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Chiral ruthenium complexes with sulfur ligands; X-ray structure of $(R)_{Ru}$-Ru(NmCp)(CO)(PPh_3)SCN (NmCp = neomenthylcyclopentadienyl)

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Abstract

The reaction of Ru(NmCp)(CO)(PPh_3)I (NmCp = neomenthylcyclopenta-dienyl) with AgSCN occurs with retention of configuration at the ruthenium to give the S-bonded Ru(NmCp)(CO)(PPh_3)SCN. This was confirmed by determining the X-ray structure of $(R)_{Ru}$-Ru(NmCp)(CO)(PPh_3)SCN. The reaction of $(S)_{Ru}$-Ru(NmCp)(CO)(PPh_3)I with $AgBF_4$ in CH_2Cl_2 followed by treatment with MeSR gave the following sulfide complexes $[(RS)_{Ru}$-Ru(NmCp)(CO)(PPh_3){S(Me)R}]BF_4 (R = CH_2Ph, Ph and ^{t}Bu). NMR studies have shown that for R = CH_2Ph the chiral sulfur centre binds to the chiral ruthenium centre with a 33% d.e. and the free energy for inversion of the S-centre is 49 ± 1 kJ mol^{-1}. In contrast, with the bulky phenyl and *tert*-butyl substituents the chiral ruthenium centre shows an overwhelming preference ($\geq 99\%$) for binding to one enantiomer of the sulfide ligand. Despite this, arguments are presented to show that this ruthenium system is not a suitable chiral auxiliary for use in synthesizing chiral sulfoxides from complexed sulphides.

Keywords: Sulfide epimerisation; Thiocyanate; Ruthenium; Stereochemistry

1. Introduction

We have previously reported the synthesis and ease of separation of the diastereomers of Ru(NmCp)(CO)(P-Ph_3)I (**1**) (NmCp = neomenthylcyclopentadienyl) which contain a chiral ruthenium center [1]. Given the configurational stability of this complex we found that it is an ideal system to investigate the stereochemistry of reactions at the ruthenium center [2]. We have extended these studies to look at the complexation of sulfur ligands and report herein results relating to thiocyanate and sulfide complexes. The latter studies are pertinent to the considerable recent interest in using chiral transition metal auxiliaries to effect the asymmetric synthesis of chiral sulfoxides by oxidation of the corresponding sulfide complexes (Scheme 1). In particular, Schenk and coworkers have developed such a cycle based upon the chiral ruthenium auxiliary [RuCp{(*S*,*S*)-chiraphos}Cl] [3]; similarly, Gladysz and co-workers have used the chiral rhenium auxiliary $[ReCp(NO)(PPh_3)]^+$ [4]. This prompted us to consider how suitable our chiral [Ru(NmCp)(CO)(PPh_3)] auxiliary would be for this purpose given the importance of enantiomerically pure sulfoxides as starting materials and chiral auxiliaries in organic synthesis [5].

2. Results and discussion

$[(S)_{Ru}$-Ru(NmCp)(CO)(PPh_3)I] reacts with AgSCN in refluxing acetone to give exclusively $[(R)_{Ru}$-Ru(NmCp)(CO)(PPh_3)SCN] (**2a**) which was fully characterised including an X-ray structure determination; the corresponding (*R*)-ruthenium iodide complex gives exclusively the corresponding (*S*)-ruthenium thiocyanate complex (**2b**). As we have stressed before, the

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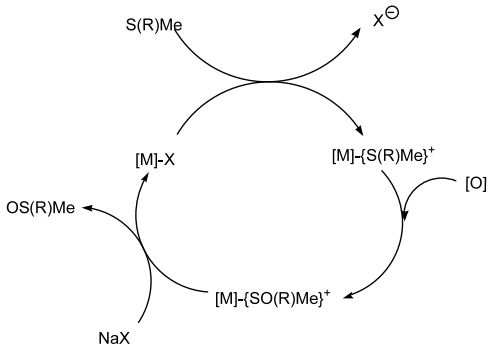


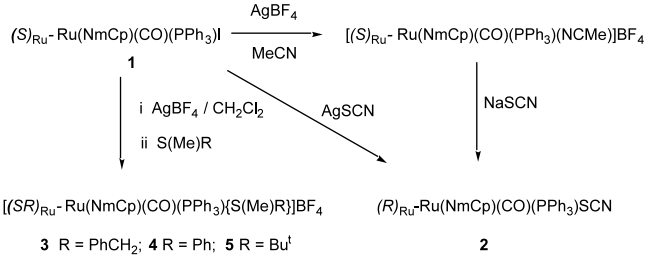
[M] = [RuCp(chiraphos)], [ReCp(NO)(PPh$_3$)] or [Ru(NmCp)(CO)(PPh$_3$)]

Scheme 1. Potential synthesis of enantiomerically pure sulfoxides.

neomenthylcyclopentadienyl ligand is an excellent 'signpost' ligand for following the stereoselectivity of such reactions [1]. Thus, using procedures detailed previously [2], we were able to follow these reactions by ^{1}H- and ^{31}P-NMR and confirmed that these reactions took place with $\geq 95\%$ stereoselectivity. The thiocyanate complex (**2**) could also be prepared indirectly from the iodide complex (**1**) via the corresponding acetonitrile complex (Scheme 2).

The thiocyanate stretch at 2107 cm^{-1} in the infrared spectrum of **2** suggested a S-bonded ligand although it has been claimed that such assignments should be applied with caution [6]. Therefore the X-ray structure was determined and, although the data are poor, it did allow us to confirm the nature of the thiocyanate bonding and to establish the absolute configuration of the product.

The X-ray structure is shown in Fig. 1 and selected bond distances and angles are tabulated in Table 1. The geometry of the ruthenium is essentially octahedral with the bond angles around ruthenium ranging from 87.8(5) to 92.5(6)°; the bond lengths of the Ru(NmCp)(CO)(PPh$_3$) fragment are similar to those observed in other structures of this type [1,2]. Obviously to minimise steric interactions the bulky triphenylphosphine ligand is almost trans to C(5), the cyclopentadienyl carbon bearing the bulky neomenthyl substituent. In keeping with the infrared spectrum the thiocyanate ligand is sulfur bonded. Surprisingly, this appears to be only the second structure determination of a thiocyanate S-bonded to ruthenium, the other being of [Ru(bpy)(CO)$_2$(SCN)$_2$] [7]. The Ru–S distance in **2a** is the exact mean of the Ru–S distances in [Ru(bpy)(CO)$_2$(SCN)$_2$] whereas the Ru–S–C bond angle of 102.9(5) in **2a** compares with a mean Ru–S–C bond angle of 105.1(4) in the bis-thiocyanate complex. It is interesting that in the closely related [RuCp(PPh$_3$)$_2$NCS] complex the thiocyanate ligand is N-bonded [8]. We note that it has been suggested that decreasing the electron density at the metal centre favours a change in the bonding from M–SCN to M–NCS [9]; this is clearly not the case here since the latter bis(triphenylphosphine) complex is more electron-rich than the carbonyl triphe-



Scheme 2.

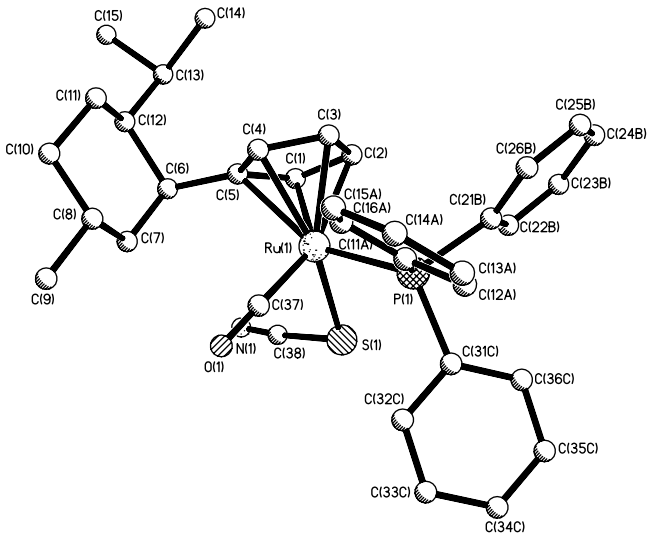


Fig. 1. Molecular structure of $(R)_{Ru}$-Ru(NmCp)(CO)(PPh$_3$)SCN.

Table 1
Selected bond lengths (Å) and bond angles (°) for $(R)_{Ru}$-Ru(NmCp)(CO)(PPh$_3$)SCN (**2a**)

[4]*Bond lengths*			
Ru(1)–C(1)	2.25(2)	Ru(1)–C(2)	2.22(2)
Ru(1)–C(3)	2.18(3)	Ru(1)–C(4)	2.18(2)
Ru(1)–C(5)	2.27(2)	(Ru1)–C(37)	1.860(13)
Ru(1)–P(1)	2.305(6)	Ru(1)–S(1)	2.430(8)
S(1)–C(38)	1.845(13)	N(1)–C(38)	1.03(2)
O(1)–C(37)	1.169(19)	C(1)–C(2)	1.34(3)
C(2)–C(3)	1.47(4)	C(3)–C(4)	1.38(3)
C(4)–C(5)	1.48(3)	C(1)–C(5)	1.42(3)
C(5)–C(6)	1.52(4)		
[4]*Bond angles*			
C(37)–Ru(1)–S(1)	92.5(4)	P(1)–Ru(1)–S(1)	89.8(2)
C(37)–Ru(1)–P(1)	87.8(4)	O(1)–C(37)–Ru(1)	168.4(17)
C(38)–S(1)–Ru(1)	102.9(5)	N(1)–C(38)–S(1)	173.0(18)
C(1)–C(2)–C(3)	107(2)	C(4)–C(3)–C(2)	110(3)
C(3)–C(4)–C(5)	105(2)	C(1)–C(5)–C(4)	107(2)
C(1)–C(5)–C(6)	122(2)	C(4)–C(5)–C(6)	131(2)
C(2)–C(1)–C(5)	111(2)	C(37)–Ru(1)–C(5)	104.2(7)
C(5)–Ru(1)–P(1)	152.8(8)	C(5)–Ru(1)–S(1)	113.5(8)
C(6)–C(5)–Ru(1)	130.7(19)	C(2)–Ru(1)–S(1)	105.4(7)

nylphosphine complex (**2a**). Obviously, steric effects are responsible, i.e. in the presence of two bulky triphenylphosphine ligands a more linear N-bonded thiocyanate is preferred over the sterically more demanding angular S-bonded thiocyanate.

In **2a** the absolute configuration of the ruthenium centre is (*R*); this complex was derived from [$(S)_{Ru}$-Ru(NmCp)(CO)(PPh_3)I indicating that the replacement of iodide by thiocyanate occurs with complete retention of configuration at the ruthenium (the change in the chiral descriptor is merely a result of a change in the ligand priority sequence i.e. in (**1**) I > NmCp > PPh_3 > CO whereas in (**2**) NmCp > SCN > PPh_3 > CO) [10]. This is consistent with the reaction taking place via a dissociative reaction, involving a configurationally stable intermediate $[Ru(NmCp)(CO)(PPh_3)]^+$ which rapidly reacts with thiocyanate. However, from our previous studies [2a], we prefer a four-centred mechanism (Scheme 3) with the added complication that silver thiocyanate is polymeric [11] and so presumably some dissociation of the polymer must precede this step.

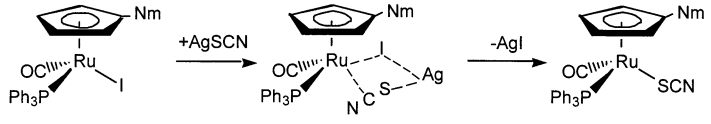
As outlined in the Introduction we were also prompted to explore the stereoselectivity of the complexation of pro-chiral sulfides by the chiral [Ru(NmCp)(CO)(PPh_3)] unit given the similar studies on related chiral systems. We initially attempted to synthesise the sulfide complexes from [$(R)_{Ru}$-Ru(NmCp)(CO)(PPh_3)(NCMe)]BF_4 since this is readily synthesised diastereomerically pure from the chiral iodide complex (**1**). Thus, [$(R)_{Ru}$-Ru(NmCp)(CO)(PPh_3)(NCMe)]BF_4 was heated under reflux in dichloromethane with an excess of benzyl methyl sulfide Unfortunately, the sulfide failed to displace the acetonitrile ligand. Therefore, we resorted to synthesising the sulfides by displacement of dichloromethane from the solvent complex [Ru(NmCp)(CO)(PPh_3)(CH_2Cl_2)]BF_4. Although this reaction proceeded readily, the dichloromethane solvent species is not very configurationally stable and therefore this led to a mixure of the ruthenium sulfide complex [Ru(NmCp)(CO)(PPh_3){S(Me)CH_2Ph}]BF_4 (**3**), which had epimerised at the ruthenium centre. Thus, the ^{31}P-NMR spectrum of the product at room temperature consisted of two peaks of equal intensity. Upon cooling to −42 °C, however, each peak split into two peaks in the ratio 2:1. These observations are consistent with the fact that for each ruthenium epimer, the chiral sulfur centre of the sulfide ligand was rapidly interconverting on the NMR time scale at room temperature, but this process could be stopped at lower temperatures. Further, at −42 °C each chiral ruthenium center shows modest stereoselectivity (i.e. d.e. 33%) in binding to one particular enantiomer of the chiral benzyl methyl sufide ligand.

The mechanism of sulphide inversion has been studied in detail and is well understood [12]. Following specific irradiation, decay of the inversion was monitored at −40 ° via the measurement of absolute peak height of all four signal. In this way the free energy of inversions were measured and found to be 49±1 kJ mol^{-1}; although this is within the range found for related systems [4,13] it is significantly greater than the 30 kJ mol^{-1} found for [RuCp(dppe)SEt_2] [14].

Different behaviour was found when a bulky sulfide i.e. MeSR (where R = Ph or ^{t}Bu) was used. The sulphide complexes [Ru(NmCp)(CO)(PPh_3){S(Me)R}]BF_4 (**4**, R = Ph; **5**, R = ^{t}Bu) were again synthesised from [Ru(NmCp)(CO)(PPh_3)(CH_2Cl_2)]BF_4 and again where found to racemic at the ruthenium centre, each compound giving rise to two peaks of equal intensity in the ^{31}P-NMR spectrum. However, in contrast to the benzyl methyl sulfide, on cooling the samples down to −71 °C two major peaks of equal intensity were observed with two other peaks ≪1% of the peak height of the major peaks. This suggests that with these bulky sulfides the chiral ruthenium centre shows an overwhelming preference for binding to one enantiomer of the sulfide ligand. This confirms the observations of Faller and Ma who noted that complexing *tert*-butyl methyl sulfide to their analogous ruthenium system $[RuCp(CO)(PPh_3)]^+$ gave 'predominantly one diastereoisomer' [15]. The major stereoisomers of [Ru(NmCp)(CO)(PPh_3){S(Me)R}]BF_4 (**4**, R = Ph; **5**, R = ^{t}Bu) each contain a neomenthylcyclopentadienyl ligand in addition to enantiomeric ruthenium and sulfur atoms so in principle it should be possible to separate them by crystallisation or chromatography but all our efforts to do so failed.

3. Conclusion

Before this ruthenium system can be developed into a useful chiral auxiliary a means of synthesising the diastereomerically pure sulfide complex has to be found. Attempts to synthesise the diastereomerically pure sulfide by changing the order of addition, (chiral ruthenium iodide complex, sulfide and then silver salt),



Scheme 3.

by using low temperatures or by the dropwise addition of the chiral ruthenium iodide complex to a mixture of the sulfide and silver salt all yielded the epimerised product. Further, although the chiral discrimination that the [Ru(NmCp)(CO)(PPh_3)] auxiliary shows towards bulky sulfides is encouraging for the asymmetric synthesis of the corresponding sulfoxides, the enantioselectivity of the sulfoxide synthesis will also depend upon the relative reactivities of the sulfide stereoisomers towards oxidation. Unfortunately, as Schenk et al. [3b] has recently shown, the oxidation of complexed sulfides in [Ru(Cp)(CO)(PPh_3)(SR^1 R^2)] not only proceeds with low diastereoselectivity but also in low yields, possibly because of concurrent oxidation of the monophosphine [3a]. Thus, although the exploratory studies reported here contribute to the general understanding of developing a chiral transition metal auxiliary, they also point to the fact that a diphosphine system such as that being investigated by Schenk is a more practical alternative to the [Ru(NmCp)(CO)(PPh_3)] auxiliary.

4. Experimental

General procedures and the synthesis of $(R)_{Ru}$- and $(S)_{Ru}$-[Ru(NmCp)(CO)(PPh_3)(NCMe)]BF_4 have been described previously [2a]. The procedure given below is an improved method of preparation of $(R)_{Ru}$- and $(S)_{Ru}$-[Ru(NmCp)(CO)(PPh_3)I] over that previously reported by us [1]. The NMR experiments were carried out on a Bruker AMX400 NMR spectrometer. The magnetisation transfer experiments were carried out and analysed as described previously [16]. The temperature was determined using a thermocouple in a 5 mm NMR tube containing CD_2Cl_2 and a Comark electronic thermometer, 5235.

4.1. Synthesis and resolution of (R,S)-[η^5-(neomenthylcyclopentadienyl]carbonyliodo-(triphenylphosphine)ruthenium (**1**)

A 250 cm^3 round-bottomed flask was charged with triruthenium dodecacarbonyl (2.1 g, 3.28 mmol), (+)-neomenthylcyclopentadiene (8.0 g, 39.4 mmol) and heptane (100 cm^3). The reaction was held at reflux temperature for 20 h. Upon cooling the solvent was removed in vacuo to yield [$\eta^?$-neomenthylcyclopentadienyl]dicarbonylruthenium dimer as a pale brown oil; ν_{max}/cm^{-1} (CO) 2003m, 1967s, 1957s, 1937s and 1786s (CH_2Cl_2). The crude product was dissolved in carbon tetrachloride (50 cm^3) and iodine was added (1.2 g, 4.92 mmol). The reaction mixture was stirred for 2 h and then the solvent was removed in vacuo to yield [$\eta^?$-neomenthylcyclopentadienyl]dicarbonyl–iodoruthenium as a red oil; ν_{max}/cm^{-1}(CO) 2039s and 1990s (CH_2Cl_2) This crude product was dissolved in xylene (125 cm^3) and freshly ground triphenylphosphine (4.0 g, 15.3 mmol) was added. The reaction mixture was held at reflux temperature for 20 h, allowed to cool and poured onto a long column (>8 inches/neutral alumina–petroleum ether) under nitrogen. (Alternatively, the xylene could be removed via high vacuum distillation.) Once the solvent had run off the title product was eluted with dichloromethane–diethyl ether (20/80 v/v) as an intense red band and collected in several sample tubes. The fractions were left in solution at room temperature for 24 h which resulted in crystallisation of the (*R*) diastereoisomer (≥90% d.e.). The (*S*) diastereoisomer was obtained from the mother liquors (≥90% d.e.). Recrystallisation of these compounds from 20% dichloromethane in diethyl ether at −20 °C was performed to increase the purity to ≥98% d.e. Overall yield of the title compound was 5.1 g (72%). Anal. Calc. for $C_{34}H_{38}IOPRu$: C, 56.59; H, 5.31; I, 17.59. Found: C, 57.07; H, 5.14; I, 17.86%. ν_{max}/cm^{-1} (CO) 1956s (CH_2Cl_2); $(R)_{Ru}$: ^{1}H-NMR ($CDCl_3$) δ (vs TMS) 7.50 (6H, m, aromatics, *meta*), 7.38 (9H, m, aromatics, *ortho* & *para*), 5.67 (1H, broad, Cp–H), 4.59 (1H, broad, Cp–H), 4.54 (1H, broad, Cp–H), 4.28 (1H, broad, Cp–H), 2.85 (1H, broad, CH), 2.21 (1H, m, CH), 1.80 (2H, m, CHs), 1.55 (2H, m, CH_2), 1.40–1.04 (4H, m, CH_2s), 0.88 (6H, m, CH_3s), 0.74 (3H, d, ^3J(HH) 6 Hz, CH_3); $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ (vs H_3PO_4) 50.0; $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ (vs TMS) 203.7 (d, CO, ^2J(CP) 21 Hz), 136.1 (d, Ar–C, ^2J(CP) 48 Hz), 133.7 (d, Ar–CH, ^4J(CP) 11 Hz *meta*), 130.2 (Ar–CH, *para*), 128.2 (d, Ar–CH, ^3J(CP) 10 Hz *ortho*), 109.6 (d, Cp–C, ^2J(CP) 6 Hz), 94.7, 85.4, 84.8, 82.1 (Cp–CHs), 48.2, 35.9, 29.6, 27.9 (CHs), 44.2, 35.4, 24.3 (CH_2s), 22.7, 22.1, 20.7 (CH_3s); $(S)_{Ru}$: ^{1}H-NMR ($CDCl_3$) δ (vs TMS) 7.50 (6H, m, aromatics, *meta*), 7.37 (9H, m, aromatics, *ortho* & *para*), 5.50 (1H, broad, Cp–H), 5.05 (1H, broad, Cp–H), 4.30 (1H, broad, Cp–H), 3.95 (1H, broad, Cp–H), 3.10 (1H, broad, CH), 2.26 (1H, m, CH), 1.92–1.55 (4H, m, CH_2s), 1.48–0.98 (4H, m, CH_2s), 0.93 (6H, m, CH_3s), 0.75 (3H, d, ^3J(HH) 6 Hz, CH_3); $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ (vs H_3PO_4) 48.7; $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ (vs TMS) 203.7 (d, CO, ^2J(CP) 20Hz), 136.0 (d, Ar–C, ^2J(CP) 48 Hz), 133.7 (d, Ar–CH, ^4J(CP) 11 Hz, *meta*), 130.2 (Ar–CH, *para*), 128.2 (d, Ar–CH, ^3J(CP) 10 Hz, *ortho*), 106.7 (d, Cp–C, ^2J(CP) 9 Hz), 98.9, 85.9, 83.5, 80.2 (Cp–CHs), 47.7, 35.1, 29.5, 28.1 (CHs), 44.16, 35.39, 24.61 (CH_2s), 22.5, 21.9, 20.5 (CH_3s); *m/z* (+ve FAB) 722 [MH^+, 60%], 694 [$MH^+ - CO$, 35], 595 [$MH^+ - I$, 65], 565 [$MH^+ - I - CO$, 100].

4.2. Synthesis of $(R)_{Ru}$-Ru(NmCp)(CO)(PPh_3)SCN (**2a**)

$(S)_{Ru}$-Ru(NmCp)(CO)(PPh_3)I (250 mg, 0.347 mmol) was dissolved in dry acetone (50 ml) and AgSCN (90 mg, 0.542 mmol) was added to this red–orange solution.

The stirred mixture was heated under reflux in the dark under nitrogen for two days then the resultant green–yellow solution was allowed to cool. The solution was filtered through Hyflo to remove silver iodide and colloidal silver and the filtrate taken to dryness to give a green–yellow solid (180 mg, 80%). Crystallization from dichloromethane–petroleum ether gave green–yellow crystals. Anal. Calc. for $C_{35}H_{38}NOPRuS$: C, 64.40; H, 5.87; N, 2.15; S, 4.91. Found C, 63.47; H, 5.81; N, 2.17; S, 5.23%. ν_{max}/cm^{-1} (CO) 1962 (s), (CN) 2107 (s) (CH_2Cl_2) ^{1}H-NMR ($CDCl_3$) δ (vs TMS) 7.41 (15H, m, aromatics), 5.39 (1H, broad, Cp–H), 4.99 (1H, broad, Cp–H), 4.38 (1H, broad, Cp–H), 4.30 (1H, broad, Cp–H), 3.15 (1H, broad, CH), 2.20–1.05 (9H, m, CH_2s, CHs), 0.94 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.90 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.76 (3H, d, ^3J(HH) 6 Hz, CH_3); $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ (vs TMS) 203.2 (d, J(PC) 19.4 Hz, CO), 134.3 (d, J(PC) 49.8 Hz, Ph–Cs), 133.3 (d, J(PC) 11.1 Hz), 130.6, 128.5 (d, J(PC) 10.4 Hz), (Ph–CHs), 110.9, (d, J(PC) 11.1 Hz, Cp–C), 101.8, 87.1, 82.8, 81.7 (Cp–CHs), 47.8, 34.8, 29.6, 28.2 (CHs), 43.8, 35.4, 24.5 (CH_2s), 22.5, 22.0, 20.6 (CH_3s); $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ (vs H_3PO_4) 50.6; m/z (+ve FAB) 653 [M^+].

4.3. Synthesis of $(S)_{Ru}$-Ru(NmCp)(CO)(PPh_3)SCN (**2b**)

This was prepared in an analogous way to the (R) diastereoisomer starting from $(R)_{Ru}$-Ru(NmCp)(CO)(PPh_3)I. ^{1}H-NMR ($CDCl_3$) δ (vs TMS) 7.47 (15H, m, aromatics), 5.44 (1H, broad, Cp–H), 4.74 (1H, broad, Cp–H), 4.51 (2H, broad, Cp–H), 2.79 (1H, broad, CH), 2.12–1.18 (9H, m, CH_2s, CHs), 0.91 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.86 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.75 (3H, d, ^3J(HH) 6 Hz, CH_3); $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ (vs H_3PO_4) 50.8.

4.4. Synthesis of $(R,S)_{Ru}$-[η^5-neomenthylcyclopentadienyl](benzyl methyl sulfide)carbonyl (triphenylphosphine)ruthenium tetrafluoroborate (**3**)

$(S)_{Ru}$-[η^5-(Neomenthylcyclopentadienyl]carbonyliodo(triphenylphosphine)ruthenium (163 mg, 0.23 mmol) and silver tetrafluoroborate (49 mg, 0.25 mmol) were charged into a Schlenck tube and freshly distilled dichloromethane (25 cm^3) was added. The resulting mixture was stirred in the absence of light for 20 h and then, to destroy any silver salts, exposed to light for 2 h. Generation of [Ru(NmCp)(CO)(PPh_3)(CH_2Cl_2)]BF_4 was confirmed by infrared spectroscopy; ν_{max}/cm^{-1}(CO) 1967s (CH_2Cl_2). Benzyl methyl sulfide (STENCH, 0.03 cm^3, 0.25 mmol) was added *via* syringe and the mixture stirred for a further 14 h. The solvent and excess benzyl methyl sulfide were removed under high vacuum. The title product was eluted as a racemic mixture from a column of neutral alumina with dichloromethane (132 mg, 70%). Anal. Calc. for $C_{42}H_{48}BF_4OPRuS$: C, 61.54; H, 5.90; S 3.91. Found: C, 61.78; H, 6.03; S 4.10%. ν_{max}/cm^{-1} (CO) 1977s (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ (vs TMS) 7.51 (18H, m, aromatics), 7.24 (22H, m, aromatics), 6.09 (1H, broad, Cp–H), 6.00 (1H, broad, Cp–H), 5.89 (1H, broad, Cp–H), 5.27 (1H, broad, Cp–H), 4.88 (1H, broad, Cp–H), 4.77 (1H, broad, Cp–H), 4.70 (1H, broad, Cp–H), 4.41 (1H, broad, Cp–H), 3.11 (1H, broad, CH), 2.62 (1H, broad, CH), 2.45 (3H, s, SCH_3), 2.40 (3H, s, SCH_3), 2.05 (2H, s, SCH_2Ph), 1.98 (2H, s, SCH_2Ph), 1.98–1.05 (18H, m, CH_2s, CHs), 1.04 (3H, d, ^3J(HH) 7 Hz, CH_3), 0.90 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.86 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.74 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.69 (6H, d, ^3J(HH) 6 Hz, CH_3s); $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ (vs H_3PO_4) 46.7, 45.7; $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ (vs TMS) 202.1, 201.8 (COs), 134.8, 134.7 (Ar–Cs, *benzyl methyl sulfide*), 133.2, 133.0 (Ar–CHs), 132.2, 132.1 (Ar–Cs), 131.4 (Ar–CHs), 130.0, 129.9 (Ar–CHs, *benzyl methyl sulfide*), 129.3, 129.1 (Ar–CHs), 128.8, 128.6, 128.4, 128.2 (Ar–CHs, *benzyl methyl sulfide*), 114.2, 114.2 (Cp–Cs), 92.9, 92.0, 89.2, 89.2, 89.2, 85.6, 84.9, 79.0 (Cp–CHs), 48.0, 47.8 (SCH_3s), 45.2, 43.6 (SCH_2Phs), 35.9, 35.6, 29.6, 29.6, 29.2, 29.2, 28.0, 28.0 (CHs), 38.3, 38.3, 35.0, 35.0, 24.2, 23.6 (CH_2s), 22.6, 22.5, 22.2, 22.0, 20.3, 20.3 (CH_3s); m/z (+ve FAB) 733 [M^+, 94%], 595 [M^+ − benzyl methyl sulfide, 100%], 565 [M^+ − benzyl methyl sulfide − CO, 63%].

4.5. Synthesis of $(R,S)_{Ru}$-[η^5-neomenthylcyclopentadienyl]carbonyl(phenyl methyl sulfide)-(triphenylphosphine)ruthenium tetrafluoroborate (**4**)

This was prepared by an analogous procedure to **3** but using phenyl methyl sulfide (thioanisole) in place of benzyl methyl sulfide. Recrystallisation (dichloromethane/ether) gave the desired product as a as a yellow solid in 64% yield. Anal. Calc. for $C_{41}H_{46}BF_4OPRuS$ C, 61.12; H, 5.75; S 3.98. Found: C, 60.61; H, 5.79; S, 3.99%. ν_{max}/cm^{-1}(CO) 1979s (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ (vs TMS) 7.50 (20H, m, aromatics), 7.31 (20H, m, aromatics), 5.39 (1H, broad, Cp–H), 5.24 (1H, broad, Cp–H), 4.92 (1H, broad, Cp–H), 4.63 (1H, broad, Cp–H), 4.57 (1H, broad, Cp–H), 4.43 (1H, broad, Cp–H), 4.13 (1H, broad, Cp–H), 3.55 (1H, broad, Cp–H), 2.97 (1H, broad, CH), 2.69 (1H, broad, CH), 2.56 (3H, s, SCH_3), 2.54 (3H, s, SCH_3), 2.29–2.07 (4H, m, CHs), 1.81–1.52 (8H, m, CH_2s), 1.40–1.00 (6H, m, CH_2s, CHs), 0.89 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.86 (3H, d, ^3J(HH) 6 Hz, CH_3), 0.80 (6H, d, ^3J(HH) 6 Hz, CH_3), 0.71 (3H, d, ^3J(HH) 5 Hz, CH_3), 0.68 (3H, d, ^3J(HH) 5 Hz, CH_3); $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ (vs H_3PO_4) 43.9, 43.0; $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ (vs TMS)

202.2, 201.9 (COs), 137.7, 137.4 (Ar–Cs, *thioanisole*), 133.3, 133.1 (Ar–CHs), 132.7, 131.9 (Ar–Cs), 131.7, 131.6 (Ar–CHs), 130.1, 130.0 (Ar–CHs, *thioanisole*), 129.4, 129.2 (Ar–CHs), 129.8, 129.7, 128.2, 128.1 (Ar–CHs, *thioanisole*), 133.1 (d, ^3J(CP) 7 Hz, Cp–C), 118.0 (d, ^3J(CP) 3 Hz, Cp–C), 104.7, 93.1, 91.6, 90.0, 90.0, 85.4, 79.8, 79.0 (Cp–CHs), 48.4, 47.8 (S*CH*$_3$s), 35.5, 35.2, 29.3, 29.0, 28.1, 28.1, 27.8, 27.1 (CHs), 44.6, 41.6, 35.0, 29.7, 24.1, 23.6 (CH_2s), 22.8, 22.4, 22.2, 21.7, 21.6, 20.5 (CH_3s); *m*/*z* (+ve FAB) 719 [M^+, 50%], 595 [M^+ − thioanisole, 100%], 565 [M^+ − thioanisole − CO, 30%].

4.6. Synthesis of (*R*,*S*)$_{Ru}$-[η^5-neomenthylcyclopentadienyl]carbonyl(*tert*-butyl methyl sulfide)(triphenylphosphine)ruthenium tetrafluoroborate (**5**)

This was isolated as a yellow oil by an analogous procedure to **3** but using *tert*-butyl methyl sulfide in place of benzyl methyl sulfide. Crystallisation (dichloromethane–ether) gave the desired product as a as a yellow solid in 85% yield. Anal. Calc. for $C_{38}H_{50}BF_4OPRuS$ C, 58.99; H, 6.51; S 4.14. Found: C, 58.79; H, 6.45; S, 4.43%. ν_{max}/cm^{-1} (CO) 1973s (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ (vs TMS) 7.55 (20H, m, aromatics), 7.36 (10H, m, aromatics), 5.90 (1H, broad, Cp–H), 5.77 (1H, broad, Cp–H), 5.69 (1H, broad, Cp–H), 5.20 (1H, broad, Cp–H), 5.14 (1H, broad, Cp–H), 4.85 (1H, broad, Cp–H), 4.55 (1H, broad, Cp–H), 4.16 (1H, broad, Cp–H), 2.93 (1H, broad, CH), 2.62 (1H, broad, CH), 2.13 (3H, s, S*CH*$_3$), 2.13 (3H, s, S*CH*$_3$), 2.43–0.77 (18H, m, CH_2s, CHs), 1.38 [9H, s, SC(*CH*$_3$)$_3$], 1.37 [9H, s, SC(*CH*$_3$)$_3$], 0.97–0.77 (12H, m, CH_3s), 0.76–0.66 (6H, m, CH_3s); ^{31}P{^{1}H}-NMR ($CDCl_3$) δ (vs H_3PO_4) 43.9, 43.0; ^{13}C{^{1}H}-NMR ($CDCl_3$) δ (vs TMS)204.1, 203.6 (COs), 133.1, 133.0 (Ar–CHs), 132.3, 132.3 (Ar–Cs), 131.6, 131.6 (Ar–CHs), 129.2, 129.1 (Ar–CHs), 116.9, 114.1 (Cp–Cs), 96.7, 95.7, 93.4, 88.9, 86.0, 84.2, 82.9, 76.4 (Cp–CHs), 50.1, 49.6 (Bu^t quaternary Cs), 48.4, 48.0 (S*CH*$_3$s), 28.6, 28.5 (^{t}Bu–*CH*$_3$s), 36.1, 35.4, 30.6, 30.6, 29.5, 28.9, 28.2, 27.9 (CHs), 44.4, 42.1, 35.1, 35.0, 24.3, 23.6 (CH_2s), 22.5, 22.3, 22.2, 21.9, 21.9, 20.4 (CH_3s); *m*/*z* (+ve FAB) 699 (M, 18%), 595 [M^+-*tert*-butyl methyl sulfide, 100], 565 [M^+ − *tert*-butyl methyl sulfide − CO, 70].

5. X-ray crystallography

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45^\circ$ on a Siemens P4 diffractometer by the omega scan method. The 2393 independent reflections (of 2529 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, and for absorption by semi-empirical methods. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.1241$ ($wR_2 = 0.3426$, 152 parameters, mean and maximum δ/σ), with allowance for the thermal anisotropy for Ru1 P1 S1 N1 O1 only. A molecule of solvent was found and refined to an occupancy of 50%. Minimum and maximum final electron density −0.821 and 1.515 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2)+(0.2000P)^2+0.00P]$ where $P = (F_o^2+2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL-93 [17] as implemented on the Viglen 486dx computer.

5.1. Crystal data for (*R*)$_{Ru}$-Ru(NmCp)(CO)(PPh_3)SCN (**2a**)

$C_{35.5}H_{38.50}Cl_{1.5}NOPRuS$; $M = 712.45$. Crystallises from chloroform as yellow blocks; crystal dimensions $0.50 \times 0.45 \times 0.23$ mm^3. Orthorhombic, $a = 13.662(6)$, $b = 16.182(10)$, $c = 17.797(5)$ Å, $U = 3935(3)$ Å^3, $Z = 4$, $D_{calc} = 1.203$ Mg m^{-3}, space group $P2_12_12_1$ (D_2^4, no. 19), Mo–K$_\alpha$ radiation ($\alpha = 0.71073$ Å), μ(Mo–K$_\alpha$) = 0.618 mm^{-1}, $F(000) = 1468$.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 213177 for compound **2a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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