition 90:10 and 50:50, are shown in Figure 3. The u.v. spectrum [Figure 3(*a*)] shows absorption at very low intensity ($\varepsilon < 1\,000$ dm^3 mol^{-1} cm^{-1}) between 390 and 600 nm, whilst stronger bands are observable below 340 nm. Reasonably, on intensity grounds, the higher energy region is dominated by excitations allied to the π–π^* system of arene moieties.[13] It is noteworthy that the intensities of the c.d. bands of (**3a**) at 250 and 216 nm [Figure 3(*b*)] are considerably higher than those of the complexes [RuCl$_2$(R)(MeCHPhNH$_2$)] [R = C$_6$H$_6$ (**3c**) or *p*-MeC$_6$H$_4$CHMe$_2$(**3d**)] (Figure 4) in which the chiral perturbation of the electronic transitions is due only to the asymmetric carbon atom present in the amine. Therefore the higher values observed for the diastereomeric mixtures of (**3a**) can be related to the dissymmetric perturbation deriving from the presence of the additional arene–ruthenium chirality in these compounds.

The diastereomers are configurationally stable in solution: no significant racemisation was observed when the enriched mixtures were heated for 24 h in ethanol at 60 °C. Heating at higher temperature or for longer periods caused some decomposition, but the u.v. and c.d. spectra did not change, so there was no racemisation. These results demonstrate that the co-ordinated arene is not displaced from ruthenium in ethanolic solution, at least in the range of temperature examined.

Experimental

All the reactions described were carried out under a dry oxygen-free nitrogen atmosphere, using conventional Schlenk-tube techniques. The arene–ruthenium complexes are air stable in the solid state. The solvents were dried and degassed before use. 1,4-Dihydro-*o*-toluic acid was prepared from *o*-toluic acid by sodium–ammonia reduction[14] and converted into its methyl ester with methyl iodide and anhydrous K$_2$CO$_3$ in acetone.[15] Triphenylphosphine, dimethylphenylphosphine, (−)(*S*)1-phenylethylamine, and (+)dehydroabietylamine were used as received from commercial suppliers. (−)(*R,R*)-1,2-Diphenyl-1,2-diaminoethane was prepared from benzaldehyde and liquid ammonia and the racemic product resolved with (+)tartaric acid.[16] The complexes [{RuCl$_2$(η^6-C$_6$H$_6$)}$_2$] and [{RuCl$_2$(η^6-*p*-MeC$_6$H$_4$CHMe$_2$)}$_2$] were prepared by a literature procedure.[8] Proton n.m.r. spectra were measured on Varian XL100, JEOL FX 200, and Varian XR 300 instruments using SiMe$_4$ as internal standard (δ values); the coupling constants, *J*, are in Hz; the aromatic protons of the methyl *o*-toluate ligand have been numbered as shown in Figure 2. I.r. spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Circular dichroism (c.d.) spectra were obtained in acetonitrile by means of a JASCO J-500 C dichrograph. Ultraviolet and visible spectra in the same solvent were obtained on a JASCO UVIDEL 710 spectrometer. Microanalyses were carried out by the ANU Microanalytical Unit, Canberra, Australia and by the Laboratorio di Microanalisi, Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa, Italy.

Preparation of Di-μ-chloro-bis[chloro(η⁶-methyl o-*toluate)]-ruthenium*(II), $[\{RuCl_2(\eta^6\text{-}o\text{-}MeC_6H_4CO_2Me)\}_2]$, (**1**).—*Method* (*a*). $RuCl_3\cdot 3H_2O$ (2.0 g, 7.65 mmol) and methyl 1,4-dihydro-*o*-toluate (4.7 g, 31.3 mmol) were dissolved in methanol (85 cm^3) and the mixture refluxed with magnetic stirring for 8 h. On standing overnight at room temperature, the red-brown microcrystalline product separated out. This was collected on a glass frit, washed several times with methanol, and sucked dry. Complex (**1**) (2.2 g) was obtained. Rotary evaporation of the filtrate to 5 cm^3 and refrigeration gave a further crop of red-brown microcrystals (0.15 g). The overall yield of (**1**) was 90% (Found: C, 32.9; H, 3.0; Cl, 21.9. $C_9H_{10}Cl_2O_2Ru$ requires C, 33.6; H, 3.1, Cl, 22.0%). I.r.: $\nu_{max.}$(CO) 1 720s cm^{-1} (Nujol). ^1H N.m.r. (100 MHz, CD_3CN): δ 6.44 (1 H, d, *J* 5.8, H^6), 6.01 (1 H, t, *J* 5.8, H^4), 5.71 (1 H, t, H^5), 5.45 (1 H, d, H^3), 3.87 (3 H, s, CO_2Me), and 2.47 (3 H, s, Me).

Method (*b*). $RuCl_3\cdot 3H_2O$ (0.2 g, 0.765 mmol) and 1,4-dihydro-*o*-toluic acid (0.82 g, 6.02 mmol) were dissolved in methanol (20 cm^3) and the deep brown solution was refluxed for 7 h. On standing overnight at room temperature the red solution deposited small deep red crystals. These were collected on a glass frit, washed several times with methanol, and sucked dry (0.036 g). Evaporation of the filtrate to half volume and cooling in the refrigerator gave a further crop of (**1**) as a red-brown solid (0.038 g). The overall yield was 30% (Found: C, 33.6; H, 3.2; Cl, 21.0%). I.r.: $\nu_{max.}$(CO) 1 720s cm^{-1} (Nujol).

Preparation of $[RuCl_2(\eta^6\text{-}o\text{-}MeC_6H_4CO_2Me)L]$ *Complexes.—Dichloro(η⁶-methyl* o-*toluate)(triphenylphosphine)-ruthenium*(II), (**2a**). Complex (**1**) (0.1 g, 0.155 mmol) and triphenylphosphine (0.13 g, 0.49 mmol) were refluxed in n-hexane (15 cm^3) for 8 h. An orange precipitate settled out below a clear supernatant on standing overnight at room temperature. This product was collected on a glass frit, washed several times with n-hexane, and sucked dry. The ^1H n.m.r. spectrum (200 MHz) of this crude product showed it to be a *ca.* 85:15 mixture of (**2a**) and unreacted (**1**). This product was shaken with acetone (20 cm^3) and filtered. Evaporation of the deep red filtrate to 4 cm^3 and addition of diethyl ether (4 cm^3) gave a pale orange precipitate. This was collected on a glass frit, washed several times with diethyl ether, and sucked dry (0.073 g, 40% yield) (Found: C, 55.5; H, 4.1; Cl, 12.2; P, 5.4. $C_{27}H_{25}Cl_2O_2PRu$ requires C, 55.5; H, 4.3; Cl, 12.1; P, 5.3%). ^1H N.m.r. (200 MHz, $CDCl_3$): δ 7.75 and 7.4 (15 H, m and m, Ph), 6.34 (1 H, d, *J* 5.5, H^6), 5.23 (1 H, dd, *J* 10.5, H^4), 4.61 (2 H, overlapping d + t, H^3 and H^5), 3.91 (3 H, s, CO_2Me), and 2.51 (3 H, s, Me).

Dichloro(dimethylphenylphosphine)(η⁶-methyl o-*toluate)-ruthenium*(II), (**2b**). This complex was synthesised similarly to (**2a**), starting from (**1**) (0.1 g, 0.155 mmol) and dimethylphenylphosphine (0.066 g, 0.48 mmol). The yield of (**2b**) was 0.08 g (55%) (Found: C, 44.4; H, 4.7; Cl, 14.7. $C_{17}H_{21}Cl_2O_2PRu$ requires C, 44.4; H, 4.6; Cl, 15.4%). ^1H N.m.r. (200 MHz, $CDCl_3$): δ 7.83, 7.52, 7.09 (5 H, multiplets, Ph), 6.13 (1 H, t, *J* 4.5, H^4 or H^6), 5.48 (1 H, m, H^6 or H^4), 5.27 (1 H, d, *J* 5.5, H^3), 4.42 (1 H, t, *J* 5, H^5), 3.84 (3 H, s, CO_2Me), 2.49 (3 H, s, Me), 1.90 (3 H, d, *J* 11.8, P*Me*MePh), and 1.81 (3 H, d, *J* 12, PMe*Me*Ph).

Preparation of $[RuCl_2RL']$ *complexes.—Dichloro(η⁶-methyl* o-*toluate)[(−)(S)1-phenylethylamine]ruthenium*(II), (**3a**). Complex (**1**) (5.0 g, 7.76 mmol) and (−)(*S*)-1-phenylethylamine (4.9 cm^3, 38 mmol) were stirred in methanol (80 cm^3) at room temperature for 5 h. A yellow-orange solid precipitated. It was filtered, washed several times with diethyl ether, and sucked dry to give 3.1 g (45% yield) of (**3a**). This was a 50:50 mixture of diastereomers, as estimated from the ratio of the intensities of the two singlets due to the CO_2Me protons [δ 3.91 and 3.97, see Figure 2(*a*)] (Found: C, 46.05; H, 4.75; Cl, 16.0; N, 3.15. $C_{17}H_{21}Cl_2NO_2Ru$ requires C, 45.85; H, 4.75; Cl, 16.05; N, 3.20%). Four crystallisations of (**3a**) from methanol–diethyl ether (3:1) gave a solid containing 90% of the less soluble diastereomer (0.43 g, 6% yield). ^1H N.m.r. (300 MHz, $CDCl_3$): δ 7.6—7.4 (5 H, m, Ph), 5.76 (1 H, t, *J* 4.7, H^4), 5.38 (1 H, d, *J* 5.7, H^6), 5.27 (1 H, d, H^3), 4.92 (1 H, t, H^5), 4.48 (1 H, m, CH), 4.12 (1 H, m, N*H*H), 3.91 (3 H, s, CO_2Me), 3.1 (1 H, m, NH*H*), 2.44 (3 H, s, Me), and 1.58 (3 H, d, *J* 6.7, CH*Me*). α ($CHCl_3$, 2.2 g dm^{-3}, 25 °C, 589.3 nm) = −75.5°. From the mother-liquor of the reaction, after five steps in which the solution was concentrated and diethyl ether was added, a solid containing 75% of the more soluble diastereomer was obtained (0.67 g, 10%). ^1H N.m.r. (300 MHz, $CDCl_3$): δ 7.6—7.4 (5 H, m, Ph), 6.2 (1 H, d, *J* 5.1, H^6), 5.62 (1 H, t, *J* 4.8, H^4), 5.16 (1 H, d, H^3), 4.88 (1 H, t, H^5), 4.48 (1 H, m, CH), 3.97 (3 H, s, CO_2Me), 3.53 (2 H, m, NH_2), 2.48 (3 H, s, Me), and 1.58 (3 H, d, *J* 6.7, CH*Me*). α ($CHCl_3$, 2 g dm^{-3}, 25 °C, 589.3 nm) = −37°.

Dichloro[(+)dehydroabietylamine](η⁶-methyl o-*toluate)-ruthenium*(II), (**3b**). Complex (**1**) (1.5 g, 2.26 (mmol) and (+)-dehydroabietylamine (1.6 g, 5.6 mmol) were stirred in methanol (20 cm^3) at room temperature for 12 h. The volume of the red-brown solution was reduced to 10 cm^3 and diethyl ether (5 cm^3) added. The red precipitate that formed at −20 °C was filtered off, washed several times with diethyl ether and dried to give 1.45 g (yield 52%) of (**3b**) as a 50:50 mixture of diastereomers (Found: C, 57.45; H, 6.80; Cl, 11.60; N, 2.25. $C_{29}H_{41}Cl_2NO_2Ru$ requires C, 57.35; H, 6.8; Cl, 11.65; N, 2.30%). ^1H N.m.r. (300 MHz, $CDCl_3$): δ 7.14, 6.97, 6.86 (6 H, multiplets, Ph), 6.3 (2 H, d, *J* 6, H^6), 6.0 (2 H, t, *J* 5.6, H^4), 5.5 (2 H, d, H^5), 5.42 (2 H, m, H^3), 3.94 and 3.93 (6 H, s and s, CO_2Me), 2.51 and 2.50 (6 H, s and s, Me), 3.2—2.7, 2.3, 1.75, 1.4 (32 H, multiplets, NH_2 and CH + CH_2 of the amine), 1.22, 1.21, 1.19 (18 H, s, d, s, Me, CH*Me*Me), and 0.95 (6 H, d, *J* 6, CHMe*Me*). The composition of (**3b**) did not change on crystallisation from methanol–diethyl ether (3:1) or dichloromethane–n-hexane (2:1).

(η⁶-Benzene)dichloro[(−)(S)-1-phenylethylamine]ruthenium-(II), (**3c**). This complex was prepared as described for (**3b**) starting from $[\{RuCl_2(\eta^6\text{-}C_6H_6)\}_2]$ (0.25 g, 0.5 mmol) and (−)(*S*)-1-phenylethylamine (0.13 cm, 1 mmol). The yield of the brown solid product was 0.33 g (90%) (Found: C, 45.10; H, 4.5; Cl, 19.05; N, 3.55. $C_{14}H_{17}Cl_2NRu$ requires C, 45.20; H, 4.10; Cl, 19.5; N, 3.75%). ^1H N.m.r. (100 MHz, $CDCl_3$): δ 7.58—7.36 (5 H, m, Ph), 5.33 (6 H, s, C_6H_6), 4.5 (1 H, m, CH), 3.91 (1 H, m, N*H*H), 3.23 (1 H, m, NH*H*), and 1.63 (3 H, d, *J* 7, CH*Me*).

*Dichloro(η⁶-*p*-cymene)[(−)(S)-1-phenylethylamine]-ruthenium*(II), (**3d**). This complex was prepared as described for (**3b**) starting from $[\{RuCl_2(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2]$ (0.252 g, 0.42 mmol) and (−)(*S*)-1-phenylethylamine (0.15 cm, 1.15 mmol). The yield of the orange-red solid was 0.3 g (85%) (Found: C, 50.45; H, 5.5; Cl, 16.45; N, 2.95. $C_{18}H_{25}Cl_2NRu$ requires C, 50.60; H, 5.9; Cl, 16.60; N, 3.30%). ^1H N.m.r. (100 MHz, $CDCl_3$): δ 7.44 (5 H, m, Ph), 5.2, 4.95, 4.74 (4 H, d, m, d, C_6H_4), 4.36 (1 H, m, C*H*Me), 3.5—3.0 (2 H, m, NH_2), 2.90 (1 H, m, C*H*Me_2), 2.11 (3 H, s, Me), 1.54 (3 H, d, *J* 6.7, CH*Me*), 1.25 (3 H, d, *J* 6.9, CH*Me*Me), and 1.19 (3 H, d, CHMe*Me*).

Preparation of Chloro[(−)(R,R)-1,2-diphenyl-1,2-diamino-

ethane](η^6-*methyl* o-*toluate*)*ruthenium*(II) *Hexafluorophosphate*, [RuCl(η^6-*o*-$MeC_6H_4CO_2Me$){(−)(N–N)}]PF_6, (**4**).—Complex (**1**) (1.81 g, 2.8 mmol) and (−)(*R*,*R*)-1,2-diphenyl-1,2-diaminoethane (1.2 g, 5.6 mmol) were stirred in methanol (20 cm^3) at room temperature for 12 h and $NaPF_6$ (0.94 g, 5.6 mmol) was added. The resulting orange solution was concentrated to 10 cm^3 and diethyl ether added until a yellow precipitate formed. This was filtered off, washed several times with diethyl ether, and dried to give 1.86 g (yield 60%) of (**4**) as a 50:50 mixture of diastereomers (Found: C, 43.75; H, 4.05; Cl, 5.8; N, 4.35; P, 5.0. $C_{23}H_{26}ClF_6N_2O_2PRu$ requires C, 44.00; H, 4.15; Cl, 5.65; N, 4.45; P, 4.95%). ^1H N.m.r. (300 MHz, CD_3OD): δ 7.3—7.1 (20 H, m, Ph), 6.71 and 6.69 (2 H, overlapping d + d, *J* 5.5, H^6), 6.24 (2 H, t, H^4), 6.1 (2 H, m, N*H*H), 5.89 (2 H, m, H^5), 5.72 (2 H, m, NH*H*), 5.6 and 5.56 (2 H, d and d, H^3), 4.1—3.8 (8 H, m, CH–CH, N*H*H, NH*H*), 3.91 and 3.89 (6 H, s and s, CO_2Me), and 2.51 and 2.50 (6 H, s and s, Me). The composition of (**4**) did not change on crystallisation from methanol–diethyl ether (3:1).

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