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Preparation of the chiral amine salts $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2R)]PF_6$, RNH_2 = α-methylbenzylamine, 1-cyclohexylethylamine, and 1-(1-naphthyl)ethylamine: X-ray single crystal structures of the diastereomeric salts $(S_{Ru}R_C)$- and $(R_{Ru}R_C)$-$[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)\{NH_2CH(Me)(Ph)\}]PF_6$

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Abstract

Diastereomeric salts $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2R)]PF_6$ containing both a chiral metal centre and an α-chiral amine ligand have been prepared. The use of diamagnetic anisotropy in their ^1H NMR spectra to distinguish the diastereomers has been supported by single crystal X-ray crystallography. The structures of the salts containing the ligands cyclohexylamine and α-methylbenzylamine (both diastereomers) have been determined at low temperature. Decomplexation of the amine ligand from purified diastereomeric salts to affect resolution of the metal centred chirality has been attempted. The chiral isonitrile ligand containing compounds $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CNCH(Me)Ph)(Cl)]$ and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CNCH(Me)Ph)(NH_3)]PF_6$ have been prepared from (*S*)-α-methylbenzylisonitrile and the single crystal X-ray structure of both diastereomeric salts of the ammine compound has been determined.

Keywords: Metal; Chirality; Diastereomers; Ruthenium; Amines; Isonitriles; X-ray

1. Introduction

The exploration and utilization of metal centred chirality in organometallic chemistry is less developed than that of carbon centres in modern organic chemistry. A major reason for this difference is the kinetic lability of most metal centres especially when monodentate ligands are present; thus studies of octahedrally coordinated Cr(III) and low-spin Co(III) complexes with ligand and metal centered chirality dominate the literature. Werner [1] reported the first resolution of a coordination compound in 1911 but the first optically active organotransition metal compounds containing a chiral metal centre were only reported in 1969 [2,3]. Brunner [4,5] has developed and reviewed this field and cautioned against common pitfalls of data interpretation when resolution of metal centres and particularly their configurational stability is reported [6–8].

We were interested in using readily available homochiral amines to effect resolution of a racemic mixture of ruthenium compounds of the general type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(L)(Cl)]$ by diastereomer formation followed by removal of the chiral auxiliary to effect resolution of the metal centre. Low-spin d^6 Ru(II) was anticipated to be reasonably configurationally stable in both five- and six-coordination but to possibly present some problems in the decomplexation step related to its kinetic inertness.

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The ammine ligand in $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_3)]PF_6$ had proved to be resistant to replacement by carbonylation and to deprotonation [9].

There are very comprehensive nomenclature systems for the unique identification of isomeric transition metal compounds but they have proved very cumbersome for routine application [10,11]. We have opted for the simple approach related to that used by organic practitioners. The stereochemical descriptors used for organometallic compounds are a modification of the Cahn–Ingold–Prelog rules and treat the cyclopentadienyl group as a single atom of atomic weight 60 for prioritization [12,13]. The structural diagrams in this paper are drawn to normally show the metal chirality denoted as $\mathbf{S}_{Ru}$ for convenience ($Cp > PPh_3 > NH_2R > CN^tBu$) but unless explicitly stated the starting materials and products represented are racemic. One of the spectroscopic probes used throughout this work is that of diamagnetic anisotropy; protons held over an aromatic ring system will normally be shielded (δ decreases) in ^1H NMR spectra while protons held over a triple bond will be deshielded (δ increases). The effect is usually observable at distances up to 4 Å and drops off rapidly although measurable effects up to 14 Å have been observed in polyaromatic systems [14,15].

2. Results and discussion

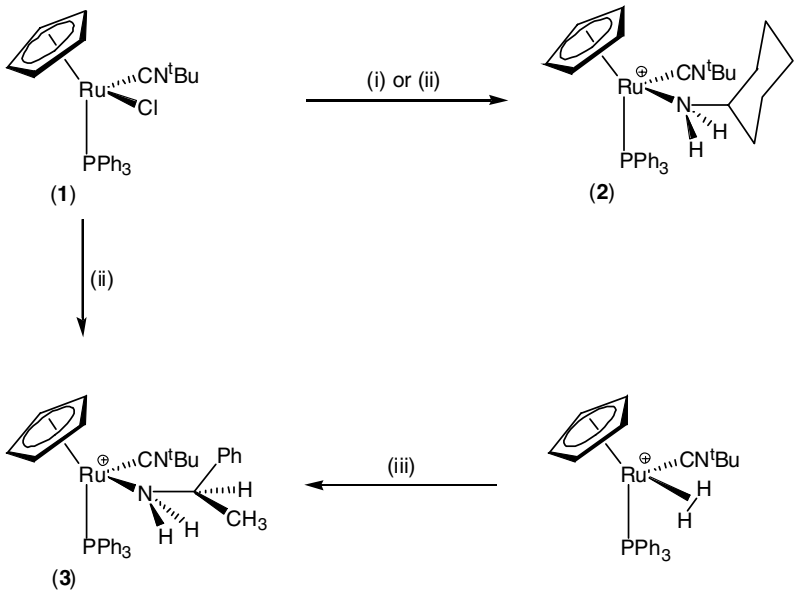
Treatment of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(Cl)]$ (**1**) with a halide abstractor in the presence of cyclohexylamine produced yellow crystalline $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2C_6H_{11})]PF_6$ (**2**). The halide abstraction system could be either thallium hexafluorophosphate in dichloromethane or the methanolic potassium hexafluorophosphate–thallium (I) carbonate mixture used previously to prepare ammine complexes [9]. The first system gave a 97% yield compared with 38% for the latter indicating some degree of competition between methanol and the amine for the solvento cationic intermediate in that synthetic route. The main features of spectroscopic interest are the differentiation of the diastereotopic NH protons by 1.21 ppm in the ^1H NMR spectrum and weak bands at 3311, 3270, and 1587 cm^{-1} in the infrared spectrum due to the amine ligand. Encouraged by the degree of chemical shift difference which suggested that one of the amine protons is oriented into the region near the phenyl rings of the triphenylphosphine ligand and hence shielded, implying strongly preferred conformations and a useful spectroscopic probe, we decided to prepare a family of cations containing *C*-chiral amines in order to investigate diastereomeric resolution. The chiral amines used were of at least 98% e.e. and the diastereomeric excesses reported below have not been recalculated; given the integration errors for routine ^1H NMR spectroscopy the diastereomeric excesses reported probably underestimate the true selectivities.

Reaction of **1** with thallium hexafluorophosphate in dichloromethane and *S*(−)-α-methylbenzylamine, *R*(−)-1-cyclohexylethylamine, or (±)-1-(1-naphthyl)ethylamine gave the salts $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2CH\{Me\}Ph)]PF_6$ (**3**), $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2CH\{Me\}Cy)]PF_6$ (**4**), and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2CH\{Me\}Np)]PF_6$ (**5**), respectively. Initial crystallization of **3** from dichloromethane–diethyl ether (1:3) at −78 °C gave fine yellow crystals, which proved to be predominantly the $\mathbf{R}_{Ru}\mathbf{S}_C$ diasteromer (**3RS**) in 74% diastereomeric excess. Concentration of the filtrate and crystallization at −25 °C gave a second set of yellow crystals, which proved to be predominantly the $\mathbf{S}_{Ru}\mathbf{S}_C$ diastereomer (**3SS**) in 98% d.e. The infrared spectrum of **3** contains four bands due to ν(NH) at 3325, 3308, 3284, and 3265 cm^{-1} confirming the presence of two diastereomers with the bands at 3325 and 3284 cm^{-1}being due to the more soluble diastereomer **3SS**. While the definitive assignment of absolute structure for the two diastereomeric salts was made by single crystal X-ray crystallography our initial assignment was made by consideration of the ^1H NMR spectra of the enriched diastereomers. The spectrum of the least soluble compound **3RS** has a cyclopentadienyl singlet resonance at δ 4.30 and a doublet at δ 1.11 for the α-methyl group whereas the more soluble compound **3SS** has these resonances at δ 4.72 and δ 1.29, respectively. The diastereomers **3RR** and **3SR** were also prepared, from *R*(+)-α-methylbenzylamine to ensure complementarity and reciprocity and this pair were used for the X-ray single crystallographic studies (Scheme 1).

Davies has demonstrated the use of α-methyl group shielding by the aromatic ring current of triphenylphosphine to distinguish stereoisomers of the metal acyls $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(COCH(Me)R)]$; in $\mathbf{S}_{Fe}\mathbf{S}_C/\mathbf{R}_{Fe}\mathbf{R}_C$ diastereomers the group resonates between δ 0.00 and δ 0.50 whereas in the $\mathbf{S}_{Fe}\mathbf{R}_C/\mathbf{R}_{Fe}\mathbf{S}_C$ diastereomers the resonance is found between δ 0.8 and δ 1.30 [16]. Fig. 1 illustrates the relative relationships between the ruthenium and iron compounds; note that the priority rules reverse the metal centre descriptors on changing from an amine group to an acyl group.

The single crystal X-ray structures of **3SR** and **3RR** (vide infra) confirm the basic conformations shown in Fig. 2 and support the additional assumption that the phenyl ring of the amine ligand shields the cyclopentadienyl protons in **3SR** and **3RS**. Our criterion is that the diastereomer with the highest ^1H NMR chemical shifts for both the cyclopentadienyl and α-methyl groups is the **RR** or **SS** diastereomer while that with the lowest values for both chemical shifts is the **RS** or **SR** isomer in the isonitrile series. Davies has published extensively on the conformational preferences of the alkyl groups in the iron acyl complexes [17]; we have not performed similar modeling studies but the close spectroscopic similarities suggest that qualitatively the structures indicated are correct, in particular that the methine hydrogen points in towards the isonitrile or carbonyl group.

While the described preparation of **3** yields an overall racemic product in that equal amounts of **3RS** and **3SS** are produced from **2** and *S*(−)-α-methylbenzylamine



(i) KPF_6, Tl_2CO_3, MeOH, amine, 60°C (ii) $TlPF_6$, amine, CH_2Cl_2, RT (iii) amine, CH_2Cl_2

Scheme 1. Synthetic routes to **2** and **3**.

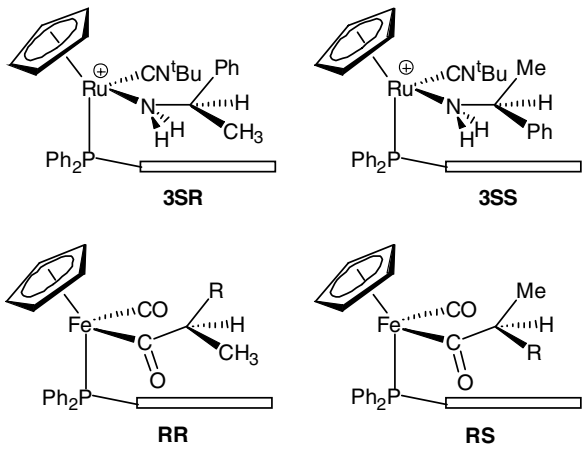


Fig. 1. Relationship of chirality descriptors to structure.

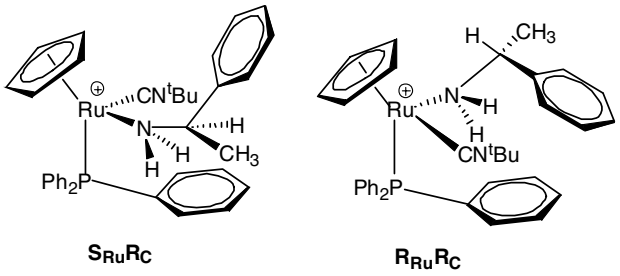
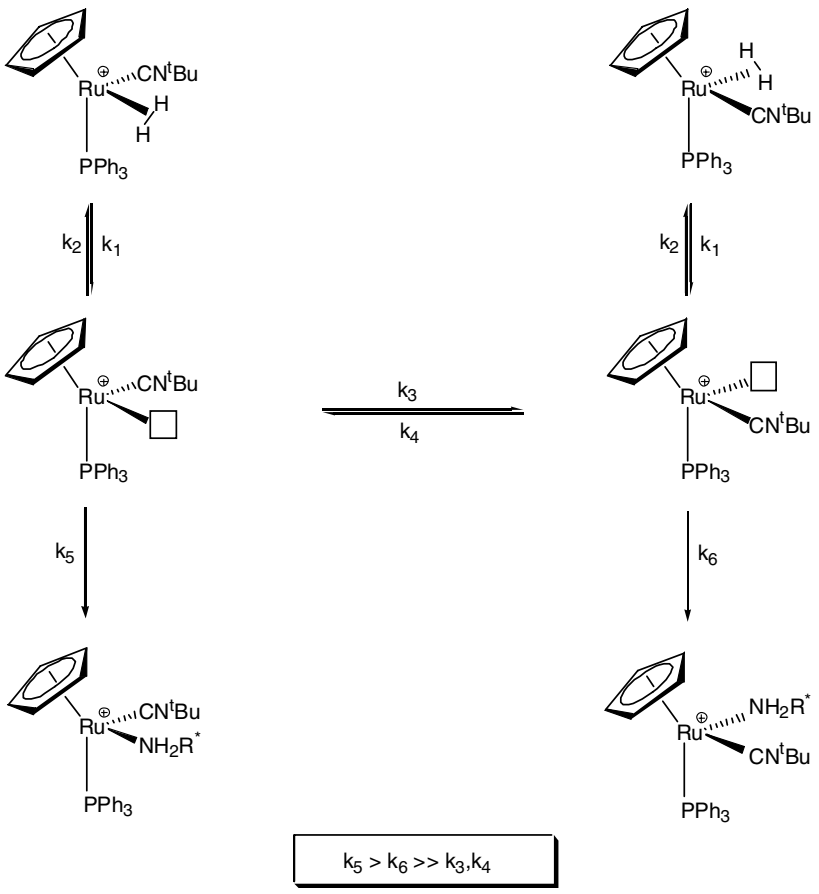


Fig. 2. Idealized solution conformation of **3SR** and **3RR**.

thermodynamically, this was not necessarily anticipated. A kinetic experiment was therefore carried out by monitoring the formation of **3SS** and **3RS** from the reaction of the molecular hydrogen cation $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(\eta^2\text{-}H_2)]PF_6$ [18] with *S*(−)-α-methylbenzylamine in deuterodichloromethane by ^1H NMR spectroscopy at room temperature. Addition of 0.3 equivalents of the amine immediately generated only **3SS** and the further addition of 0.7 equivalents of amine subsequently generated **3RS** within 10 min; the final ratio of diastereomers was 50:50 and remained unchanged after 1 h at room temperature. Under the ambient conditions the Lewis acid fragment $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]^+$ formed initially does not racemise and despite a kinetic preference for **3SS** the lack of racemization prevents diastereomeric induction. Under these conditions there is no interconversion of **3SR** and **3SS** as evidenced both by this experiment and from monitoring enriched samples over a period of days. Further, the single crystals used for the X-ray structural determinations of **3RR** and **3SR**, respectively were each dissolved in CD_2Cl_2 at 22 °C and ^1H NMR spectra of the solutions were immediately obtained; in each case the appropriate single diastereomer was the only observed species and the other diastereomers, **3SR** and **3RR**, respectively, were not observed after several hours.

There has been a considerable history of investigating the ease of racemization of chiral at metal compounds [4–8] with the general conclusion that such centres are often not stereochemically rigid; we conclude that in this case the rate of racemization is much less than the rate of complexation and that none of the ligands attached to ruthenium in the final products reversibly dissociate (Scheme 2).

The salt $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2CH\{Me\}\text{-}Cy)]PF_6$ (**4**) was also enriched on initial crystallization to produce **4SR** as the least soluble diastereomeric salt in 61% d.e. and the more soluble isomer **4RR** in 79% d.e.



Scheme 2. Curtin–Hammett scheme for the interconversion of **3**.

Similarly a single crystallization of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2CH\{Me\}Np)]PF_6$ (**5**) gave the **RS/SR** product in 73% d.e. and the more soluble **RR/SS** product in 56% d.e. A further recrystallization of the **RS/SR** product increased the diastereomeric excess up to 91%; both products in this case being racemic because racemic (±)-1-(1-naphthyl)ethylamine was used. In contrast to the large difference in ^{1}H NMR chemical shift, (0.43 ppm), for the cyclopentadienyl resonances of **3RS** and **3SS** these resonances differ by 0.001 ppm for the diastereomers of **4** suggesting that the aromatic ring of the amine in **3** can shield these protons. In the case of **5** which also contains an aromatic group in the amine ligand the separation is 0.54 ppm for the diastereomers.

Further diastereomeric enrichment of **3** and **5** was carried out to establish the principle and usually a maximum of three crystallizations was sufficient to give products of ca. 98.5% d.e. for **3** and **5**. Enrichment of **4** was not explored fully because the spectroscopic parameters of **4** made accurate quantitation problematic beyond the 90% d.e. level.

The reaction of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CO)Cl]$ (**6**) with thallium hexafluorophosphate and *S*(−)-α-methylbenzylamine in dichloromethane produced a very low yield (3%) of yellow crystals of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CO)(NH_2CH\{Me\}Ph)]PF_6$ (**7**). The two diastereomeric salts were again partially separable with the $\mathbf{R_{Ru}S_C}$ product (**7RS**) being the least soluble. The assignment of $\mathbf{R_{Ru}}$ stereochemistry in this diastereomeric salt was made by comparing the cyclopentadienyl resonances in the ^{1}H NMR spectra at δ 5.13 and 4.57 with the lower chemical shift being assigned to **7RS** and the higher to **7SS**; this reflects the pattern found for the diastereomers of **3** and **5** induced by the orientation of the aromatic substituent on the amine ligand. The small quantity of **7SS** obtained after the initial crystallization which gave a sample of **7RS** in 42% d.e. combined with the low chemical yield, prevented the full assignment of the ^{1}H NMR spectrum and means that we have used a single parameter in this case.

Decomplexation of the bound amine from diastereomerically enriched samples of **3**, **4**, or **7** should produce enantiomerically enriched samples of the metal moieties. A variety of procedures was explored using $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2C_6H_{11})]PF_6$ (**2**) as a model compound. Reaction of **2** with carbon monoxide (5 atm., 294 K, 120 h.) in dichloromethane, with iodomethane or tetraethylammonium fluoride or tetraethylammonium cyanide in dichloromethane, with methanolic sodium methoxide, with sodium iodide or sodium azide in acetone, with lithium triethylborohydride in THF (all at 294 K, 1–48 h), or with 2-methyl-1-butanethiol in refluxing methanol gave in each case high recovery (>80%) of

2 and no other tractable products. Treatment of **2** with excess sodium iodide and excess trimethylamine-*N*-oxide in methanol under reflux generated [(η^5-C_5H_5)-Ru(PPh_3)(CN^tBu)(I)] (**8**) in moderate yield together with recovered **2**. Since this reaction probably proceeds by the generation of iodine and its subsequent reaction with **2** we proceeded to react **2** with iodomethane in refluxing 1,2-dichloroethane or by photolysis of a solution in dichloromethane containing iodine. Careful optimization of these reactions suggested initial conditions for the attempted decomplexation of **3**, the chiral metal centre target. Samples of **3RS** (90% d.e.) and **3SS** (96% d.e.) were converted via the iodomethane route into **8** in 98% and 82% isolated yield, respectively. A sample of **3RS** of the same purity was also converted via the photolysis route in 54% isolated yield.

The samples of **8** obtained were assayed for enantiomeric purity by two methods; reaction with *S*(−)-α-methylbenzylamine to regenerate **3RS** and **3SS** and by a ^{1}H NMR spectroscopic method. Addition of *R*(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol (*R*(−)-TFAE) to racemic **8** causes doubling of the cyclopentadienyl and *tert*-butyl resonances with the optimum separation (300 MHz: 5.7 and 3.6 Hz, respectively) occurring on addition of 1.2 equivalents of TFAE. Both methods confirmed that the samples of **8** obtained on decomplexation from **3RS** and **3SS** were racemic (±2%). The high chemical stability of **3** and the nature of the forcing conditions required to produce **8** demonstrates that our resolution strategy was unsuccessful.

The reaction of a secondary amine ligand could potentially generate an additional chiral centre and [(η^5-C_5H_5)-Ru(PPh_3)(CN^tBu)(Cl)] (**1**) was reacted with diethylamine and $TlPF_6$ in dichloromethane to confirm that a secondary amine could ligate to the ruthenium centre. The orange-yellow crystals of [(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)($NHEt_2$)]PF_6 (**9**) were moderately air-sensitive and showed a single band at 3269 cm^{-1} (ν_{NH}) in the infrared spectrum in contrast to the two bands seen for a primary amine containing cation. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **9** demonstrated that the ethyl groups of the diethylamine ligand were diastereotopic as expected. *S*(−)-*N*-methyl-1-phenylethylamine reacted similarly to yield yellow crystalline [(η^5-C_5H_5)-Ru(PPh_3)(CN^tBu)(NH(Me)CH{Me}Ph)]PF_6 (**10**) as a mixture of four diastereomers in the ratio 9.6%:38.5%:3.9%:48.0% while concentration of the initial mother-liquor and crystallization produced the same diastereomers in the ratio 21.7%:52.2%:8.7%:17.4%. While these precise ratios reflect the degree of crystallization achieved they also indicate the relative stability of the nitrogen chiral centres, these being freely selectable under the reaction conditions unlike the ruthenium and carbon chiralities, one of which is not racemisable under the conditions and the other of which is set. Analysis of the ^{1}H NMR spectra of these mixtures using the criteria established above for the relative disposition of the metal and carbon chiralities suggests the assignments $\mathbf{S_{Ru}S_NS_C}$:$\mathbf{S_{Ru}R_NS_C}$:$\mathbf{R_{Ru}R_NS_C}$:$\mathbf{R_{Ru}S_NS_C}$ for the diastereomers (Table 1). In particular the cyclopentadienyl group and α-methyl resonances reflect the neighbouring phenyl ring induced shieldings. The *N*-methyl group shieldings also reflect the existence of two diastereomers with these groups pointing towards the isonitrile unsaturation (deshielded) and two with these groups pointing away (shielded).

Calculation of the total quantities of each diastereomer *isolated* reveals the overall ratio is 12.3%:41.4%:4.9%:41.4%; fortuitously the quantity of **10RSS** and **10SRS** material is similar and demonstrates that the metal centre prefers to induce opposite chirality at the nitrogen centre. While the *isolated* material does not represent 100% of the theoretical yield it is clear that a preference of at least 4:1 is present. Fig. 3 below shows all four diastereomers.

The conformations shown are those that can be reasonably predicted based upon the structures of the diastereomeric salts of **3RR** and **3SR** analyzed earlier by ^{1}H NMR spectroscopy and confirmed by X-ray single crystal structure determination. It is clear that the *N*-methyl group would prefer to be external (**SRS**,**RSS**) rather than internal (**RRS**,**SSS**) on steric grounds.

Table 1
Comparison of chemical shifts for the diastereomers of **3** and **10**

Assignments	3RS	3SS	10RSS	10RRS	10SRS	10SSS
C*Ph*	7.25	6.97	7.05	6.65	6.80	6.15
C_5H_5	4.29	4.72	4.64	4.74	4.81	4.83
C*H*Me	3.35	3.34	3.63	3.73	3.88	3.78
N*H*	3.69, 1.87	3.49, 2.13	2.05	obscured	2.51	1.85
NH*Me*			2.29	2.53	2.23	2.46
CH*Me*	1.11	1.30	1.34	1.40	1.55	1.50
C*Me*$_3$	1.30	1.25	1.25	1.18	1.30	1.26

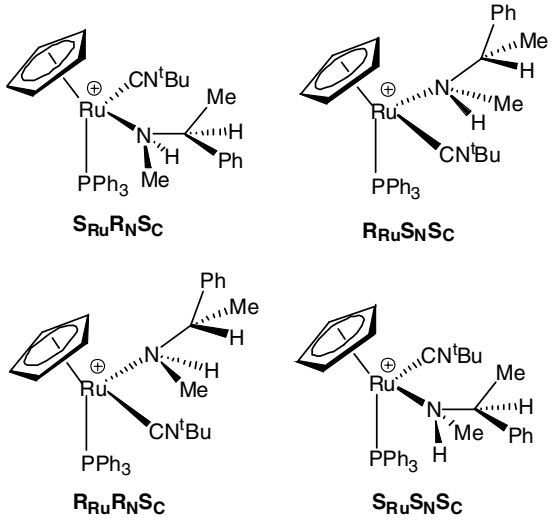


Fig. 3. The diastereomers of **10** derived from *S*(−)-*N*-methyl-1-phenylethylamine.

An alternative method to produce a ruthenium complex resolved at the metal centre which could be taken on further in asymmetric chemistry would involve the preparation of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CNZ)(Cl)]$, where Z contains a chiral element. Combining our experience of the amine chemistry and the utility of the ring shielding effect as a spectroscopic probe we decided to use *S*(−)-α-methylbenzylisonitrile (*S*(−)-Ph(Me)CHNC) as a ligand. A sample of *S*(−)-α-methylbenzylamine was determined to be >99.6% e.e by ^{1}H NMR spectroscopy using *R*(−)-TFAE as a chiral auxiliary [19]. Conversion of this amine to the isonitrile was achieved in 50% yield by a phase transfer Hofmann carbylamine procedure; polarimetry and subsequent reactions indicate that the optical purity was retained in the product.

Reaction of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(Cl)]$ with *S*(−)-α-methylbenzylisonitrile in hot toluene gave a bright orange powder after chromatography in 45% yield. Characterization of this material showed it to be a racemic mixture of the diastereomeric salts $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CNCH(Me)Ph)(Cl)]$ (**11SS**,**11RS**). The solid and solution infrared spectra of the product contained bands at 2102 and 2104 cm^{-1} assignable to *ν*(CN), while the mass spectrum contained the parent ion and then subsequent losses of the chloro group and the isonitrile group. It proved possible with considerable effort to enrich a sample to 30% d.e. by crystallization from toluene–hexane mixtures in order to assign the individual ^{1}H NMR parameters to each diastereomer. The ^{1}H NMR spectroscopic signals of the C*H*Me (*δ* 4.87 and 4.70) and CH*Me* (*δ* 1.29 and 1.39) groups were baseline resolved in the diastereomer mixture and could be used quantitatively. The remoteness of the chiral centre in **11** in comparison to the amine complexes such as **3** did not permit complete confidence in an absolute assignment because the linear isonitrile functionality removes the α-methyl group away from the ring current of the triphenylphosphine aromatic rings, but after looking at the solid state structures of **12**, we assign the signals at *δ* 4.87 and 1.29 to **11SS**.

The mixture (**11SS**,**11RS**) was converted into the ammine salts $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CNCH(Me)Ph)(NH_3)]PF_6$ (**12SS**,**12RS**) by means of ammonium hexafluorophosphate and thallium carbonate in hot methanol with a view to improving the separation of the diastereomeric centres by crystallization. It should be noted that the ruthenium chirality descriptors reverse when the chloro ligand is replaced by the ammine ligand. Thus, assuming retention at the metal centre, **11SS** produces **12RS** and **11RS** produces **12SS**. The yellow crystalline product obtained in 47% yield proved to an equimolar mixture of the diastereomeric salts. All attempts to effect partial resolution failed and indeed single crystals of **12** proved to contain both diastereomeric centres. In particular the single crystal used for the X-ray single crystal structure determination was later dissolved in CD_2Cl_2 and confirmed this point and that the equimolar mixture was perfectly configurationally stable in solution.

3. X-ray crystal structures

The X-ray single crystal structure of **2** was determined at 223 K; many crystals of **2** were examined under a polarizing microscope and found to be twinned but a few single crystals were located and examined. The crystal used for the data collection was of an acceptable quality for the intended purpose. The crystal specimens of **3RR** and **3SR** were of very high optical quality and highly faceted; it would be possible to resolve a mixed sample by triage, picking the diastereomers apart under a microscope. Both structures were determined at 233 K (Table 2).

The crystal of **2** contained molecules with the *R*-configuration at ruthenium and the absolute structure parameter of 0.31(8) reflects the correct choice for the single chiral centre. Analysis of a second crystal revealed that it only contained molecules with an *S*-configuration at ruthenium (Rogers *η* 1.11(12)), thus the bulk sample is probably best described as a racemic conglomerate. The unit cell also contained one molecule of dichloromethane per cation. Racemic twin refinement was attempted on the data obtained for the first crystal and did not significantly improve the refinement; the nature of the sample did not suggest that further exploration was necessary or required.

The overall geometry of the cation is pseudo octahedral as expected with the cyclohexyl group in a chair conformation with the proton on C(41) pointing in towards the isonitrile ligand (Fig. 4). One of the amine protons points towards the centre of a phenyl ring while the other is oriented away as anticipated providing the origin of the chemical shift differentiation in the ^{1}H NMR spectrum. The ruthenium–nitrogen bond length of 2.172(8) Å compares with 2.190(5), 2.216(2) and 2.174(8) Å for

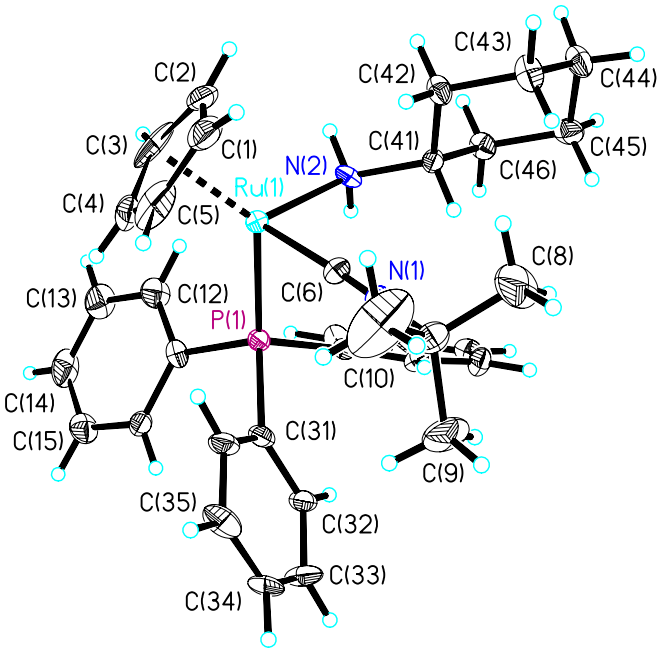


Fig. 4. The cation present in **2** showing 25% probability ellipsoids.

Table 2
Crystallographic data collection parameters for **2**, **3SR**, **3RR**, and (**12RS**,**12SS**)

Identification code	**2** · CH_2Cl_2	**3SR**	**3RR**	(**12RS**,**12SS**)
Empirical formula	$C_{35}H_{44}Cl_2F_6N_2P_2Ru$	$C_{36}H_{40}F_6N_2P_2Ru$	$C_{36}H_{40}F_6N_2P_2Ru$	$C_{32}H_{32}F_6N_2P_2Ru$
Formula weight	840.63	777.71	777.71	721.61
Temperature (K)	223(2)	233(2)	233(2)	233(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
Unit cell dimensions				
a (Å)	11.048(3)	10.083(2)	9.444(2)	9.902(4)
b (Å)	16.983(3)	18.628(3)	18.932(3)	17.934(8)
c (Å)	11.204(2)	10.704(2)	11.022(2)	18.283(9)
α (°)	90	90	90	90
β (°)	114.04(2)	117.68(2)	115.13(1)	92.63(4)
γ (°)	90	90	90	90
Volume (Å^3)	1919.9(8)	1780.4(6)	1784.1(6)	3243(3)
Z	2	2	2	4
Density (calculated) (Mg/m^3)	1.454	1.451	1.448	1.478
Absorption coefficient (mm^{-1})	0.687	0.589	0.588	0.641
F(000)	860	796	796	1464
Crystal size (mm^3)	$0.35 \times 0.25 \times 0.25$	$0.40 \times 0.35 \times 0.30$	$0.55 \times 0.40 \times 0.25$	$0.45 \times 0.20 \times 0.14$
Θ range for data collection (°)	1.99–27.50	2.28–31.07	2.04–31.07	2.27–25.09
Index ranges	$-1 \leqslant h \leqslant 14$, $-22 \leqslant k \leqslant 1$, $-14 \leqslant l \leqslant 13$	$-2 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 27$, $-15 \leqslant l \leqslant 14$	$-2 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 27$, $-16 \leqslant l \leqslant 15$	$0 \leqslant h \leqslant 11$, $-1 \leqslant k \leqslant 21$, $-21 \leqslant l \leqslant 21$
Reflections collected	5598	7316	7368	6726
Independent reflections [R_{int}]	4865 [0.0356]	5859 [0.0209]	5835 [0.0276]	6342 [0.0499]
Completeness to θ_{max} (%)	99.2	99.8	99.4	99.3
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	4864/1/433	5859/18/424	5835/34/460	6342/1/776
Goodness-of-fit on F^2	1.096	1.024	1.085	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0712$, $wR_2 = 0.1755$	$R_1 = 0.0330$, $wR_2 = 0.0755$	$R_1 = 0.0333$, $wR_2 = 0.0867$	$R_1 = 0.0544$, $wR_2 = 0.1111$
R indices (all data)	$R_1 = 0.0988$, $wR_2 = 0.1905$	$R_1 = 0.0425$, $wR_2 = 0.0808$	$R_1 = 0.0398$, $wR_2 = 0.0918$	$R_1 = 0.0945$, $wR_2 = 0.1290$
Absolute structure parameter	0.31(8)	0.00(3)	−0.01(3)	0.03(6)
Largest differential peak and hole (e Å^{-3})	1.703 and −0.640	0.554 and −0.453	0.561 and −0.614	0.529 and −0.377

$[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(NH_2CH_2Ph)]BF_4$ [20], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(P\{OMe\}_3)(NH_2CMe_3)]SO_3CF_3$ [21], and $[(\eta^5\text{-}C_5H_5)Ru(Cy_2PCH_2CH_2PCy_2)(NH_2C_8H_{17})]SO_3CF_3$ [22], respectively.

The structures of **3SR** (Fig. 5) and **3RR** (Fig. 6) have the same gross geometry as that found in **2**, and are both absolute structure determinations with parameter values of −0.01(3) and 0.00(3), respectively. The ruthenium–nitrogen bond lengths are 2.168(3) and 2.184(3) Å, respectively, and there are other small metric differences at the ruthenium centre (Table 3). These differences for the diastereomeric cations are likely to be due to steric factors such as the disposition of the benzyl group. The most striking structural difference between **3RR** and **3SR** is the position of the α-methyl group caused by the preference of the benzyl hydrogen atom to point inwards towards the isonitrile group in both diastereomers. The proximity of the α-methyl group in **3SR** to the aromatic rings of the triphenylphosphine ligand and of the α-phenyl group to the cyclopentadienyl ring hydrogens supports the earlier ^{1}H NMR spectroscopic analysis where both these interactions produce shielding relative to **3RR**. The differentiation of the two NH resonances in the ^{1}H NMR spectrum of each diastereomeric salt can also be seen to be a consequence of shielding from aromatic rings. It is implicit in this analysis that the solid state structures and solution structures for each diastereomeric cation are similar; given that rotation around the Ru(1)–N(1) bond and about the N(1)–C(8) bond is likely to be restricted in both diastereomers this is a reasonable outcome.

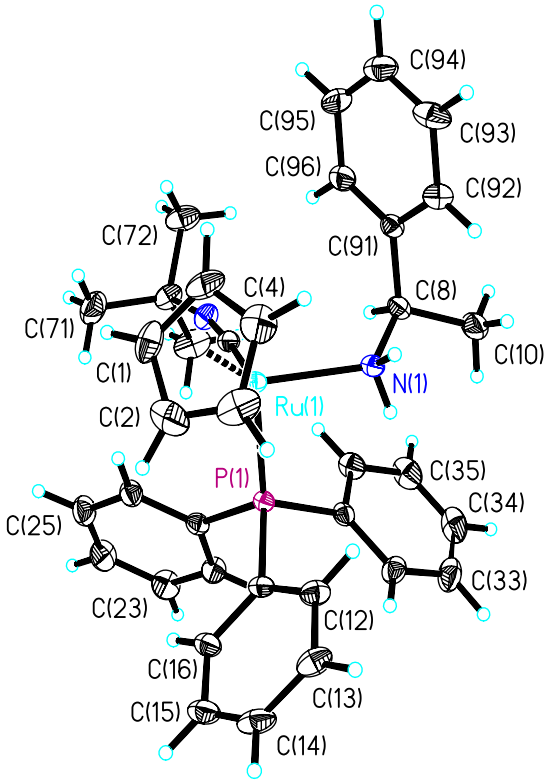


Fig. 5. The cation present in **3SR** showing 25% probability ellipsoids.

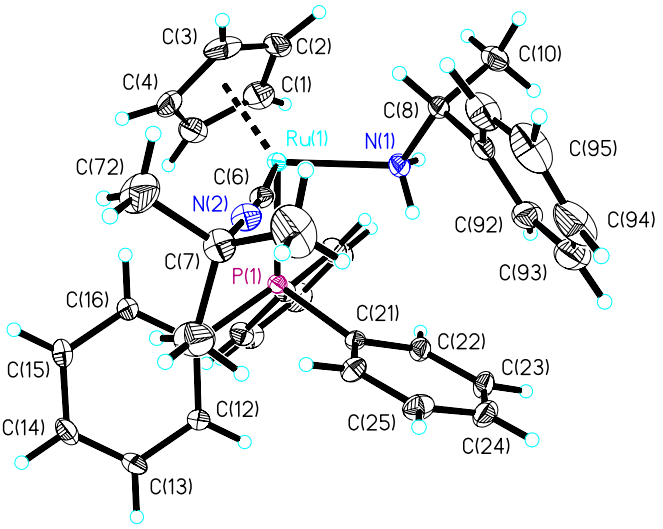


Fig. 6. The cation present in **3RR** showing 25% probability ellipsoids.

Table 3
Selected bond lengths (Å) and bond angles (°) for **3RR** and **3SR**

	3SR	3RR
Ru(1)–P(1)	2.2948(10)	2.2964(10)
Ru(1)–N(1)	2.184(3)	2.168(3)
Ru(1)–C(6)	1.936(3)	1.946(4)
P(1)–Ru(1)–N(1)	89.71(9)	90.53(9)
P(1)–Ru(1)–C(6)	89.16(10)	88.79(10)
N(1)–Ru(1)–C(6)	95.65(13)	90.10(15)
Ru(1)–N(1)–C(8)	121.6(2)	118.1(2)
Ru(1)–C(6)–N(2)	171.9(3)	175.2(4)
C(6)–N(2)–C(7)	169.0(4)	176.5(2)

The X-ray single crystal structure of **12** was carried out at 233 K and the crystal contained both diastereomers of the cation in the unit cell, permitting both a relative and an absolute structure determination. The outcome is that the isonitrile ligand was confirmed to be of *S*-configuration. Visual comparison of the two diastereomeric cations suggests why the **12RS** (Fig. 7) and **12SS** (Fig. 8) compounds are difficult to fractionally separate and do co-crystallize; the volumes and molecular shapes are very similar in that only the disposition of the α-methyl group perturbs the near mirror symmetry in the unit cell (see Table 4).

4. Conclusions

Diastereomers containing only two chiral centres can be designated as *p*-(RR or SS) or *n*-(RS or SR) [23,24]. The most soluble diastereomeric salts in dichloromethane are the *p*-forms of **3**, **4**, **5**, and **7**; possibly this relationship will also hold if small modifications are made to these generic molecules (e.g., change of cyclopentadienyl group, use of PR_2Ph in place of PPh_3, ring *para*-substitution at phenyl rings of phosphine or amine). The use of ring shielding effects in ^{1}H NMR spectroscopy has proved a useful tool in determining diastereomer ratio and relative assignment

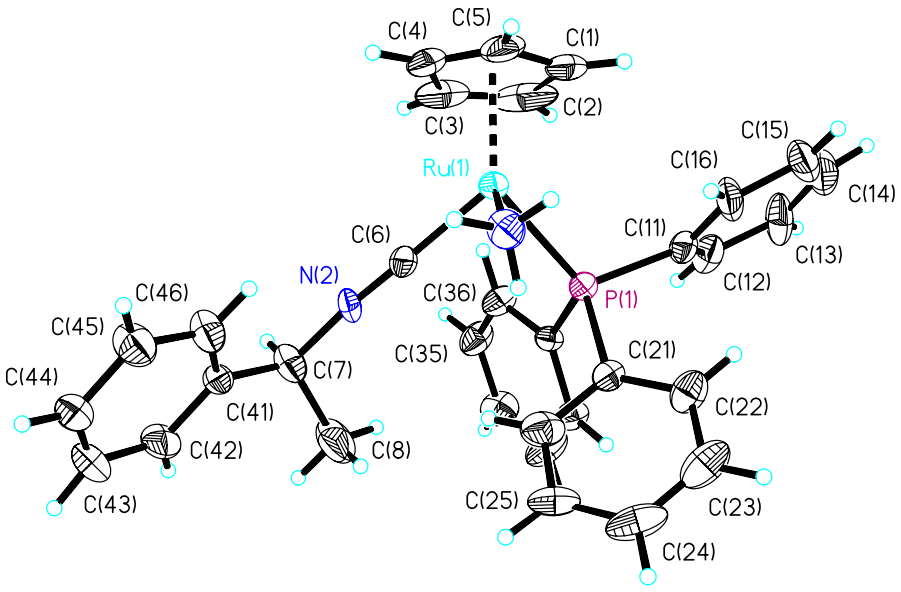


Fig. 7. The cation present in **12RS** showing 25% probability ellipsoids.

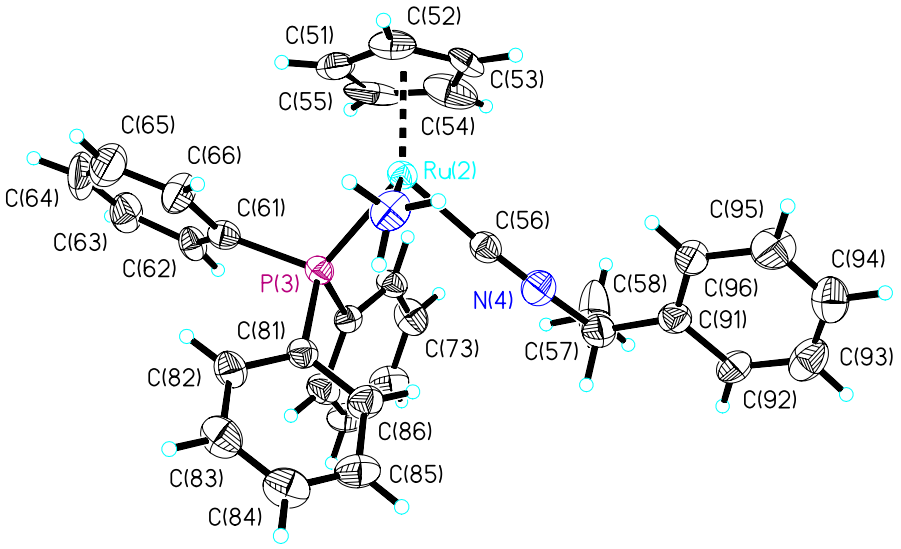


Fig. 8. The cation present in **12SS** showing 25% probability ellipsoids.

Table 4
Selected bond lengths (Å) and bond angles (°) for **12RS** and **12RR**

	12RS		**12RR**
Ru(1)–P(1)	2.301(3)	Ru(2)–P(3)	2.298(3)
Ru(1)–N(1)	2.153(9)	Ru(2)–N(3)	2.182(9)
Ru(1)–C(6)	1.917(14)	Ru(2)–C(56)	1.913(15)
C(6)–N(2)	1.156(15)	C(56)–N(4)	1.175(17)
P(1)–Ru(1)–N(1)	91.5(3)	P(3)–Ru(1)–N(3)	91.5(3)
P(1)–Ru(1)–C(6)	88.6(3)	P(3)–Ru(2)–C(56)	88.4(4)
N(1)–Ru(1)–C(6)	91.4(4)	N(3)–Ru(2)–C(56)	89.7(5)
Ru(1)–C(6)–N(2)	177.7(11)	Ru(2)–C(56)–N(4)	176.6(12)
C(6)–N(2)–C(7)	174.6(12)	C(56)–N(4)–C(57)	165.5(15)

for this family of compounds and extends the work of Davies on cyclopentadienyliron compounds. The crystallographic work illustrates some of the variations possible when one or more chiral centres are present. For example **2** crystallized as a racemic conglomerate where each single crystal is itself homochiral but the bulk sample is racemic, **3** can be crystallized to yield single crystals of each of the four diastereomers, while **12** generated by using a homochiral ligand produces single crystals containing both possible diastereomers.

All of the cationic compounds in this work are configurationally stable in solution at room temperature for periods in excess of one week. In particular the single crystal actually used for each structural measurement was redissolved and monitored by ^{1}H NMR spectroscopy within minutes of solution and then periodically. The solution spectra exactly mirrored the composition determined in the crystal. The nature of the ligands used in this study

and the strong metal–ligand bonding undoubtedly prevents epimerization which has been found to be a major problem elsewhere [6–8]. Indeed the bond strengths in compounds such as **2** and **3** prevented our ultimate aim of producing resolved at ruthenium materials for subsequent asymmetric synthesis.

5. Experimental

5.1. General comments

All reactions and preparations were carried out using conventional Schlenk tube techniques and all solvents were degassed prior to use. Chromatographic work-ups were performed with columns made up of Grade IV neutral alumina prepared with petroleum ether (40–60 °C). Cyclohexylamine and diethylamine were dried over barium oxide and distilled before use. *R*(+)- and *S*(−)-α-methylbenzylamine (99.6% e.e.) were supplied by Seal Sands Chemicals Ltd. The amines *R*(−)-α-cyclohexylethylamine (98% e.e.) and (±)-1-(1-naphthyl)ethylamine from Aldrich were used as supplied. *S*(−)-*N*-methyl-1-phenylethylamine (98% e.e.) was supplied by Fluka Chemika. *R*(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol (99.5% e.e., Aldrich) was dried under reduced pressure at 70 °C overnight. Photolysis reactions were performed using a P.W. Allen A409 medium pressure mercury lamp (313, 366 nm). Infrared spectra were recorded on a Perkin–Elmer 1710 FT-IR instrument calibrated against polystyrene film and only significant absorption bands are reported. Optical rotation measurements were made on an Optical Activity Ltd. AA–100 polarimeter. Nuclear magnetic resonance spectra were recorded on Bruker AC300 (300.13 MHz, ^{1}H NMR; 75.47 MHz, ^{13}C; 121.49 MHz, ^{31}P) and Avance 400 (400.13 MHz, ^{1}H NMR; 100.61 MHz, ^{13}C; 161.98 MHz, ^{31}P) spectrometers. All ^{1}H and ^{13}C NMR chemical shifts are expressed in ppm relative to $SiMe_4$ (0.0 ppm) and ^{31}P shifts relative to $P(OPh)_3$ (126.5 ppm). All spectra were measured at room temperature and homonuclear decoupling and DEPT spectra were obtained when appropriate. Elemental analyses were obtained by Butterworth Laboratories, London. Mass spectral analyses were performed by Fast Atom Bombardment (FAB) on a Kratos Concept S1 Spectrometer. Crystal structure data were collected on a Siemens R3m/V Diffractometer at 233 K for $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2Cy)]PF_6$ (**2**), ($S_{Ru}R_C$)- and ($R_{Ru}R_C$)-$[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2CHMePh)]PF_6$ (**3SR**) and (**3RR**), and at 293 K for $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CNCH(Me)Ph)(NH_3)]PF_6$ (**12**). The starting compounds $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)Cl]$ (**1**) [25,26], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CO)Cl]$ (**6**) [27], and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)I]$ (**8**) [28] were prepared by the published literature procedures.

The optical purity of the *R*(+)- and *S*(−)-α-methylbenzylamines was checked by ^{1}H NMR spectroscopy using *R*(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol [19]. The optical purity of the *R*(−)-α-cyclohexylethylamine and *S*(−)-*N*-methyl-1-phenylethylamine was not verified.

5.2. Preparation of *S*(−)-α-methylbenzylisonitrile {*S*(−)-CNCHMePh}

The published procedure for the synthesis of *tert*-butylisonitrile was adapted [29,30]. A two-neck round-bottomed flask (500 ml) equipped with a magnetic stirrer bar, a reflux condenser, and a pressure equalising dropping funnel was charged with sodium hydroxide (24 g, 0.6 mol). Stirring was commenced and deionized water (3 × 30 ml) was added in portions to maintain smooth stirring. The funnel was charged with a mixture of *S*(−)-α-methylbenzylamine (20 ml, 0.158 mol), chloroform (15 ml, 0.188 mol) and benzyltriethylammonium chloride (0.4 g, 1.75 mmol) in dichloromethane (30 ml). The mixture was added dropwise to the stirred, warm solution (at ca. 45 °C) over a 30-min period. The reaction mixture began to reflux slowly 10 min after initiation of the addition and subsided within 2 h; stirring was continued for an additional hour. The reaction mixture was diluted with ice and deionized water (1:1, 150 ml), and the organic layer (pale yellow) was separated and retained. The colourless aqueous layer was extracted with dichloromethane (2 × 30 ml), and the combined extracts were successively washed with deionized water (20 ml), aqueous sodium chloride solution (5% w/w, 20 ml), and dried over excess anhydrous magnesium sulphate for 1 h.

The drying agent was removed by filtration, washed with dry dichloromethane (10 ml), and the pale yellow combined filtrate and washings were distilled at ca. 65 °C using a Vigreux column (1.5 cm × 10 cm) to remove the solvent (dichloromethane).

The remaining yellow solution was placed under nitrogen, and distilled under reduced pressure to remove final traces of dichloromethane, unreacted chloroform (at 25 °C, 13 mmHg), and any excess *S*(−)-α-methylbenzylamine (34–39 °C, 3 mmHg). Finally, the fraction which distilled at 29–30 °C (0.01 mmHg) was collected as a colourless oil. Yield 11.0 ml (50%).

IR (neat): ν_{max} 2140vs cm^{-1} (CN). ^{1}H NMR ($CDCl_3$): δ 7.29–7.42 (m, 5H, Ph), 4.81 (q{1:1:1}t, 1H, ^{3}J(HH) 7 Hz and ^{2}J(NH) 2 Hz, C*H*MeN), 1.67 (d{1:1:1}t, 3H, ^{3}J(HH) 7 Hz and ^{3}J(NH) 2 Hz, CH*Me*N) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.6 (t, *J*(CN) 4.5 Hz, *C*N), 138.6 (s, C_{ipso}, Ph), 128.9 (s, C_{ortho}, Ph), 128.3 (s, C_{para}, Ph), 125.4 (s, C_{meta}, Ph), 53.8 ({1:1:1}t, ^{1}J(NC) 6 Hz, N*C*HPh), 25.1 (s, CH*Me*). Optical rotation $[\alpha]_{589}$ −30.5° (21°C, neat *d* 0.97 g cm^{-1}).

{Lit. [31] IR: ν_{max} 2141 (CN), 759, 698 cm^{-1}; ^{1}H NMR: δ 7.20 (m, 5H, Ph), 4.70 (m, 1H, C*H*MeN), 1.60 (d, 3H, CH*Me*N) ppm. ^{13}C{^{1}H} NMR (proton coupled): δ 157.0 (t, *J*(CN) 4.3 Hz, *C*N), 53.8 (dt, N*C*HPh), 25.0 (q, CH*Me*) ppm. Lit. [32,33] IR: ν_{max} 3000, 2950, 2160 (CN), 1600, 1500, 770, 700 cm^{-1}; ^{1}H NMR (CCl_4): δ 7.35 (s, 5H, Ph), 4.83 (q{1:1:1}t, 1H, ^{3}J(HH) 7 Hz and ^{2}J(NH) 2 Hz, C*H*MeN, 1.68 (d{1:1:1}t, 3H, ^{3}J(HH) 7 Hz and ^{3}J(NH) 2 Hz, CH*Me*N; Optical rotation [33,34] $[\alpha]_{589}$ −30° (20 °C, neat)}.

*5.2.1. [(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2Cy)]PF_6 (**2**)*

A Schlenk tube was charged with a solution of **1** (1.00 g, 1.83 mmol) in dichloromethane (40 ml), thallium hexafluorophosphate (1.60 g, 4.58 mmol), and a magnetic stirrer bar. The orange solution was stirred in the dark under nitrogen at room temperature for 1 h to give a tomato-orange suspension. Excess cyclohexylamine (2 ml, 17.48 mmol) was added and the solution was stirred in the dark at room temperature overnight. Filtration, evaporation of the filtrate under reduced pressure, and crystallization of the yellow residue from dichloromethane and diethylether (1:3, 40 ml) at −30 °C for 2 days afforded bright yellow crystals of **2**. Yield 1.34 g (97%). (Calc. for $C_{34}H_{42}F_6N_2P_2Ru \cdot CH_2Cl_2$: C, 50.00; H, 5.28; N, 3.33. Found: C, 49.93; H, 5.33; N, 3.30%). IR (Nujol): ν_{max} 3311w, 3270w, 1587vw (NH), 2121m (CN), and 842s cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2): δ 7.2–7.5 (m, 15H, PPh_3), 4.74 (s, 5H, C_5H_5), 3.20 (br.t, 1H, $^{2,3}J$(HH) 11 Hz, NH), 1.99 (br.d, 1H, ^2J(HH) 12 Hz, NH), 0.7–1.90 (m, 11H, Cy), 1.25 (s, 9H, C*Me*$_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.20 (d, C_{ipso}, PPh_3), 133.77 (d, ^2J(PC) 11 Hz, C_{ortho}), 131.05 (s, C_{para}), 129.14 (d, ^3J(PC) 10 Hz, C_{meta}), 81.94 (s, C_5H_5), 59.29 (s, C_1, Cy), 58.00 (s, *C*Me$_3$), 35.82 (s, C_2, Cy), 33.13 (s, C_3, Cy), 30.73 (s, C*Me*$_3$), 25.49 (s, C_4 and C_5, Cy), 25.29 (s, C_6, Cy) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 59.91 (s, PPh_3), −145.40 (septet, ^1J(PF) 712 Hz, PF_6) ppm. MS (FAB): 611 $[M - PF_6]^+$(50%), 512(100), 429(41).

*5.2.2. ($S_{Ru}R_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMePh$)]PF_6 (**3SR**)*

A solution of **1** (0.23 g, 0.42 mmol) in dichloromethane (30 ml) was treated with thallium hexafluorophosphate (0.42 g, 1.20 mmol) and excess *R*(+)-α-methylbenzylamine (0.8 ml, 6.21 mmol). This yellow-orange solution was stirred in the dark at room temperature for 24 h. After filtration and solvent removal from the filtrate under reduced pressure, fine yellow crystals were obtained by crystallizing the residue at −30 °C from dichloromethane and diethylether (1:3, 20 ml) overnight. Yield 0.19 g (58%) 80% d.e. (Calc. for $C_{36}H_{40}F_6N_2P_2Ru.CH_2Cl_2$: C, 51.51; H, 4.91; N, 3.25. Found: C, 50.93; H, 4.82; N, 3.39%.) IR (Nujol): ν_{max} 3307w, 3264w, 1580vw (NH), 2115m (CN), 1712w (Ph overtone), and 840s cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2): δ 7.25–7.51 (m, 15H, PPh_3), 7.21–7.25 (m, 5H, Ph), 4.30 (s, 5H, C_5H_5), 3.71 (br.t, 1H, $^{2,3}J$(HH) 11 Hz, NH), 3.35 (m, 1H, NC*H*Me), 1.88 (br.d, 1H, ^2J(HH) 11 Hz, NH), 1.30 (s, 9H, C*Me*$_3$), 1.11 (d, 3H, ^3J(HH) 7 Hz, Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.09 (d, C_{ipso}, PPh_3), 133.78 (d, ^2J(PC) 11 Hz, C_{ortho}), 131.11 (s, C_{para}), 129.26 (d, ^3J(PC) 10 Hz, C_{meta}), 128.86 (s, C_{para}, Ph), 127.42 (s, C_{meta}, Ph), 81.71 (s, C_5H_5), 61.76 (s, N*C*HPh), 30.82 (s, C*Me*$_3$), 25.34 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 60.04 (s, PPh_3), −145.30 (septet, ^1J(PF) 712 Hz, PF_6) ppm. MS (FAB): 633 $[M - PF_6]^+$(21%), 512(100), 429(54).

*5.2.3. ($R_{Ru}R_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMePh$)]PF_6 (**3RR**)*

The mother-liquor from the crystallization procedure above was reduced in volume (to ca. 10 ml) under reduced pressure, and was left to crystallize out at −80 °C for 2 days, producing yellow crystals which were isolated by filtration. Yield 0.07 g (21%) 98% d.e.

IR (Nujol): ν_{max} 3325w, 3284w, 1591w (NH), 2126s (CN), 1712w (Ph overtone) and 840s cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2): δ 7.23–7.45 (m, 15H, P*Ph*$_3$), 6.96–6.98 (m, 5H, Ph), 4.72 (s, 5H, C_5H_5), 3.49 (br.t, 1H, $^{2,3}J$(HH) 10 Hz, NH), 3.35 (m, 1H, NC*H*Me), 2.12 (br.d, 1H, ^2J(HH) 10 Hz, NH), 1.29 (d, 3H, ^3J(HH) 7 Hz, Me), 1.25 (s, 9H, C*Me*$_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.11 (d, C_{ipso}, PPh_3), 133.63 (d, ^2J(PC) 11 Hz, C_{ortho}), 130.98 (s, C_{para}), 129.17 (d, ^3J(PC) 8 Hz, C_{meta}), 128.23 (s, C_{para}, Ph), 126.21 (s, C_{meta}, Ph), 81.81 (s, C_5H_5), 61.65 (s, N*C*HPh), 30.65 (s, C*Me*$_3$), 22.63 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 59.08 (s, PPh_3) ppm.

*5.2.4. ($R_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMePh$)]PF_6 (**3RS**)*

To a solution of **1** (0.16 g, 0.29 mmol) in dichloromethane (30 ml) was added thallium hexafluorophosphate (0.4 g, 1.15 mmol) and excess *S*(−)-α-methylbenzylamine (0.8 ml, 6.21 mmol). This yellow/orange solution was stirred overnight in the dark, at room temperature. After solvent removal under reduced pressure, fine yellow crystals were obtained by crystallising the residue at −80 °C from dichloromethane and diethylether (1:3, 20 ml) overnight. Yield 0.13 g (57%) 74% d.e.

*5.2.5. ($S_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMePh$)]PF_6 (**3SS**)*

The mother-liquor from above was concentrated to low volume (to ca. 10 ml) under reduced pressure, and was left to crystallize out in the dark at −30 °C for 7 h, from which yellow crystals were isolated. Yield 0.05 g (22%) 98% d.e.

*5.2.6. ($S_{Ru}R_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMeCy$)]PF_6 (**4SR**)*

To a solution of **1** (0.21 g, 0.384 mmol) in dichloromethane (30 ml) was added thallium (I) hexafluorophosphate (0.40 g, 1.15 mmol) and excess *R*(−)-1-cyclohexylethylamine (1.0 ml, 6.81 mmol). This orange solution was stirred at room temperature in the dark under nitrogen for 67 h. After solvent removal under reduced pressure, fine yellow crystals were obtained by crystallising the yellow residue at −30 °C from dichloromethane and diethylether (1:3, 40 ml) overnight. Yield 0.13 g (43%) 61% d.e. (Calc. for $C_{36}H_{46}F_6N_2P_2Ru \cdot CH_2Cl_2$: C, 51.16; H, 5.57; N, 3.22. Found: C, 52.98; H, 5.57; N, 3.45%.) IR (Nujol): ν_{max} 3312m, 3275w, 1584w (NH), 2116s (CN), 1721br.w (Ph overtone) and 843vs cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2): δ 7.28–7.50 (m, 15H, PPh_3), 4.744 (s, 5H, C_5H_5), 3.15 (br.dd, 1H, $^{2,3}J$(HH) 12, 6 Hz, NH), 2.09 (qd, 1H, $^{3,3}J$(HH) 6, 4 Hz, NC*H*Me), 1.24 (s, 9H, C*Me*$_3$), 0.70 (d, 3H, ^3J(HH)

7 Hz, Me), 0.7–0.98, 1.05–1.45 and 1.65–1.74 (m, 11H, $^{2,3,3}J$(HH) 12, 12, 4 Hz, Cy) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 133.77 (d, ^1J(PC) 44 Hz, C_{ipso}, P*Ph*$_3$), 133.71 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), 131.10 (s, C_{para}, PPh_3), 129.24 (d, ^3J(PC) 9 Hz, C_{meta}, PPh_3), 81.88 (s, C_5H_5), 60.99 (s, N*C*HCy), 42.59 (s, C_1, Cy), 30.66 (s, C*Me*$_3$), 26.84 (s, C_2, Cy), 26.71 (s, C_3, Cy), 26.34 (s, C_4 and C_5, Cy), 25.49 (s, C_6, Cy), 17.02 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 59.57 (s, PPh_3) ppm. MS (FAB): 639 $[M - PF_6]^+$(20%), 512(100), 429(31).

5.2.7. ($R_{Ru}R_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMeCy$)]PF_6 (**4RR**)

The mother-liquor from above was concentrated to low volume (ca. 10 ml) under reduced pressure, and was then left to crystallize out in the dark at −30 °C overnight, from which yellow crystals were isolated. Yield 0.11 g (37%) 79% d.e.

IR (Nujol): ν_{max} 3315w, 3274w, 1585w (NH), 2121m (CN), 1725br.w (Ph overtone) and 843s cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2): δ 7.28–7.51 (m, 15H, PPh_3), 4.745 (s, 5H, C_5H_5), 2.95 (br.t, 1H, $^{2,3}J$(HH) 11 Hz, NH), 2.00 (m, 1H, NC*H*Me), 1.26 (s, 9H, C*Me*$_3$), 0.99 (d, 3H, ^3J(HH) 7 Hz, Me), 0.52–0.70, 1.0–1.3 and 1.60–1.83 (m, 11H, $^{2,3,3}J$(HH) 11, 11, 4 Hz, Cy) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.02 (d, ^1J(PC) 44 Hz, C_{ipso}, PPh_3), 133.83 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), 131.12 (s, C_{para}, PPh_3), 129.22 (d, ^3J(PC) 10 Hz, C_{meta}, PPh_3), 81.95 (s, C_5H_5), 61.35 (s, N*C*HCy), 45.22 (s, C_1, Cy), 30.74 (s, C*Me*$_3$), 29.61 (s, C_2, Cy), 27.04 (s, C_3, Cy), 26.50 (s, C_4 and C_5, Cy), 25.91 (s, C_6, Cy), 16.24 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 59.68 (s, PPh_3) ppm.

5.2.8. ($R_{Ru}S_C$,$S_{Ru}R_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMe\{1\text{-}C_{10}H_7\}$)]$PF_6$ (**5RS,5SR**)

An orange solution of **1** (0.20 g, 0.366 mmol) and thallium (I) hexafluorophosphate (0.40 g, 1.15 mmol) in dichloromethane (30 ml) was stirred for 90 min to give a tomato-orange solution. Excess (±)-1-(1-naphthyl)ethylamine (1.0 ml, 6.21 mmol) was added. The mixture was stirred at room temperature in the dark under nitrogen for 52 h to give a bright yellow solution. After solvent removal under reduced pressure, the yellow treacly solid was washed with diethylether (2 × 15 ml). Extraction with dichloromethane (2 × 15 ml), filtration, and concentration under reduced pressure (ca. 10 ml) gave a yellow solution. Addition of diethylether (30 ml) afforded fine yellow crystals on storing at −30 °C under nitrogen overnight. Yield 0.05 g (17%) 73% d.e.

IR (Nujol): ν_{max} 3303w, 3271vw, 1587vw (NH), 2108m (CN) and 843vs cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2): δ 7.93–7.97 (m, 2H, Np), 7.88 (d, 1H, ^3J(HH) 8 Hz, Np), 7.24–7.63 (m, 19H, Np and PPh_3), 4.35 (m, 1H, NC*H*Me), 4.23 (s, 5H, C_5H_5), 3.68 (br.t, 1H, $^{2,3}J$(HH) 11 Hz, NH), 2.15 (br.d, 1H, ^2J(HH) 11 Hz, NH), 1.29 (d, 3H, ^3J(HH) 7 Hz, Me), 1.23 (s, 9H, C*Me*$_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 138.97 (s, C_{ipso}, Np), 134.18 and 130.82 (s, 2× $C_{bridging}$, Np), 133.66 (d, ^1J(PC) 45 Hz, C_{ipso}, PPh_3), 133.71 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), 131.19 (s, C_{para}, PPh_3), 129.67, 128.96, 126.81, 126.34, 126.09, 123.19, and 122.57 (s, 7× C_{aryl}, Np), 129.32 (d, ^3J(PC) 10 Hz, C_{meta}, PPh_3), 81.50 (s, C_5H_5), 58.34 (s, N*C*HNp), 30.68 (s, C*Me*$_3$), 25.53 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 59.46 (s, PPh_3) ppm.

5.2.9. ($R_{Ru}R_C$,$S_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMe\{1\text{-}C_{10}H_7\}$)]$PF_6$ (**5RR,5SS**)

The mother-liquor from above was reduced in volume (ca. 10 ml) under reduced pressure, and was then left to crystallize out in the dark at −30 °C for 46 h, from which yellow crystals were isolated. Yield 0.07 g (23%) 56% d.e. of the least soluble (**5RS,5SR**). (Calc. for $C_{40}H_{42}F_6N_2P_2Ru \cdot 0.5CH_2Cl_2$: C, 55.90; H, 4.98; N, 3.22. Found: C, 56.29; H, 4.75; N, 3.40%.) IR (Nujol): ν_{max} 3314w, 3257w, 1587w (NH), 2108m (CN) and 841s cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2): δ 7.70 (m, 2H, Np), 7.20–7.59 (m, 19H, Np and PPh_3), 7.40 (t, 1H, ^3J(HH) 7 Hz, Np), 4.35 (m, 1H, NC*H*Me), 4.77 (s, 5H, C_5H_5), 3.84 (br.t, 1H, $^{2,3}J$(HH) 11 Hz, NH), 3.05 (br.d, 1H, ^2J(HH) 11 Hz, NH), 1.42 (d, 3H, ^3J(HH) 7 Hz, Me), 1.21 (s, 9H, C*Me*$_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ ~133.58 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), ~133.37 (d, ^1J(PC) 45 Hz, C_{ipso}, PPh_3), ~129.13 (d, ^3J(PC) 10 Hz, C_{meta}, PPh_3), 128.30, 126.65, 126.25, 122.25, and 121.90 (s, C_{aryl}, Np), 81.81 (s, C_5H_5), 56.93 (s, N*C*HNp), 30.78 (s, C*Me*$_3$), 22.95 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 59.57 (s, PPh_3) ppm. MS (FAB): 682 $[M - PF_6]^+$(34%), 511(100), 428(44).

5.2.10. ($R_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CO)-($NH_2CHMePh$)]PF_6 (**7RS**)

To a yellow-brown solution of **6** (0.50 g, 1.02 mmol) in dichloromethane (30 ml) was added thallium hexafluorophosphate (0.81 g, 2.33 mmol) and *S*(−)-α-methylbenzylamine (1 ml, 7.76 mmol). The brown mixture was stirred under nitrogen at 45–50 °C for 17.5 h (overnight) to give a cream brown suspension. Filtration, washing the off-white residue with dichloromethane (3 × 5 ml) gave a brown filtrate. After solvent removal under reduced pressure, the brown residue was extracted with diethylether (5 × 10 ml) and filtered to give a yellow solution. This was placed onto an alumina column (2 × 15 cm), the excess amine was eluted with light petroleum ether (60 ml) and the pale yellow product band was eluted with dichloromethane (60 ml) to give a pale yellow solution. After solvent removal under reduced pressure, a mustard yellow powder was obtained by crystallising the residual oil from diethylether (10 ml) at −80 °C for 54 h. Yield 0.04 g (5%) 42% d.e. (Calc. for $C_{32}H_{31}F_6NOP_2Ru$: C, 53.19; H, 4.32; N, 1.94. Found: C, 53.30; H, 4.60; N, 1.75%.) IR (Nujol): ν_{max} 3306w, 3267w, 1587vw (NH), 1950sh.w, 1941m (CO) and 843s cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2/$CDCl_3$): δ 7.55–7.60 and 7.34–7.40 (m, 15H, PPh_3), 7.26 (m, 5H, Ph), 4.57 (s, 5H, C_5H_5), 4.26 (br.t, 1H, $^{2,3}J$(HH) 11 Hz, NH), 3.26 (br.sextet {br.m}, 1H,

^3J(HH) 7 Hz, NC*H*Me), 1.95 (br.d, 1H, ^2J(HH) 11 Hz, NH), 1.09 (d, 3H, ^3J(HH) 7 Hz, CH*Me*) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2/CDCl_3$): δ 203.92 (d, ^2J(PC) 19 Hz, CO), 134.34 (d, C_{ipso}, PPh_3), 133.95 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), 132.11 (s, C_{para}, P*Ph*$_3$), 129.92 (d, ^3J(PC) 10 Hz, C_{meta}, PPh_3), 129.54 (s, C_{ortho}, Ph), 129.12 (s, C_{para}, Ph), 128.12 (s, C_{meta}, Ph), 86.39 (s, C_5H_5), 64.19 (s, N*C*HPh), 25.59 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2/CDCl_3$): δ 55.58 (s, PPh_3) ppm. MS (FAB): 578 $[M - PF_6]^+$(37%), 457(63), 429(100).

5.2.11. ($S_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMePh$)]PF_6 (**7SS**)

The partial data was obtained from the spectra obtained from the sample of (**7RS**) above.

^1H NMR ($CD_2Cl_2/CDCl_3$): δ 7.40–7.52 and 7.27–7.34 (m, 15H, P*Ph*$_3$), 6.95 (m, 5H, Ph), 5.13 (s, 5H, C_5H_5), 1.39 (d, 3H, ^3J(HH) 7 Hz, CH*Me*) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2/CDCl_3$): δ 142.67 (s, C_{ipso}, PPh_3), 133.85 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), 131.56 (s, C_{para}, PPh_3), 129.38 (d, ^3J(PC) 10 Hz, C_{meta}, PPh_3), 127.03 (s, C_{meta}, Ph), 86.71 (s, C_5H_5), 64.06 (s, N*C*HPh), 23.17 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2/CDCl_3$): δ 54.25 (s, PPh_3) ppm.

5.2.12. [(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)($NHEt_2$)]PF_6 (**9**)

A Schlenk tube was charged with a solution of **1** (0.20 g, 0.37 mmol) in dichloromethane (30 ml), thallium hexafluorophosphate (0.19 g, 0.54 mmol), and a magnetic stirrer bar. The orange solution was stirred in the dark under nitrogen at room temperature for 1 h to give a tomato-orange suspension. Excess diethylamine (0.4 ml, 3.87 mmol) was added and the solution was stirred in the dark at room temperature overnight. Filtration, evaporation of the filtrate under reduced pressure, and crystallization of the yellow residue from dichloromethane and diethylether (1:3, 20 ml) at −30 °C afforded orange-yellow crystals of **9**. Yield 0.16 g (60%).

IR (Nujol): ν_{max} 3269w, 1613vw (NH), 2129m, 2062sh.w (CN), and 841s cm^{-1} (PF_6). ^1H NMR (CD_2Cl_2): δ 7.26–7.49 (m, 15H, PPh_3), 4.78 (s, 5H, C_5H_5), 2.78 (m, 2H, $^{2,3}J$(HH) 7 Hz, CH_2CH_3), 2.67 (m, 2H, $^{2,3}J$(HH) 7 Hz, CH_2CH_3), 1.68 (br.s, 1H, NH), 1.20 (s, 9H, C*Me*$_3$), 1.08 (t, 3H, $^{2,3}J$(HH) 7 Hz, CH_2CH_3), 0.44 (t, 3H, $^{2,3}J$(HH) 7 Hz, CH_2 CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 133.88 (d, C_{ipso}, PPh_3), 133.37 (d, ^2J(PC) 11 Hz, C_{ortho}), 131.32 (s, C_{para}), 129.52 (d, ^3J(PC) 10 Hz, C_{meta}), 82.08 (s, C_5H_5), 58.45 (s, *C*Me$_3$), 56.13, 51.54 (2s, CH_2), 30.45 (s, C*Me*$_3$), 14.67, 14.08 (2s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.3 (s, PPh_3), −145.40 (septet, ^1J(*P*F) 712 Hz, PF_6) ppm. MS (FAB): 585 $[M - PF_6]^+$(15%), 512(100), 454(9), 429(37).

5.2.13. [(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)(NH(*Me*)-*CHMePh*)]PF_6 (**10**)

A solution of **1** (0.20 g, 0.37 mmol) in dichloromethane (30 ml) was treated with thallium hexafluorophosphate (0.20 g, 0.57 mmol) and excess *S*(−)-*N*-methyl-1-phenylethylamine (0.25 ml, 1.72 mmol). This yellow-orange solution was stirred in the dark at room temperature for 24 h. After filtration and solvent removal from the filtrate under reduced pressure, fine yellow crystals were obtained by crystallizing the residue at −30 °C from dichloromethane and diethylether (1:3, 15 ml) overnight. Yield 0.18 g (62%). IR (Nujol): ν_{max} 3263w, 1585vw (NH), 2122s (CN), and 841br.s cm^{-1} (PF_6). MS (FAB): 647 $[M - PF_6]^+$(11%), 511(100), 454(11), 429(38).

The ^1H NMR spectrum of the crystals revealed four diastereomers were present; integration of the cyclopentadienyl ligand singlets produced a ratio of 5:20:2:25 for **SSS**:**SRS**:**RRS**:**RSS**. Concentration of the mother-liquor above to ca. 7 ml and cooling to −25 °C gave yellow crystals, yield 0.05 g. (17%), whose spectrum showed the diastereomer ratio to be 5:12:2:4.

10RSS: ^1H NMR (CD_2Cl_2): δ 7.33–7.54 (m, 15H, PPh_3), 7.05 (m, 5H, Ph), 4.64 (s, 5H, C_5H_5), 3.63 (quintet, 1H, ^3J(HH) 7 Hz, NHC*H*), 2.29 (d, 3H, ^3J(HH) 6 Hz, NHCH_3), 2.05 (br.q, 1H, ^3J(HH) 6 Hz, NH), 1.34 (d, 3H, ^3J(HH) 6 Hz, CHCH_3), 1.25 (s, 9H, Bu) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 139.68 (s, C_{ipso}, Ph), 133.40 (d, J(PC) 44 Hz, C_{ipso}, PPh_3), 133.39 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), 131.39 (s, C_{para}, PPh_3), 129.61 (d, ^3J(PC) 10 Hz, C_{meta}, PPh_3), 129.08 (s, C_{ortho}, Ph), 128.97 (s, C_{para}, Ph), 127.85 (s, C_{meta}, Ph), 82.18 (s, C_5H_5), 68.08 (s, N*C*HPh), 58.57 (s, *C*Me$_3$), 45.70 (s, NHCH_3), 30.48 (s, C*Me*$_3$), 23.99 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.3 (s, PPh_3) ppm.

10SRS: ^1H NMR (CD_2Cl_2): δ 7.32–7.51 (m, 15H, PPh_3), 6.80 (m, 5H, Ph), 4.81 (s, 5H, C_5H_5), 3.88 (qd, 1H, ^3J(HH) 7 Hz, ^4J(PH) 1.8 Hz, NHC*H*), 2.51 (br.s, 1H, N*H*CH$_3$), 2.23 (d, 3H, ^3J(HH) 6 Hz, NHCH_3), 1.55 (d, 3H, ^3J(HH) 7 Hz, CHCH_3), 1.30 (s, 9H, Bu) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 139.41 (s, C_{ipso}, Ph), 133.52 (d, J(PC) 44 Hz, C_{ipso}, PPh_3), 133.56 (d, ^2J(PC) 10 Hz, C_{ortho}, PPh_3), 131.39 (s, C_{para}, PPh_3), 129.62 (d, ^3J(PC) 9 Hz, C_{meta}, PPh_3), 129.64 (s, C_{ortho}, Ph), 127.82 (s, C_{para} + C_{meta}, Ph), 82.44 (s, C_5H_5), 65.73 (s, N*C*HPh), 58.62 (s, *C*Me$_3$), 41.35 (s, NHCH_3), 30.75 (s, C*Me*$_3$), 24.80 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.1 (s, PPh_3) ppm.

10SSS: ^1H NMR (CD_2Cl_2): δ 6.15 (m, 5H, Ph), 4.83 (s, 5H, C_5H_5), 3.78 (q, 1H, ^3J(HH) 7 Hz, NHC*H*), 2.51 (br.s, 1H, N*H*CH$_3$), 2.46 (d, 3H, ^3J(HH) 6 Hz, NHCH_3), 1.85 (br.s, 1H, *NH*CH$_3$), 1.50 (d, 3H, ^3J(HH) 7 Hz, CHCH_3), 1.26 (s, 9H, Bu) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 82.30 (s, C_5H_5), 60.79 (s, *C*Me$_3$), 47.18 (s, NHCH_3), 30.64 (s, C*Me*$_3$), 14.75 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 55.7 (s, PPh_3) ppm.

10RRS: ^1H NMR (CD_2Cl_2): δ 6.65 (m, 5H, Ph), 4.74 (s, 5H, C_5H_5), 3.73 (qd, 1H, ^3J(HH) 7 Hz, ^4J(PH) 1.8 Hz, NHC*H*), 2.53 (d, 3H, ^3J(HH) 6 Hz, NHCH_3), 1.40 (d, 3H, ^3J(HH) 7 Hz, CHCH_3), 1.18 (s, 9H, Bu) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 81.65 (s, C_5H_5), 41.05 (s, NHCH_3), 30.36 (s, C*Me*$_3$), 20.80 (s, CH*Me*) ppm.

*5.2.14. ($R_{Ru}S_C$,$R_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)-(CNCHMePh)Cl] (**11RS,11SS**)*

A suspension of **1** (0.70 g, 0.964 mmol) and excess (*S*)-α-methylbenzylisonitrile (0.5 ml, 3.58 mmol) in toluene (30 ml) was stirred and heated under reflux at 100 °C under nitrogen for 24 h. The cooled orange solution was reduced in volume (to ca. 10 ml) under reduced pressure and put onto an alumina column (1.5 × 20 cm.). PPh_3 was eluted with toluene (20 ml) and the orange product band eluted with dichloromethane (30 ml) and ultimately acetone (10 ml) to give an orange solution. Solvent removal under reduced pressure gave a frothy orange solid. Wash with petroleum ether (b.p. 40–60 °C, 2 × 10 ml) followed by drying under reduced pressure afforded a bright orange powder. Yield 0.26 g (45%) [**11SS**:**11RS** 49:51].

Recrystallization of a small sample (0.15 g) from toluene and hexane (1:3, 20 ml) at −30 °C for 16 h afforded an oily orange solid after filtration and solvent removal under reduced pressure. Yield 0.02 g [**11SS**:**11RS** 65:35].

IR (Nujol): ν_{max} 2104, 2102s cm^{-1} (CN). MS (FAB): 595 $[M]^+$(38%), 560(85), 429(93).

11SS: ^{1}H NMR ($CDCl_3$): δ 7.41–7.54 and 7.22–7.33 (m, 15H, PPh_3), 7.10–7.13 and 7.03–7.06 (m, 5H, Ph), 4.87 (q, 1H, ^3J(HH) 7 Hz, C*H*Me), 4.55 (s, 5H, C_5H_5), 1.39 (d, 3H, ^3J(HH) 7 Hz, CH*Me*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.65 (d, ^1J(PC) 44 Hz, C_{ipso}, P*Ph*$_3$), 133.71 (d, ^2J(PC) 11 Hz, C_{ortho}, P*Ph*$_3$), 129.41 (s, C_{para}, PPh_3), 128.65 (s, C_{para}, Ph), 127.82 (d, ^3J(PC) 11 Hz, C_{meta}, PPh_3), 125.37 (s, C_{meta}, Ph), 81.66 (s, C_5H_5), 56.20 (s, N*C*HPh), 25.01 (s, CH*Me*) ppm.

11RS: ^{1}H NMR ($CDCl_3$): δ 7.41–7.54 and 7.22–7.33 (m, 15H, P*Ph*$_3$), 7.10–7.13 and 7.03–7.06 (m, 5H, Ph), 4.70 (q, 1H, ^3J(HH) 7 Hz, C*H*Me), 4.53 (s, 5H, C_5H_5), 1.29 (d, 3H, ^3J(HH) 7 Hz, CH*Me*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.47 (d, ^1J(PC) 44 Hz, C_{ipso}, PPh_3), 133.71 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), 129.41 (s, C_{para}, PPh_3), 128.65 (s, C_{para}, Ph), 127.82 (d, ^3J(PC) 11 Hz, C_{meta}, PPh_3), 125.37 (s, C_{meta}, Ph), 81.66 (s, C_5H_5), 56.09 (s, N*C*HPh), 25.01 (s, CH*Me*) ppm.

*5.2.15. ($R_{Ru}S_C$,$R_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)-(CNCHMePh)(NH_3)]PF_6 (**12RS,12SS**)*

A mixture of (**11RS**,**11SS**) (0.21 g, 0.353 mmol), ammonium hexafluorophosphate (0.25 g, 1.54 mmol), and thallium (I) carbonate (0.50 g, 1.07 mmol) in methanol (40 ml) was stirred at 60 °C for 22 h. Removal of the solvent under reduced pressure and crystallization of the residue from dichloromethane–diethylether (1:3, 40 ml) at −30 °C afforded yellow crystals of (**12RS**,**12SS**). Total yield 0.12 g (47%) [racemate]. (Calc for $C_{32}H_{32}F_6N_2P_2Ru \cdot 3CH_2Cl_2$: C, 43.06; H, 3.92; N, 2.87. Found: C, 43.56; H, 3.63; N, 3.13%.) IR (Nujol): ν_{max} 3370m, 3296w, 1622w (NH), 2119br.s (CN) and 838br.vs cm^{-1} (PF_6). ^{1}H NMR ($(CD_3)_2CO$): δ 7.36–7.58 (m, 30H, P*Ph*$_3$), 7.25–7.36 and 7.11–7.14 (m, 10H, Ph), 5.21 (q, 1H, ^3J(HH) 7 Hz, C*H*Me) and 5.19 (q, 1H, ^3J(HH) 7 Hz, C*H*Me), 4.88 (s, 10H, C_5H_5), 2.60 (br, 6H, NH_3), 1.52 (d, 3H, ^3J(HH) 7 Hz, CH*Me*), 1.43 (d, 3H, ^3J(HH) 7 Hz, CH*Me*) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 135.41 (d, ^1J(PC) 45 Hz, C_{ipso}, PPh_3), 134.29 (d, ^2J(PC) 11 Hz, C_{ortho}, PPh_3), 131.29 (s, C_{para}, PPh_3), 129.58 (d, ^3J(PC) 10 Hz, C_{meta}, PPh_3), 128.88 (s, C_{ortho}, PPh_3), 126.48 (s, C_{para}, Ph), 126.36 (s, C_{meta}, Ph), 82.52 (s, C_5H_5), 57.38 (s, N*C*HPh), 25.22 (s, CH*Me*), 25.09 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.47 (s, PPh_3) and 58.17 (s, PPh_3) ppm. MS (FAB): 577 $[M - PF_6]^+$(24%), 560(100), 429(53).

5.3. Decomplexation of amine ligands

*5.3.1. [(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)(NH_2Cy)]PF_6 (**2**)*

Method A. Complex **2** (0.10 g, 0.13 mmol), trimethylamine *N*-oxide dehydrate (0.05 g, 0.45 mmol), and sodium iodide (0.08 g, 0.53 mmol) were placed in a Fischer–Porter bottle and suspended in methanol (30 ml). After heating and stirring at 85 °C for 48 h the solvent was removed under reduced pressure. Extraction with dichloromethane (30 ml) gave an orange-red solution which was washed with water (3 × 10 ml). The dichloromethane layer was dried with anhydrous magnesium sulphate, filtered and the solvent removed. The orange foam (0.09 g) was identified as a mixture (70:30) of **8** and unreacted **2** by ^{1}H NMR and infrared spectroscopies.

Method B. A Fischer–Porter bottle was charged with **2** (0.20 g, 0.27 mmol), iodomethane (2 ml, 32 mmol), and 1,2-dichloroethane (30 ml). Heating and stirring for 22 h at 120 °C gave a dark red solution. Cooling, removal of solvent, and washing the residue with petroleum ether (2 × 5 ml) then water (3 × 5 ml) gave a red solid which was dried under reduced pressure and identified as **8** (0.16 g, 95%) by ^{1}H NMR and infrared spectroscopies.

Method C. A stirred solution of **2** (0.10 g, 0.13 mmol) and iodine (0.10 g, 0.39 mmol) in dichloromethane was photolyzed for 24 h at room temperature. The product solution was washed with sodium thiosulfate solution (10%, 3 × 20 ml), the separated organic layer was washed with water (3 × 20 ml), then dried with granular calcium chloride. Removal of the solvent under reduced pressure gave **8** (0.08 g, 95%).

*5.3.2. ($S_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMePh$)]PF_6 (**3SS**)*

A sample of **3RS** (96% d.e.) was treated under Method B above. The isolated **8** was recrystallized from dichloromethane and petroleum ether. Analysis of the ^{1}H NMR spectra obtained in the absence and presence of *R*(−)-TFAE (1.05 equiv) showed the product to be a racemic mixture of **8R** and **8S**.

*5.3.3. ($R_{Ru}S_C$)-[(η^5-C_5H_5)Ru(PPh_3)(CN^tBu)-($NH_2CHMePh$)]PF_6 (**3RS**)*

A sample of **3RS** (90% d.e.) was treated under Method B above. The isolated **8** was treated with thallium hexafluorophosphate and excess *S*(−)-*N*-methyl-1-phenylethylamine using the procedures described earlier. The crude product

before crystallization was shown by ^{1}H NMR spectroscopy to be a racemic mixture of **3RS** and **3SS**.

A sample of **3RS** (90% d.e.) was treated under Method C above. The product **8** was analyzed by the ^{1}H NMR–TFAE method and by conversion back to **3**. Both methods revealed the original sample of **8** to be racemic.

5.4. X-ray crystallography

The crystals of **2**, **3SR**, **3RR**, and **12** were grown by slow layer diffusion of diethyl ether into dichloromethane solutions. Suitable crystal specimens were mounted on a glass fibre with epoxy resin and cooled on the goniometer head by means of nitrogen gas. Precession photographs and intensity data were collected on a Siemens R3m/V diffractometer using graphite monochromatized Mo Kα X-rays. Cell dimensions were obtained from 25 to 50 centred reflections with 2θ values from 20° to 32°. Intensity data were collected using a 2θ–θ scan technique. The intensities of three reflections measured periodically showed a decrease of less than 1% over the data collection for all four datasets. An empirical absorption correction was applied using azimuthal scan data for twelve selected reflections. The structures were solved by standard heavy atom routines and refined by full-matrix least-squares methods. All non-hydrogen atoms were given anisotropic temperature factors. Hydrogen atoms were placed in the models at calculated positions and allowed to ride on their respective carbon atoms. The hexafluorophosphate anions were rotationally disordered in both **3SR** and **3RR** and were modeled by simple partial occupancy methods. Table 2 contains the collection and solution parameters for all four determinations.

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Appendix A. Supplementary data

The supplementary crystallographic data for this paper are contained in the deposition files CCDC-277650 (**2**), CCDC-277651 (**3SR**), CCDC-277652 (**3RR**), and CCDC-277653 (**12**). These data can be obtained free of charge via ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK: fax +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.01.016.

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