Synthesis of Halfsandwich Ruthenium Complexes of Sulfinic Acid Esters [1]

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Dedicated to Prof. Dr. Dr. h.c. Max Schmidt on the occasion of his 75th birthday

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Ruthenium Complexes, Sulfur Ligands, Diastereoselective Alkylations

A series of halfsandwich ruthenium sulfinato complexes $[CpRu(PR'_3)_2(SO_2R)]$ (R = Me, CH_2Ph, C_2H_4Ph, Ph, 4-C_6H_4Me; $PR'_3 = PMe_3$, 1/2 dppm) with various electronic and steric environments around the ruthenium centre, have been prepared by insertion of SO_2 into a ruthenium carbon bond, by a direct ligand exchange reaction, or by oxidation of thiolato complexes with 3-chloroperoxybenzoic acid. The chiral complexes $[CpRu(CO)(PPh_3)(SO_2R)]$ (R = Me, CH_2Ph, Ph) were obtained similarly by oxidation of the corresponding thiolates with magnesium monoperoxyphthalate. Alkylation of the sulfinato complexes with oxonium salts $[R''_3O]X$ (R'' = Me, Et; X = BF_4, PF_6) gave ruthenium complexes of sulfinic acid esters, $[CpRu(L)(L')(S(O)(OR'')R)]X$ in high yields and, for the chiral complexes, up to 82% de. The esters may be detached from the metal by ligand exchange with acetonitrile. Stronger nucleophiles such as I^- or SMe^- dealkylate the coordinated sulfinic acid esters.

Introduction

One of the most notable features of transition metal complexes is their ability to activate coordinated substrates to undergo reactions not observed with the free ligands [2, 3]. This fascinating aspect of transition metal chemistry is usually rationalised by taking into account the framework of σ and π bonding as well as backbonding between the metal centre and the ligand [4 - 6]. Electron-rich transition metal fragments tend to increase the electron density on the ligand, hence activating it for electrophilic additions.

Electron-rich ruthenium thiolate complexes $[CpRu(PR'_3)_2(SR)]$ are readily alkylated under mild conditions to give cationic thioether complexes $[CpRu(PR'_3)_2(RSR'')]^+$ [7]. The same class of complexes was even shown to form stable adducts $[CpRu(PR'_3)_2(S(SO_2)R)]$ with the weak Lewis acid SO_2 [8]. We have discussed this unusual reactivity in terms of the ability of the ruthenium centre to increase the electron density on the thiolate sulfur atom and hence to considerably increase its nucleophilicity. In this context it seemed interesting to study the effect of complexes of the type $[CpRu(L)(PR'_3)]^+$ (L = CO, PR'_3) on other sulfur-containing ligands. We chose sulfinate anions which are more challenging substrates due to the fact that the potentially nucleophilic oxygen atom is separated by two bonds from the metal centre. In addition the sulfinate anion when coordinated to a stereogenic ruthenium centre offers the potential of a diastereoselective functionalisation of one of either diastereotopic oxygen atoms. We have shown previously that chiral ruthenium complexes can be efficiently used as chiral auxiliaries in a variety of highly diastereoselective transformations [9 - 14]. Hence we should be able to obtain esters of sulfinic acids stereoselectively in the coordination sphere of a ruthenium complex. Such systems are valuable building blocks with sulfur centered chirality [15]. Earlier work by Wojcicki and co-workers has shown that the corresponding iron sulfinato complex $[CpFe(CO)(PPh_3)(SO_2Me)]$ can be protonated as well as alkylated at oxygen and forms stable adducts with BF_3 [16, 17]. No reports on the diastereoselectivities of these transformations were, however, included.

In this contribution we describe the effect of the electron rich transition metal fragments $[CpRu(L)(PR_3)]^+$ (L = CO, PR_3) on the nucleophilicity of a coordinated sulfinate anion and the exploitation of this effect in the synthesis of cationic ruthenium

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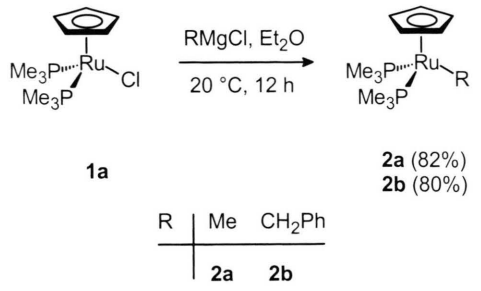
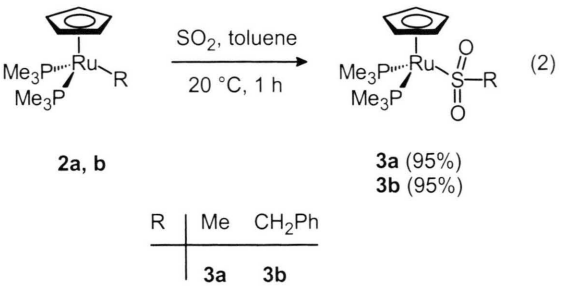
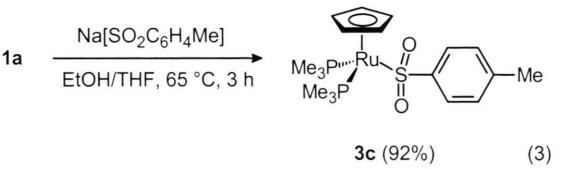




complexes of sulfinic acid esters. Furthermore, we will discuss the factors influencing the diastereoselectivity of the alkylation reaction.



Synthesis of the Sulfinato Complexes [CpRu(L)(PR'$_3$)(SO$_2$R)]

Initially we decided to start our investigation using the highly electron rich ruthenium fragment [CpRu(PMe$_3$)$_2$]$^+$. As a common starting material we chose [CpRu(PMe$_3$)$_2$(Cl)] (**1a**), which had been shown earlier to react readily with Grignard reagents [18]. Similarly, the alkyl complexes **2a, b** were obtained in excellent yields (eq. (1)).

It is worth noting that chloro Grignard reagents are preferred over their bromo or iodo analogs, since with these heavier halide ions considerable amounts of the bromo or iodo complexes [CpRu(PMe$_3$)$_2$(X)] are formed as side products, which are inseparable from the desired compounds. The alkyl complexes are air sensitive yellow oils, which are readily soluble in hexane, benzene, or halogenated solvents. The NMR spectroscopic data of **2a, b** are in perfect accordance with the proposed structures. The most notable features are the couplings ^2J(*P*Ru*C*) and ^3J(*P*Ru*CH*) which split the ^{13}C and ^{1}H NMR signals of the metal bound alkyl groups into triplets. The methyl resonances of the PMe$_3$ ligands appear as virtual triplets in the ^{1}H NMR spectra and as characteristic X parts of ABX spin systems [19] in the ^{13}C NMR spectra.

Passing dry gaseous SO$_2$ through solutions of **2a, b** in toluene results in quantitative formation of the desired sulfinato complexes [CpRu(PMe$_3$)$_2$(SO$_2$R)] (**3a, b**) (eq. (2)).

Sulfinato complexes are also available by a direct ligand substitution reaction as shown in the following example. Reaction of **1a** with Na[SO$_2$(4-C$_6$H$_4$Me)] in a 1:1 EtOH/THF solvent mixture under reflux gives [CpRu(PMe$_3$)$_2$(SO$_2$(4-C$_6$H$_4$Me))] (**3c**) in almost quantitative yield (eq. (3)).

The use of this particularly polar solvent mixture is crucial for the success of the reaction and points towards a dissociative ligand substitution mechanism involving a cationic 16 valence electron ruthenium species.

The sulfinato complexes are pale yellow crystalline substances which are readily soluble in toluene and chlorinated solvents. Compared to their alkyl counterparts **2a, b**, they are fairly air stable and can be stored for weeks. The solids **3a-c** are apparently quite hygroscopic and therefore do not give reproducible analytical data. In the NMR spectra the α carbon as well as the α SO$_2$CH proton resonances are shifted to lower field as expected. The most notable features of these complexes are their ν (S=O) absorptions in the infrared spectra at 1156 - 1132 and 1028 - 1020 cm^{-1}, respectively. A direct comparison between these values of the sulfinato complexes, which can formally be regarded as metalla-sulfones, and those of a diorgano-sulfone (Me$_2$SO$_2$; ν (S=O): 1314 and 1134 cm^{-1} [20]) reveal that the S=O bond order is significantly reduced.

We then turned our attention to the less electron-rich arylphosphine sulfinato complexes [CpRu(dppm)(SO$_2$R)] (**5a-d**). In order to cut the previous synthetic route by one step we decided to use the thiolate complexes [CpRu(dppm)(SR)] (**4a-d**) as precursors. Compound **4d** has not been reported before and was obtained in good yield using our standard one-pot synthesis [7]. We have recently reported that this class of compounds can be selectively oxidised with dimethyldioxirane [21] to give the corresponding sulfinato complexes. In the present case,

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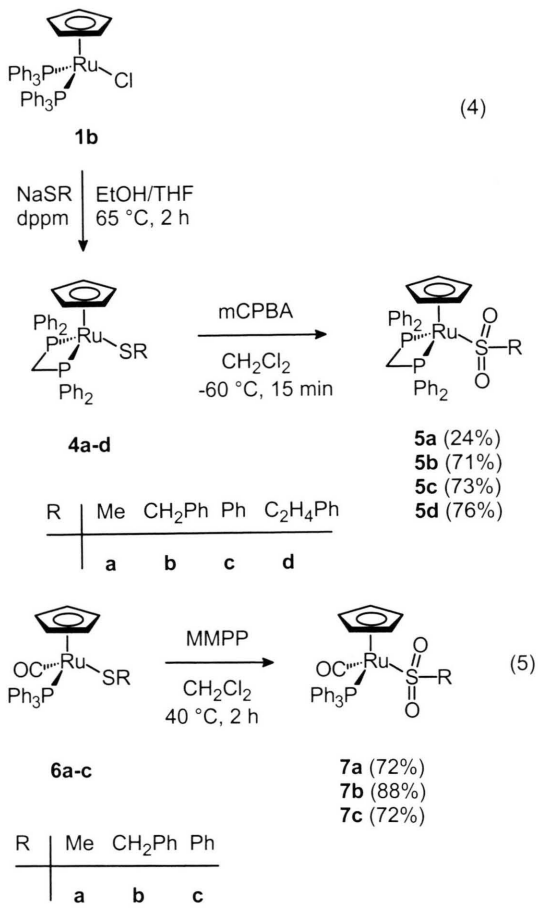
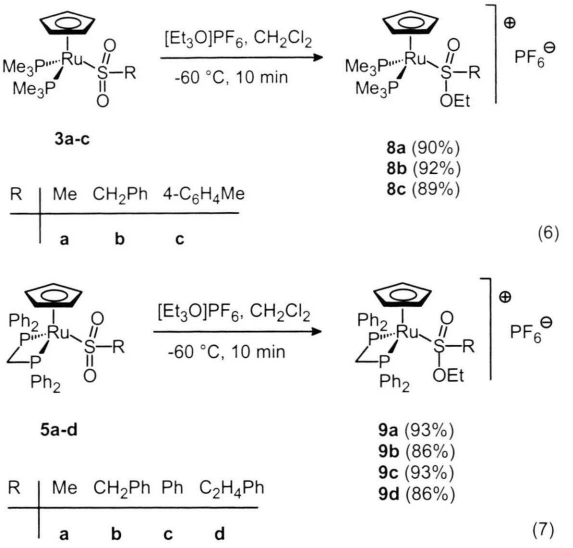


however, a commercially available peracid such as mCPBA (3-chloroperoxybenzoic acid) can be used as a substitute which cleanly oxidises the complexes **4a-d** to the corresponding sulfinato complexes **5a-d** in good yields (eq. (4)).

A similar oxidation protocol using MMPP (magnesium monoperoxyphthalate) gave sulfinato complexes with metal-centred chirality (eq. (5)).

The new sulfinato complexes **5a-d** and **7a-c** again are air-stable yellow crystalline solids which are soluble in toluene and chlorinated solvents. All of them exhibit the expected spectroscopic properties featuring low field ^{1}H and ^{13}C resonances for both α-carbon and CH groups. The carbonyl complexes **7a-c** show infrared ν (CO) absorptions between 1960 and 1980 cm^{-1} indicating that the sulfinato anion is a less electron donating ligand in comparison with the thiolate group. The ν(S=O) absorptions are in the range expected for *S*-bound sulfinato complexes [22, 23]. The carbonyl complexes



7a-c show ν (S=O) bands at somewhat higher wavenumbers indicating a reduced back bonding of the metal HOMO into the sulfinato LUMO. The decreased S=O bond order should result in an increase in electron density at the sulfinato oxygen atoms and, therefore, in an enhanced nucleophilicity. Subsequent investigations have shown this to be the case.

Synthesis of Cationic Sulfinic Acid Ester Complexes [CpRu(L)(PR'$_3$)(SO(OR'')R)]X

Following earlier work of Wojcicki [17] we chose oxonium salts [R''$_3$O]X as alkylating agents. Treatment of the sulfinato complexes **3a-c** and **5a-d** with [Et$_3$O]PF$_6$ in dichloromethane at –60 °C resulted in clean reactions to produce cationic sulfinic acid ester complexes **8a-c** and **9a-d** in excellent yields (eqs (6), (7)).

The new sulfinic acid ester complexes were obtained as colourless solids which are soluble in polar media such as chlorinated hydrocarbons or acetone. In alcoholic solvents they decompose to give back the sulfinato complexes. The ^{31}P NMR spectra exhibit AB spin systems indicating the inequivalence of the phosphorus nuclei due to the stereogenic centre at sulfur. Similarily the methylene protons of the ethyl groups appear as distinct AB parts of ABX$_3$ spin systems. The chemical shifts in both the ^{1}H and ^{13}C NMR spectra are very similar to those of the free ligands [15]. The infrared spectra of the complexes show a

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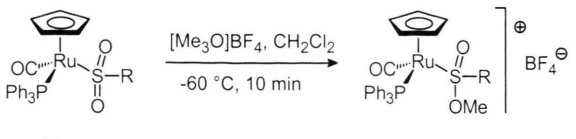
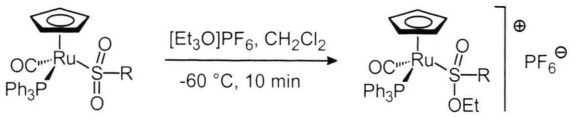


R	Me	CH_2Ph	Ph
	a	b	c

(8)



R	CH_2Ph	Ph
	11a	11b

(9)

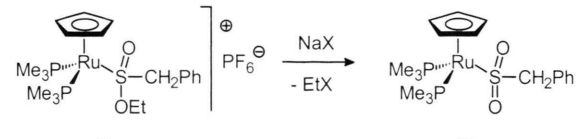
medium strong S=O stretching absorption around 1145 cm^{-1}.

Stereochemistry is an important issue in the alkylation reaction, since in compounds with an additional element of chirality, the sulfinato oxygen atoms are diastereotopic. Therefore, we turned our attention to the CO substituted complexes **7a-c**. In the corresponding iron series an extensive variety of highly diastereoselective transformations of various substrates [CpFe(CO)(PPh_3)(X)] have been reported, in particular by Davies *et al.* [24 - 26]. Alkylation of **7a-c** with either $[Me_3O]BF_4$ or $[Et_3O]PF_6$ gave the diastereomeric sulfinic acid ester complexes **10a-c** and**11a, b** in excellent yields and varying diastereoselectivities (eqs (8), (9)).

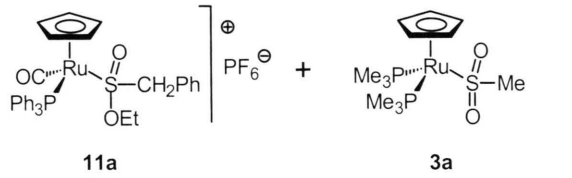
The products are pale yellow crystalline solids which are soluble in chlorinated hydrocarbons and acetone. In the infrared spectra the S=O stretching absorption could not be identified unambiguously. The CO stretching frequency is shifted to still higher values if compared to the starting materials, which is a result of the decreased electron density at the metal centre due to the cationic nature of these complexes.

Reactivity of Cationic Sulfinic Acid Ester Complexes

In order to gain some preliminary insight into the reactivity of the new complexes we studied the reaction of compound **8b** with nucleophiles. Reaction with NaSMe and NaI resulted in complete dealkylation of the complex, giving back the corresponding



X = I, SMe (10)



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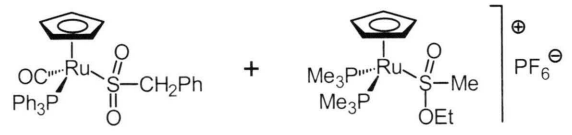

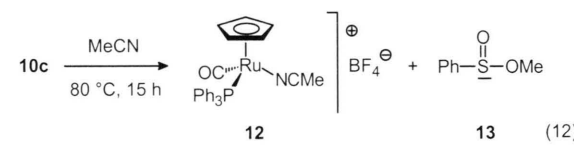

(12)

sulfinato complex **3b** and presumably EtI or EtSMe which were lost during workup (eq. (10)).

In order to further demonstrate the capability of the new sulfinic acid ester complexes to act as alkylating agents, a crossover experiment between the ester complex **11a** and the electron rich and therefore more nucleophilic sulfinato complex **3a** was carried out. After 4h under reflux a 10% transfer of the ethyl group was observed giving the expected crossover products **7b** and **8a** respectively (eq. (11)).

Refluxing a solution of **10c** in acetonitrile resulted in an abstraction of the sulfinic acid ester ligand, yielding the acetonitrile complex **12** [27] and PhS(O)OMe (**13**) (eq. (12)).

13 was identified by its known spectroscopic properties [28]. It should be mentioned that we have recently reported such a demetalation procedure and suggested a cycle to efficiently recover the quite precious ruthenium starting materials [1, 14].

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Discussion

Electron-rich ruthenium sulfinato complexes, which can be formally regarded as metalla-sulfones, are characterised by a significantly reduced S=O bond order if compared to regular diorgano-sulfones. This reduced bond order is not only expressed in their low S=O stretching frequencies but also in their enhanced nucleophilicity at oxygen. It should be kept in mind that sulfones can only be arylated at oxygen using diazonium salts [29]. The two mesomeric structures shown in equation 13 adequately describe these properties.

The reason behind this change of structure and reactivity can be explained in terms of back bonding from the metal HOMO into the ligand LUMO. By taking advantage of this metal activating effect we have been able to synthesise esters of sulfinic acids in the coordination sphere of a ruthenium complex. Alkylation of the diastereotopic sulfinato oxygen atoms can proceed with moderate to good diastereoselectivity, depending on the steric demand of the alkylating agent and, more importantly, on the nature of the chiral ruthenium complex. In particular, the combination of a very small ligand such as CO and the bulky triphenylphosphine can give rise to a selectivity of up to 91:9.

The cationic sulfinic acid ester complexes are readily dealkylated by nucleophiles. This suggests that they might be useful reagents, having the potential to act as enantioselective alkylating agents.

Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of dry nitrogen using suitably purified solvents. $[CpRu(PMe_3)_2(Cl)]$ (**1a**) [30], $[CpRu(PPh_3)_2(Cl)]$ (**1b**) [31] and the thiolato complexes [CpRu(dppm)(SR)] (R = Me (**4a**), CH_2Ph (**4b**), Ph (**4c**)), [CpRu(CO)(PPh_3)(SR)] (R = Me (**6a**), CH_2Ph (**6b**), Ph (**6c**)) [7] were obtained as described in the literature. 3-Chloroperoxybenzoic acid (mCPBA) was dried under vacuum at 80 °C and titrated iodometrically. Magnesium-monoperoxyphthalate hexahydrate (MMPP) and all other reagents were used as purchased.

The following analytical instruments were used: IR: Perkin-Elmer 283, Bruker IFS 25; NMR: Bruker AMX 400 (^{1}H, 400 MHz, TMS; ^{13}C, 100 MHz, TMS; ^{31}P, 162 MHz, H_3PO_4). Chemical shifts δ in [ppm], coupling constants J in [Hz]. Signals of aryl groups and signals of the CH_2 group of the dppm ligand are uncharacteristic and have been omitted from the lists of spectral data. PF_6^- salts exhibit a septet at $\delta = -144.0$ ppm ($J = 710$ Hz) in their ^{31}P NMR spectra. Melting or decomposition points were determined in closed capillaries in a copper block and are uncorrected.

[CpRu(PMe$_3$)$_2$(R)] (**2a, b**)

To a solution of **1a** (0.69 g, 1.95 mmol) in diethylether (50 ml), 4 ml of a 0.5 M RMgCl solution (2.00 mmol) in diethylether was added at room temperature. After 12 h the reaction mixture was quenched with methanol (1 ml) and evaporated under vacuum. The residue was extracted with hexanes (100 ml) and filtered over celite. Removal of the solvent under vacuum yielded the alkyl complexes as yellow oils.

2a: Yield 0.53 g (82%), yellow oil. – ^{1}H NMR (C_6D_6): 4.20 (s, 5H, Cp), 1.11 (vt, N = 9.4 Hz, 18H, PCH_3), 0.13 (t, J = 6.7 Hz, 3H, $RuCH_3$). – ^{13}C NMR (C_6D_6): 80.3 (s, Cp), 23.0 (X-part of ABX system, N = 26 Hz, PCH_3), –28.5 (t, J = 14 Hz, $RuCH_3$). – ^{31}P NMR (C_6D_6): 13.5 (s).

2b: Yield 0.64 g (80%), yellow oil. – ^{1}H NMR (C_6D_6): 4.21 (s, 5H, Cp), 2.31 (t, J = 6.9 Hz, 2H, $RuCH_2$) 1.08 (vt, N = 8.2 Hz, 18H, PCH_3). – ^{31}P NMR (C_6D_6): 12.4 (s).

[CpRu(PMe$_3$)$_2$(SO$_2$R)] (**3a, b**)

A solution of the alkyl complex (1.00 mmol) in toluene (50 ml) was treated for 5 min with dry gaseous SO_2. A color change to red and back again to yellow was observed. The mixture was stirred for 1 h at room temperature and then evaporated to 5 ml under vacuum. Addition of hexane caused the product to crystallize.

3a: Yield: 0.36 g (95%), yellow crystalline powder, m. p. 151 °C (dec). – IR (Nujol): 1132, 1020 cm^{-1} (SO). – ^{1}H NMR ($CDCl_3$): 4.37 (s, 5H, Cp), 3.03 (s, 3H, SO_2CH_3), 1.21 (vt, N = 8.8 Hz, 18H, PCH_3). – ^{13}C NMR ($CDCl_3$): 82.9 (s, Cp), 62.6 (s, SCH_3), 22.8 (X part of ABX system, N = 31 Hz, PCH_3). – ^{31}P NMR ($CDCl_3$): 11.4 (s).

3b: Yield: 0.43 g (95%), yellow crystalline powder, m. p. 181 °C (dec). – IR (Nujol): 1156, 1028 cm^{-1} (SO). – ^{1}H NMR ($CDCl_3$): 4.64 (s, 5H, Cp), 4.06 (s, 2H, SCH_2), 1.49 (vt, N = 9.3 Hz, 18H, PCH_3). – ^{13}C NMR ($CDCl_3$): 82.7 (s, Cp), 78.9 (s, SCH_2), 22.8 (X part of ABX system, N = 32 Hz, PCH_3). – ^{31}P NMR ($CDCl_3$): 10.5 (s).

[CpRu(PMe$_3$)$_2$(SO$_2$(4-C$_6$H$_4$Me))] (**3c**)

A solution of **1a** (0.33 g 1.00 mmol) and sodium toluenesulfinate (0.20 g 1.12 mmol) in a mixture of ethanol (10 ml) and THF (10 ml) was heated under reflux for 3 h.

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The solvent was removed under vacuum, the residue extracted with benzene (10 ml) and filtered over celite. The filtrate was taken to dryness and the residue recrystallised from benzene/hexane.

Yield 0.43 g (92%), yellow crystalline powder, m. p. 176 °C (dec). – IR (Nujol): 1144, 1020 cm^{-1} (SO). – ^1H NMR ($CDCl_3$): 4.52 (s, 5H, Cp), 2.32 (s, 3H, CH_3), 1.51 (vt, N = 9.2 Hz, 18H, PCH_3). – ^{13}C NMR ($CDCl_3$): 83.7 (s, Cp), 22.8 (X part of ABX system, N = 32 Hz, PCH_3), 21.1 (s, CH_3). – ^{31}P NMR ($CDCl_3$): 11.2 (s).

[CpRu(dppm)(SCH_2CH_2Ph)] (**4d**)

A solution of **1b** (0.73 g 1.00 mmol), $NaSCH_2CH_2Ph$ (0.19 g 1.20 mmol), and dppm (0.46 g 1.20 mmol) in a mixture of THF (20 ml) and ethanol (15 ml) was heated for 2 h under reflux. The solvent was removed under vacuum and the residue purified by column chromatography (silica gel, eluent Et_2O/THF 2:1). The broad yellow band was collected, evaporated, and the residue further purified by recrystallisation from toluene/hexane.

Yield: 0.58 g (84%), yellow crystalline powder, m. p. 163 °C (dec). $C_{38}H_{36}P_2RuS$ (687.8): Calcd C 66.36, H 5.28. Found C 66.36, H 5.26%.

^1H NMR ($CDCl_3$): 4.82 (s, 5H, Cp), 2.85 (AA'XX' system, N = 16.9 Hz, 2H, SCH_2), 2.65 (AA'XX' system, N = 17.1 Hz, 2H, $PhCH_2$). – ^{13}C NMR ($CDCl_3$): 78.5 (s, Cp), 41.5 (s, SCH_2), 37.9 (s, $PhCH_2$). – ^{31}P NMR ($CDCl_3$): 15.8 (s).

[CpRu(dppm)(SO_2R)] (**5a-d**)

A suspension of 3-chloroperoxybenzoic acid (85%, 82 mg, 0.42 mmol) in dichloromethane (5 ml) was slowly added at –60 °C to a solution of the thiolate complex (0.20 mmol) in dichloromethane (5 ml). The mixture was stirred for 15 min at that temperature with the colour changing from orange *via* dark red / yellow to purple. The solvent was removed under vacuum and the crude product purified by column chromatography eluting with CH_2Cl_2/acetone 2:1 (two components-column: upper layer 10 cm Al_2O_3, basic, activity grade I; lower layer 10 cm Al_2O_3, neutral, activity grade I). The first yellow band contained the product which was further purified by crystallisation from benzene/hexane.

5a: Yield 37 mg (24%), yellow crystalline powder. The spectroscopic data are identical to those previously reported [23].

5b: Yield: 100 mg (71%), yellow crystalline powder, m. p. 212 °C (dec). $C_{37}H_{34}O_2P_2RuS$ (705.8): Calcd C 62.97, H 4.86. Found C 63.25, H 4.88%.

IR (Nujol): 1156, 1024 cm^{-1} (SO). – ^1H NMR ($CDCl_3$): 4.82 (s, 5H, Cp), 3.45 (s, 2H, SCH_2). – ^{13}C NMR ($CDCl_3$): 82.6 (s, Cp), 74.1 (s, SCH_2). – ^{31}P NMR ($CDCl_3$): 13.4 (s).

5c: Yield: 100 mg (73%), yellow crystalline powder, m. p. 221 - 223 °C (dec). $C_{36}H_{32}O_2P_2RuS$ (691.7): Calcd C 62.51, H 4.66. Found C 62.76, H 4.61%.

IR (Nujol): 1132, 1016 cm^{-1} (SO). – ^1H NMR ($CDCl_3$): 4.87 (s, 5H, Cp). – ^{31}P NMR ($CDCl_3$): 12.5 (s).

5d: Yield: 110 mg (76%), yellow crystalline powder, m. p. 238 °C (dec). $C_{38}H_{36}O_2P_2RuS$ (719.8): Calcd C 63.41, H 5.04. Found C 63.12, H 5.13%.

IR (Nujol): 1144, 1020 cm^{-1} (SO). – ^1H NMR ($CDCl_3$): 4.89 (s, 5H, Cp), 3.24, (AA'XX' system, N = 16.9 Hz, 2H, SCH_2), 2.85 (AA'XX' system, N = 16.9 Hz, 2H, $PhCH_2$). – ^{13}C NMR ($CDCl_3$): 81.8 (s, Cp), 72.6 (s, SCH_2), 31.7 (s, $PhCH_2$). – ^{31}P NMR ($CDCl_3$): 13.9 (s).

[CpRu(CO)(PPh_3)(SO_2R)] (**7a-c**)

A solution of the thiolate complex (0.86 mmol) and magnesium monoperoxyphthalate hexahydrate (0.50 g, 1.00 mmol) in dichloromethane (20 ml) was heated under reflux for 2 h. The solvent was removed in vacuum and the residue filtered over a 5 cm Al_2O_3 plug, eluting with 30 ml CH_2Cl_2/acetone 2:1. The filtrate was taken to dryness and the product further purified by crystallisation from benzene/hexane.

7a: Yield: 0.33 g (72%), yellow crystalline powder, m. p. 189 - 191 °C (dec). The spectroscopic data are identical to those previously reported [21].

7b: Yield: 0.46 g (88%), yellow crystalline powder, m. p. 173 - 174 °C (dec). $C_{31}H_{27}O_3PRuS$ (611.7): Calcd C 60.87, H 4.45. Found C 60.89, H 4.31%.

IR (Nujol): 1960 (CO), 1172, 1040 cm^{-1} (SO). – ^1H NMR ($CDCl_3$): 4.24 (s, 5H, Cp), 4.30, 4.20 (AB system, J = 12.0 Hz, 2H, SCH_2). – ^{13}C NMR ($CDCl_3$): 203.2 (d, J = 18 Hz, CO), 89.3 (s, Cp), 78.5 (s, SCH_2). – ^{31}P NMR ($CDCl_3$): 47.3 (s).

7c: Yield: 0.37 g (72%), yellow crystalline powder, m. p. 168 - 171 °C (dec). $C_{30}H_{25}O_3PRuS$ (597.6): Calcd C 60.29, H 4.22. Found C 60.04, H 4.24%.

IR (Nujol): 1980 (CO), 1176, 1036 cm^{-1} (SO). – ^1H NMR ($CDCl_3$): 4.70 (s, 5H, Cp). – ^{31}P NMR ($CDCl_3$): 47.3 (s).

Alkylation of the sulfinato complexes

To a solution of the sulfinato complex (0.10 mmol) in dichloromethane (5 ml) either $[Et_3O]PF_6$ (24 mg, 0.09 mmol) or $[Me_3O]BF_4$ (14 mg, 0.09 mmol) was added at –60 °C. The mixture was allowed to warm slowly to room temperature. The solvent was removed under reduced pressure, the residue washed three times with benzene (3 ml) and recrystallised from dichloromethane/hexane.

[CpRu(PMe_3)$_2$($S(O)(OEt)Me$)]PF_6 (**8a**)

Yield: 50 mg (90%), colourless crystalline powder, m. p. 76 - 79 °C (dec).

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$C_{14}H_{31}F_6O_2P_3RuS$ (571.4): Calcd C 29.43, H 5.47. Found C 30.02, H 5.54%.

IR (Nujol): 1133 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.32 (s, 5H, Cp), 4.31, 4.11 (ABX_3 system, J = 9.7, 7.1 Hz, 2H, OCH_2), 3.58 (s, 3H, SCH_3), 1.71 (vt, N = 8.8 Hz, 18H, PCH_3), 1.38 (t, J = 7.1 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 85.6 (s, Cp), 60.5 (s, OCH_2), 57.4 (s, SCH_3), 20.9 (m, PCH_3), 14.5 (s, CH_3). – ^{31}P NMR (acetone-d_6): 7.6, 7.3 (AB system, J = 40 Hz).

[CpRu(PMe$_3$)$_2$(S(O)(OEt)CH$_2$Ph)]PF$_6$ (**8b**)

Yield: 60 mg (92%), colourless crystalline powder, m. p. 76 - 79 °C (dec). $C_{20}H_{35}F_6O_2P_3RuS$ (647.5): Calcd C 37.10, H 5.45. Found C 37.08, H 5.69%.

IR (Nujol): 1168 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.27 (s, 5H, Cp), 5.01, 4.68 (AB system, J = 13.4 Hz, 2H, SCH_2), 4.11, 3.83 (m, 2H, OCH_2), 1.70 (d, J = 10.0 Hz, 9H, PCH_3), 1.50 (d, J = 9.9 Hz, 9H, PCH_3), 0.79 (t, J = 7.1 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 86.6 (s, Cp), 77.4 (s, SCH_2), 63.0 (s, OCH_2), 22.4 (d, J = 32 Hz, PCH_3), 22.3 (d, J = 31 Hz, PCH_3), 15.6 (s, CH_3). – ^{31}P NMR (acetone-d_6): 7.3, 5.3 (AB system, J = 41 Hz).

[CpRu(PMe$_3$)$_2$(S(O)(OEt)(4-C$_6$H$_4$Me))]PF$_6$ (**8c**)

Yield: 58 mg (89%), colourless crystalline powder, m. p. 79 - 80 °C (dec). $C_{20}H_{35}F_6O_2P_3RuS$ (647.54): Calcd C 37.10, H 5.45. Found C 36.83, H 5.26%.

IR (Nujol): 1144 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.13 (s, 5H, Cp), 3.97, 3.49 (ABX_3 system, J = 9.9, 7.1 Hz, 2H, OCH_2), 2.44 (s, 3H, CH_3), 1.78 (d, J = 10.0 Hz, 9H, PCH_3), 1.54 (d, J = 10.0 Hz, 9H, PCH_3), 1.25 (t, J = 7.1 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 151.5, (s, SC), 85.3 (s, Cp), 63.7 (s, OCH_2), 22.8 (d, J = 34 Hz, PCH_3), 22.2 (d, J = 34 Hz, PCH_3), 21.9 (s, CH_3), 15.9 (s, CH_3). – ^{31}P NMR (acetone-d_6): 7.7, 7.5 (AB system, J = 41 Hz).

[CpRu(dppm)(S(O)(OEt)Me)]PF$_6$ (**9a**)

Yield: 75 mg (93%), colourless crystalline powder, m. p. 109 °C (dec). $C_{33}H_{35}F_6O_2P_3RuS$ (803.7): Calcd C 49.32, H 4.39. Found C 47.02, H 4.18%.

IR (Nujol): 1151 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.49 (s, 5H, Cp), 3.48 (ABX_3 system, J = 9.6, 7.1 Hz, 2H, OCH_2), 3.02 (s, 3H, SCH_3), 0.98 (t, J = 7.1 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 85.1 (s, Cp), 60.3 (s, OCH_2), 55.8 (s, SCH_3), 14.5 (s, CH_3). – ^{31}P NMR (acetone-d_6): 7.2, 6.2 (AB system, J = 86 Hz).

[CpRu(dppm)(S(O)(OEt)CH$_2$Ph)]PF$_6$ (**9b**)

Yield: 75 mg (86%), colourless crystalline powder, m. p. 109 °C (dec). $C_{39}H_{39}F_6O_2P_3RuS$ (879.8) Calcd C 53.24, H 4.47. Found C 52.46, H 4.71%.

IR (Nujol): 1168 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.32 (s, 5H, Cp), 4.29, 3.89 (AB system, J = 13.4 Hz, 2H, SCH_2), 2.95 - 2.89 (m, 2H, OCH_2), 0.79 (t, J = 7.1 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 85.1 (s, Cp), 75.0 (s, SCH_2), 63.5 (s, OCH_2), 14.2 (s, CH_3). – ^{31}P NMR (acetone-d_6): 6.6, 4.7 (AB system, J = 84 Hz).

[CpRu(dppm)(S(O)(OEt)Ph)]PF$_6$ (**9c**)

Yield: 80 mg (93%), colourless crystalline powder, m. p. 137 - 140 °C (dec). $C_{38}H_{37}F_6O_2P_3RuS$ (865.8): Calcd C 52.72, H 4.31. Found C 53.07, H 4.58%.

IR (Nujol): 1148 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.40 (s, 5H, Cp), 3.21, 3.16 (ABX_3 system, J = 9.9, 7.1 Hz, 2H, OCH_2), 0.95 (t, J = 7.1 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 151.9 (s, SC), 85.7 (s, Cp), 63.5 (s, OCH_2), 14.5 (s, CH_3). – ^{31}P NMR (acetone-d_6): 6.0 (s).

[CpRu(dppm)(S(O)(OEt)CH$_2$CH$_2$Ph)]PF$_6$ (**9d**)

Yield: 77 mg (86%), colourless crystalline powder, m. p. 139 - 140 °C (dec). $C_{40}H_{41}F_6O_2P_3RuS$ (893.8): Calcd C 53.75, H 4.62. Found C 53.44, H 4.65%.

IR (Nujol): 1154 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.56 (s, 5H, Cp), 3.49 (m, 2H, OCH_2), 3.42 (m, 1H, SCH_2), 3.24 (m, 1H, SCH_2), 2.57 (m, 2H, $PhCH_2$), 1.08 (t, J = 7.0 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 85.0 (s, Cp), 73.0 (s, SCH_2), 62.8 (s, OCH_2), 28.0 (s, $PhCH_2$), 14.5 (s, CH_3). – ^{31}P NMR (acetone-d_6): 6.4, 5.1 (AB system, J = 86 Hz).

[CpRu(PPh$_3$)(CO)(S(O)(OMe)Me)]BF$_4$ (**10a**)

This compound was obtained as a 50:50 mixture of diastereoisomers. Yield: 57 mg (89%), colourless crystalline powder, m. p. 113 °C (dec). $C_{26}H_{26}BF_4O_3PRuS$ (637.4): Calcd C 48.99, H 4.11. Found C 48.13, H 4.13%.

IR (Nujol): 2008 (CO) cm^{-1}. *Both diastereoisomers:* ^1H NMR (acetone-d_6): 5.57 (s, 5H, Cp), 5.27 (s, 5H, Cp), 3.57 (s, 3H, CH_3), 3.50 (s, 3H, CH_3), 3.47 (s, 3H, CH_3), 3.40 (s, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 203.2 (s, br, CO), 200.8 (s, br, CO), 92.1 (s, Cp), 91.3 (s, Cp), 69.3 (s, SCH_3), 52.9 (s, OCH_3), 52.7 (s, OCH_3). – ^{31}P NMR (acetone-d_6): 43.1 (s), 42.2 (s).

[CpRu(PPh$_3$)(CO)(S(O)(OMe)CH$_2$Ph)]BF$_4$ (**10b**)

This compound was obtained as a 70:30 mixture of diastereoisomers. Yield: 65 mg (91%), colourless crystalline powder, m. p. 124 - 126 °C (dec). $C_{32}H_{30}BF_4O_3PRuS$ (713.5): Calcd C 53.87, H 4.24. Found C 53.95, H 4.32%.

IR (Nujol): 2012 (CO) cm^{-1}. – *Major diastereoisomer:* ^1H NMR (acetone-d_6): 5.41 (s, 5H, Cp), 5.11, 4.72 (AB system, J = 12.9 Hz, 2H, SCH_2), 3.24 (s, 3H, OCH_3). – ^{13}C

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NMR (acetone-d_6): 199.6 (d, J = 20 Hz, CO), 91.4 (s, Cp), 74.6 (s, SCH_2), 52.8 (s, OCH_3). – ^{31}P NMR (acetone-d_6): 42.0 (s). *Minor diastereoisomer:* ^{1}H NMR (acetone-d_6): 5.60 (s, 5H, Cp), 4.94, 4.62 (AB system, J = 13.6 Hz, 2H, SCH_2), 3.49 (s, 3H, OCH_3). – ^{13}C NMR (acetone-d_6): 200.3, (d, J = 20 Hz, CO), 90.9 (s, Cp), 75.1 (s, SCH_2), 53.4 (s, OCH_3). – ^{31}P NMR (acetone-d_6): 41.9 (s).

[CpRu(PPh$_3$)(CO)(S(O)(OMe)Ph)]BF$_4$ (**10c**)

This compound was obtained as a 66:34 mixture of diastereoisomers. Yield: 64 mg (91%), colourless crystalline powder, m.p. 124 - 126 °C (dec). $C_{31}H_{28}BF_4O_3PRuS$ (699.5): Calcd C 53.23, H 4.04. Found C 52.95, H 3.82%.

IR (Nujol): 2008 (CO) cm^{-1}. *Major diastereoisomer:* ^{1}H NMR (acetone-d_6): 5.28 (s, 5H, Cp), 2.98 (s, 3H, OCH_3). – ^{13}C NMR (acetone-d_6): 200.1 (s, br, CO), 91.9 (s, Cp), 52.6 (s, OCH_3). – ^{31}P NMR (acetone-d_6): 42.5 (s). *Minor diastereoisomer:* ^{1}H NMR (acetone-d_6): 5.50 (s, 5H, Cp), 3.20 (s, 3H, OCH_3). – ^{13}C NMR (acetone-d_6): 200.1, (s, br, CO), 92.0 (s, Cp), 53.7 (s, OCH_3).– ^{31}P NMR (acetone-d_6): 43.1 (s).

[CpRu(PPh$_3$)(CO)(S(O)(OEt)CH$_2$Ph)]PF$_6$ (**11a**)

This compound was obtained as a 91:9 mixture of diastereoisomers. Yield: 71 mg (91%), colourless crystalline powder, m.p. 126 - 129 °C (dec). $C_{33}H_{32}F_6O_3P_2RuS$ (785.7): Calcd C 50.45, H 4.11, S 4.08. Found C 49.53, H 3.97, S 3.97%.

IR (Nujol): 2009 (CO) cm^{-1}. *Major diastereoisomer:* ^{1}H NMR (acetone-d_6): 5.33 (s, 5H, Cp), 5.02, 4.76 (AB system, J = 13.3 Hz, 2H, SCH_2), 4.03, 3.67 (ABX_3 system, J = 9.6, 7.1 Hz, 2H, OCH_2), 0.87 (t, J = 7.1 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 200.6 (d, J = 18 Hz, CO), 91.7 (s, Cp), 74.8 (s, SCH_2), 64.7 (s, OCH_2), 17.4 (s, OCH_3). – ^{31}P NMR (acetone-d_6): 42.1 (s). *Minor diastereoisomer:* ^{1}H NMR (acetone-d_6): 5.63 (s, 5H, Cp), 5.17, 4.76 (AB system, J = 13.0 Hz, 2H, SCH_2), 3.99, 3.65 (m, 2H, OCH_2), 1.25 (t, J = 7.0 Hz, 3H, CH_3). – ^{31}P NMR (acetone-d_6): 41.9 (s).

[CpRu(PPh$_3$)(CO)(S(O)(OEt)Ph)]PF$_6$ (**11b**)

This compound was obtained as a 60:40 mixture of diastereoisomers. Yield: 71 mg (92%), colourless crystalline powder, m.p. 121 - 122 °C (dec). $C_{32}H_{30}F_6O_3P_2RuS$ (771.7): Calcd C 49.81, H 3.92. Found C 49.82, H 3.48%.

IR (Nujol): 2008 (CO) cm^{-1}. *Major diastereoisomer:* ^{1}H NMR (acetone-d_6): 5.46 (s, 5H, Cp), 3.82, 3.49 (ABX_3 system, J = 9.9, 7.0 Hz, 2H, OCH_2), 1.09 (t, J = 7.0 Hz, 3H, CH_3). – ^{31}P NMR (acetone-d_6): 42.6 (s). *Minor diastereoisomer:* ^{1}H NMR (acetone-d_6): 5.35 (s, 5H, Cp), 4.19, 4.17 (ABX_3 system, J = 9.9, 7.1 Hz, 2H, OCH_2), 0.96 (t, J = 7.1 Hz, 3H, CH_3). – ^{31}P NMR (acetone-d_6): 43.3 (s).

Reaction of [CpRu(PMe$_3$)$_2$(S(O)(OEt)CH$_2$Ph)]PF$_6$ (**8b**) *with NaI and NaSMe*

A suspension of **8b** (65 mg, 0.10 mmol) and either NaI (15 mg, 0.10 mmol) or NaSMe (7 mg, 0.10 mmol) in dichloromethane (3 ml) was stirred for 24 h at 20 °C. The solvent was removed under reduced pressure and the residue examined by NMR spectroscopy to show [CpRu(PMe$_3$)$_2$(SO_2CH_2Ph)] (**3b**) exclusively.

Crossover experiment between [CpRu(CO)(PPh$_3$)(S(O)(OEt)CH$_2$Ph)]PF$_6$ (**11a**) *and [CpRu(PMe$_3$)(SO_2CH_3)]* (**3a**)

A solution of **11a** (32 mg, 0.04 mmol) and **3a** (20 mg, 0.05 mmol) in dichloromethane (5 ml) was heated for 4 h under reflux. The solvent was removed under reduced pressure and the residue examined by NMR spectroscopy to show, besides the starting materials, 10% of the crossover products [CpRu(CO)(PPh$_3$)(SO_2CH_2Ph)] (**7b**) and [CpRu(PMe$_3$)$_2$(S(O)(OEt)CH_3)]PF_6 (**8a**)

Ligand exchange reaction

A solution of **10c** (50 mg, 0.07 mmol) in acetonitrile (5 ml) was heated for 2 h under reflux. The solvent was removed in vacuum and the residue dissolved in acetone-d_6 and examined by NMR spectroscopy, which showed the quantitative formation of [CpRu(CO)(PPh$_3$)($NCCH_3$)]-BF_4 (**12**) {^{1}H NMR (acetone-d_6): 5.31 (s, 5H, Cp), 2.11 (s, 3H, NCMe). ^{31}P NMR (acetone-d_6): 49.0 (s)} and PhS(O)OMe (**13**). The sulfinic acid ester **13** was separated from the reaction mixture by extraction with diethylether (10 ml). It exhibited spectroscopic properties identical to those described in [28].

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