Synthesis and Oxidation of Ruthenium Allyl Thioether Complexes Bearing Phosphite and Phosphonite Coligands [1]

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Ruthenium Complexes, Thioether, Sulfoxide, Epoxide, Dimethylidioxidane

Halfsandwich ruthenium thiolate complexes bearing electron-withdrawing phosphite or phosphonite ligands were prepared from [CpRu(PPh₃)₂(SR)] (R = Ph, CH₂Ph, Me) and triphenylphosphite or (S,S)-bis(binaphthylphosphonito)ethane (bbpe), respectively. Reaction with 1-bromo-3-methyl-2-buten in the presence of NH₄PF₆ gave the corresponding allylthioether complexes [CpRu(PR₃)₂(S(R)CH₂CH=CM₂)]PF₆. Treatment with an excess of dimethylidioxidane (DMD) transformed the triphenylphosphite derivatives into diastereomeric (oxiranyl-methyl)sulfoxide complexes with 18 - 80% de. NMR monitoring of the reaction revealed that the oxidant attacks the sulfur atom and the C=C double bond with comparable rates. Similar oxidation of the bbpe complexes gave mixtures of four diastereoisomers with ratios of (64 : 15 : 13 : 8) and (51 : 24 : 15 : 10), respectively.

Introduction

Oxygen transfer to unsaturated thioethers usually gives sulfoxides and sulfones, before the electrophilic oxygen-transfer reagent attacks the C=C double bond [2]. In a previous publication of this series we have shown that this ordering can be partially reversed by coordination of the sulfur atom to a [CpRu(P-P)]⁺ complex, where (P-P) denotes a chelating bidentate phosphine ligand [3]. In these cases the formation of sulfones was suppressed completely, but the first oxygen transfer still took place exclusively at the thioether function:

Withdrawing phosphite ligands in place of the strongly donating diphosphines. In doing so it might be possible to redirect the first oxygen transfer to the C=C double bond. In addition, with the use of chiral, enantiomerically pure phosphites there is the possibility of achieving a double asymmetric oxidation.

Synthesis of Thiolate and Thioether Complexes

Thiolate complexes 1a-c, which are readily obtained from [CpRu(PPh₃)₂Cl] [4] and NaSR [5, 6], react with triphenylphosphite in boiling toluene to give the thiolate derivatives 2a-c in good yields:

2a-c are yellow, somewhat air-sensitive crystalline solids which are readily soluble in most organic solvents. Their ¹H and ¹³C NMR spectra (see experimental section) show the signals of all groups present; a characteristic feature of the ³¹P NMR spectra is the low-field resonance at 140 ppm. For the synthesis of electronically sim-
Table I. Important NMR spectroscopic data of the thioether complexes 5a-c, 6a, b.

<table>
<thead>
<tr>
<th>No.</th>
<th>13C NMR</th>
<th>31P NMR</th>
<th>( J(\text{P-P}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp</td>
<td>SC</td>
<td>C((\alpha))</td>
<td>C((\beta))</td>
</tr>
<tr>
<td>5a</td>
<td>84.9(^{b})</td>
<td>152.3(^{c})</td>
<td>48.7</td>
</tr>
<tr>
<td>5b</td>
<td>84.9(^{b})</td>
<td>42.3</td>
<td>49.6</td>
</tr>
<tr>
<td>5c</td>
<td>85.2(^{d})</td>
<td>26.5(^{b})</td>
<td>44.6(^{b})</td>
</tr>
<tr>
<td>6a</td>
<td>85.9</td>
<td>149.7(^{c})</td>
<td>48.2</td>
</tr>
<tr>
<td>6b</td>
<td>85.3</td>
<td>70.8</td>
<td>42.0</td>
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</table>

\(^{a}\) Recorded in acetone-\(d_{6}\); aryl and phosphine signals are uncharacteristic and have been omitted; \(^{b}\) \( J(\text{C-P}) \) 3 Hz; \(^{c}\) \( J(\text{C-P}) \) 6 Hz; \(^{d}\) \( J(\text{C-P}) \) 2 Hz; \(^{e}\) \( J(\text{P-P}) \) 3 Hz; \(^{f}\) \( J(\text{P-P}) \) 16 Hz.

The thiolate complexes 1a, b undergo ligand exchange with 3 as described above, yielding the enantiomerically pure derivatives 4a, b as yellow crystalline powders (eq. (3)).

Their dissymmetric structure is apparent from separate NMR signals for the two phosphorus nuclei and, in 4b, the diastereotopic methylene protons. Although 2a-c and 4a, b are less nucleophilic than the corresponding phosphine-substituted thiolate complexes such as 1a-c [6], they are still rapidly allylated with 1-bromo-3-methyl-2-butene (eqs. (4), (5)). The reaction has to be carried out at 0 °C and the mixture worked up after 45 min in order to avoid any substitution of the allyl thioether ligand by bromide ion.

The new thioether complexes are isolated in high yields as colorless, air-stable crystalline solids which dissolve readily in polar organic solvents such as dichloromethane or acetone. The allylation is accompanied by a downfield shift of the \(^{1}\text{H}\) and \(^{13}\text{C}\) resonances of the R group at sulfur and, for 5a-c, an upfield shift of the \(^{31}\text{P}\) resonance (Table I). Again, the \(^{1}\text{H}\) signals of diastereotopic methylene groups are split into well-resolved AB systems.

ilar but chiral, enantiomerically pure complexes a readily available \(C_2\)-symmetric chelating phosphite was required. The candidate of choice was the bis(binaphthylphosphonito)ethane 3 (bbpe), which was obtained in high yield as a colorless crystalline solid from (S)-1,1'-binaphthyl-2,2'-diol and 1,2-bis(dichlorophosphino)ethane (eq. (2)) (The \((R,R)\)-enantiomer of 3 has been reported independently [7]).
Table II. Important NMR spectroscopic data of the complexes 7a-c, 8a, b, A and B'.

<table>
<thead>
<tr>
<th>No.</th>
<th>13C NMR</th>
<th>SC</th>
<th>C(α)</th>
<th>C(β)</th>
<th>C(γ)</th>
<th>CH₃</th>
<th>CH₃</th>
<th>31P NMR</th>
<th>J(P-P)</th>
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<tr>
<td></td>
<td>Cp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P(A)</td>
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<tr>
<td>7a'</td>
<td>85.0b</td>
<td>134.5c</td>
<td>48.5</td>
<td>62.2</td>
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<td>18.5</td>
<td>24.1</td>
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<td>66.7</td>
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<td>57.40</td>
<td>58.2</td>
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<td>8a'''</td>
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<td>56.59</td>
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<td>8b'</td>
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<td>B</td>
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<td>50.8</td>
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a Recorded in acetone-d₆; aryl and phosphine signals are uncharacteristic and have been omitted; b, t, J(C-P) 2 Hz; c, t, J(C-P) 4 Hz; d, t, J(C-P) 3 Hz.

Scheme 2.

Oxygen Transfer Reactions

The oxidation of complexes 5a-c and 6a, b with dimethyldioxirane is quite slow and requires a fourfold excess of DMD in order to reach completion (eqs. (6), (7)).

The reaction is accompanied by a fair amount of decomposition, but the desired products are readily purified by column chromatography. We were unable to obtain crystals of sufficient quality for an X-ray study. The sulfoxide complexes 7a-c and 8a, b are similar in appearance to their starting materials. 7a, b are formed in surprisingly good diastereoselectivity when compared with the corresponding dppe and dppe complexes [3]. On the other hand, the asymmetric induction brought about by the bbpe ligand 3 (eq. (7)) is comparable to the selectivity achieved with (S,S)-CHIRAPHOS [3]. The oxidation of the thioether function leads to a sizable downfield shift of the 13C resonances of the adjacent carbon atoms while new signals in the range typical of epoxides appear at the expense of the olefinic resonances (Table II).

In order to gain some insight into the course of the oxidation, the reaction of 5c at -10 °C with an
equimolar amount of DMD was followed by $^1$H, $^{13}$C, and $^{31}$P NMR. The mixture of products consisted of 25\% starting material 5c, 15\% doubly oxidized product 7c, 25\% sulfoxide complex A, and 35\% epoxide B. This demonstrates that electrophilic attack at sulfur and at the C=C double bond occurs at almost identical rates (Scheme 2).

**Discussion**

Thiolate ligands are very strong $\sigma$- and $\pi$-donors and as such are capable of stabilizing coordinatively unsaturated intermediates [8]. As a result, the substitution of adjacent ligands in low-valent transition metal complexes is greatly accelerated. We have taken advantage of this effect in a number of ligand exchange reactions using the complexes [CpRu(PPh$_3$)$_2$(SR)] as readily accessible starting materials [3, 6, 9]. Similarly, the reactions described by equations (1) and (3) reach completion within 2 h. The losses in yield are mainly due to the good solubility of these phosphite complexes.

The alkylation of terminal thiolate ligands provides an easy access to complexes of thioethers [6, 8, 10]. Occasionally the use of alkyl halides for this purpose may pose a problem since the strongly nucleophilic halide anion will substitute the weakly donating thioether ligand [11]. In our case, this secondary reaction was safely avoided by limiting the reaction time to the necessary minimum.

As for the oxygen transfer reactions, we relied on dimethyldioxirane (DMD), a highly reactive, yet surprisingly clean and selective oxidant [12]. DMD has recently been employed successfully in organometallic chemistry to perform various types of oxygen additions and insertions [13]. In particular, the oxidation of coordinated thioethers to sulfoxides was achieved in high yields and in many instances also with very high diastereoselectivities [14]. The systems studied here, however, appear to be somewhat more sensitive with regard to metal oxidation and subsequent decomposition.

The fairly high diastereoselectivity of the formation of 7a, b (eq. (6)) is surprising, particularly in view of the fact that two parallel reaction paths are involved (see Scheme 2). The second steps of both paths apparently favor the same diastereoisomer. In the previously investigated series the relative configuration of the major diastereoisomer was in one case identified by X-ray crystallography as (R,R,S,S) [3]. Compounds 7 and 8 do not provide any clear-cut spectroscopic handle from which the relative (7) or absolute (8) configurations of the two new stereocenters could be derived with certainty. The diastereoselectivity achieved in the oxidation of the bbpe complexes 6a, b (eq (8)) is similar to what we have found with the analogous (S,S)-CHIRAPHOS complexes [3]. Nevertheless, in view of the many ways to sterically and/or electronically modify binaphthyl-derived phosphonite ligands [15] we are certain that complexes such as 4, 6 and 8 provide ample opportunities for improvement.

**Experimental Section**

All experiments were carried out in Schlenk tubes under an atmosphere of nitrogen using suitably purified solvents. [CpRu(PPh$_3$)$_2$Cl] [4] and the thiolato complexes 1b, c were obtained as described in the literature [3]. Dimethyldioxirane was employed as a 0.08 - 0.12 M solution in acetone [16], all other reagents were used as purchased. NMR: Bruker AMX 400 (6[ppm], $^{1}$H, 400 MHz, TMS; $^{13}$C, 100 MHz, TMS; $^{31}$P, 162 MHz, H$_2$PO$_4$). The NMR signals of the aryl groups and the bbpe ligand are uncharacteristic and have therefore been omitted from the lists of spectral data.

$[\text{CpRu(PPh}_3)_2\text{(SR)}] \quad (1a)$

This complex was obtained in analogy to a published procedure [3]. Yield: (87\%), red crystalline powder, m.p. 73 °C (dec).

C$_{47}$H$_{40}$P$_2$RuS (799.9)  
Calcd C 70.57 H 5.04 S 4.01\%,  
Found C 70.90 H 5.13 S 3.95\%.

$^1$H NMR (benzene-d$_6$): 4.12 (s, C$_8$H$_5$).  
$^{13}$C NMR (benzene-d$_6$): 83.8 (t, $^2$J(C-P) 2 Hz, C$_8$H$_5$), 152.3 (t, $^3$J(C-P) 4 Hz, SC).  
$^{31}$P NMR (benzene-d$_6$): 40.3 (s).

$[\text{CpRu(P(OPh)_3}_2\text{(SR)}] \quad (2a-c)$

A mixture of 1a-c (0.50 mmol) and P(OPh)$_3$ (0.39 g, 1.25 mmol) in 20 ml of toluene was heated under reflux for 2 h. The solution was evaporated to dryness and the residue dissolved in diethyl ether and chromatographed over a silica column (20 cm) using diethyl ether as an eluent. The yellow band was collected and evaporated to dryness, and the residue was dissolved in a mixture of diethyl ether/hexanes. The solution was cooled with liquid nitrogen to induce crystallization.

2a: Yield (64\%), yellow crystalline powder, m.p. 35 °C (dec).
The synthesis of 6a, b was accomplished following the procedure given above for 5a-c.

To a stirred suspension of 2a-c or 4a, b (0.50 mmol) and NH₄PF₆ (0.11 g, 0.7 mmol) in acetone (20 ml) 1-bromo-3-methyl-2-butene (0.22 g, 0.75 mmol) was added at 0 °C. After 45 min the mixture was evaporated to dryness and the residue dissolved in dichloromethane/acetone 4:1 and filtered over a short silica column (5 cm). After evaporation the product was recrystallized from dichloromethane/diethyl ether.

5a: Yield (91%), yellow crystalline powder, m.p. 54 °C (dec).

A mixture of 1a, b (0.50 mmol) and bbpe (0.35 g, 0.53 mmol) in 20 ml of toluene was heated under reflux for 90 min. The solution was then evaporated to dryness and the residue dissolved in benzene and filtered through celite. After evaporation of the solvent the residue was treated with hexanes in an ultrasonic bath to induce crystallization.

4a: Yield (77%), yellow crystalline powder, m.p. 182 °C (dec).

The synthesis of 6a, b was accomplished following the procedure given above for 5a-e.
6a: Yield (91%), yellow crystalline powder, m.p. 220 °C (dec).

C₅₈H₇₂O₃P₃RuS (1148.1)
Calcd C 60.68 H 4.13 S 2.79%.
Found C 60.85 H 4.17 S 2.40%.

¹H NMR (acetone-d₆): 1.14 (s, CH₃), 1.49 (s, CH₃),
3.60 (dd, 3J(H-H) 13.6 Hz, 3J(H-H) 8.0 Hz, CH₂), 4.00
(dd, 3J(H-H) 12.4 Hz, 3J(H-H) 8.0 Hz, CH₂), 5.12-5.22
(m, CH), 5.19 (s, C₅H₅).

6b: Yield (93%), yellow crystalline powder, m.p. 205 °C (dec).

C₅₉H₇₆O₃P₃RuS (1162.1)
Calcd C 60.98 H 4.25 S 2.76%.
Found C 60.50 H 4.41 S 2.68%.

¹H NMR (acetone-d₆): 1.51 (s, CH₃), 1.64 (s, CH₃),
3.63-3.90 (m, CH₂), 3.77 (dd, 3J(H-H) 12.4 Hz, CH₂Ph),
4.16 (d, 3J(H-H) 12.4 Hz, CH₂Ph), 4.75 (s, C₅H₃), 5.28-
5.38 (m, CH).

[CpRu(P(OPh)₃)₂(RS(O)R')PF₆] (7a-c)

A solution of the thioether complex 5a-c (0.2 mmol) in
acetone (20 ml) was treated at 20 °C with four 0.2 mmol
aliquots of DMD and stirred for 2 d. The mixture was
then evaporated to dryness and the residue dissolved in
dichloromethane and chromatographed over a silica col-
umn (20 cm) using dichloromethane/diethyl ether 1:1 as an
eluent. After evaporation of the solvent the product
was recrystallized from dichloromethane/hexanes.

7a: Yield (57%), light yellow crystalline product, m.p. 64 °C (dec).

C₅₁H₇₆O₃P₃RuS (1142.0)
Calcd C 54.69 H 4.33 S 2.81%.
Found C 55.05 H 5.21 S 2.60%.

¹H NMR (acetone-d₆), major (90%) diastereomer: 0.75
(s, CH₃), 1.06 (s, CH₃), 2.64 (dd, 3J(H-H) 13.6 Hz, 3J(H-
H) 6.0 Hz, CH₂), 2.78 (t, 3J(H-H) 6.0 Hz, CH₂), 3.22 (dd,
3J(H-H) 13.6 Hz, 3J(H-H) 6.0 Hz, CH₂), 5.16 (s, C₅H₃);
minor (10%) diastereomer: 0.95 (s, CH₃), 1.22 (s, CH₃),
5.05 (s, C₅H₃).

7b: Yield (61%), light yellow crystalline product, m.p. 68 °C (dec).

C₅₃H₇₄O₃P₃RuS (1156.0)
Calcd C 55.07 H 4.45 S 2.77%.
Found C 55.22 H 4.70 S 2.73%.

¹H NMR (acetone-d₆), major (86%) diastereomer: 1.05
(s, CH₃), 1.09 (s, CH₃), 2.56 (dd, 3J(H-H) 8.0 Hz, 3J(H-
H) 2.8 Hz, CH₂), 2.88 (dd, 3J(H-H) 14.8 Hz, 3J(H-H)
8.0 Hz, CH₂), 3.22 (dd, 3J(H-H) 14.8 Hz, 3J(H-H) 2.8 Hz,
CH₂), 4.03 (d, 3J(H-H) 14.0 Hz, CH₂Ph), 4.29 (d, 3J(H-H)
14.0 Hz, CH₂Ph), 5.14 (s, C₅H₃); minor (14%) diastere-
omer: 1.18 (s, CH₃), 1.28 (s, CH₃), 5.10 (s, C₅H₃).

7c: Yield (47%), light yellow crystalline product, m.p. 138 °C (dec).

C₅₇H₇₄O₃P₃RuS (1079.9)
Calcd C 52.27 H 4.39 S 2.97%.
Found C 51.21 H 4.82 S 2.58%.

¹H NMR (acetone-d₆), major (59%) diastereomer: 1.23
(s, CH₃), 1.49 (s, CH₃), 3.18 (dd, 3J(H-H) 14.0 Hz, 3J(H-
H) 9.2 Hz, CH₂), 3.31-3.38 (m, CH₂), 3.50 (d, 3J(H-H)
14.0 Hz, CH₂), 3.56 (s, CH₃), 5.34 (s, C₅H₃); minor (41%)
diastereomer: 1.32 (s, CH₃), 1.36 (s, CH₃), 3.31-3.38 (m,
CH₂), 3.33 (s, CH₃), 3.66 (dd, 3J(H-H) 14.4 Hz, 3J(H-H)
7.6 Hz, CH₂), 4.02 (dd, 3J(H-H) 14.4 Hz, 3J(H-H) 3.2 Hz,
CH₂), 5.33 (s, C₅H₃).

[CpRuthbpe](RS(O)R')PF₆ (8a, b)

The synthesis of 8a, b was accomplished following the
procedure given above for 7a-c.

8a: Yield (44%), light yellow crystalline product, m.p. 191 °C (dec).

C₅₅H₇₄O₃P₃RuS (1180.0)
Calcd C 59.03 H 4.01 S 2.72%.
Found C 58.04 H 4.21 S 2.59%.

¹H NMR (acetone-d₆), major (64%) diastereomer: 0.84
(s, CH₃), 0.90 (s, CH₃), 2.18-2.72 (m, CH), 3.89 (dd,
3J(H-H) 14.8 Hz, 3J(H-H) 5.6 Hz, CH₃), 4.30 (dd, 3J(H-
H) 14.8 Hz, 3J(H-H) 5.6 Hz, CH₂), 5.21 (s, C₅H₃); second
(15%) diastereomer: 1.06 (s, CH₃), 1.13 (s, CH₃), 2.18-
2.72 (m, CH), 3.81 (dd, 3J(H-H) 15.2 Hz, 3J(H-H) 7.2 Hz,
CH₂), 4.46 (dd, 3J(H-H) 15.2 Hz, 3J(H-H) 4.4 Hz, CH₂),
4.70 (s, C₅H₃); third (13%) diastereomer: 1.18 (s, CH₃),
1.19 (s, CH₃), 2.18-2.72 (m, CH), 4.45 (dd, 3J(H-H) 14.4
Hz, 3J(H-H) 3.6 Hz, CH₂), 5.37 (s, C₅H₃); fourth (8%) diastereomer: 0.97 (s, CH₃), 1.04 (s, CH₃), 2.18-2.72 (m,
CH), 4.16 (dd, 3J(H-H) 14.4 Hz, 3J(H-H) 5.6 Hz, CH₂),
4.20 (dd, 3J(H-H) 14.4 Hz, 3J(H-H) 4.8 Hz, CH₂), 5.50
(s, C₅H₃).

8b: Yield (47%), light yellow crystalline product, m.p. 207 °C (dec).

C₅₉H₇₄O₃P₃RuS (1194.1)
Calcd C 59.35 H 4.14 S 2.69%.
Found C 59.18 H 4.51 S 2.55%.

¹H NMR (acetone-d₆), major (51%) diastereomer: 1.39
(s, CH₃), 1.52 (s, CH₃), 2.28-2.84 (m, CH), 3.32 (dd,
3J(H-H) 14.4 Hz, 3J(H-H) 8.0 Hz, CH₂), 3.91 (dd, 3J(H-
H) 14.4 Hz, 3J(H-H) 2.4 Hz, CH₂), 3.94 (d, 3J(H-H)
14.8 Hz, CH₂Ph), 4.27 (d, 3J(H-H) 14.8 Hz, CH₂Ph), 4.75
(s, C₅H₃); second (24%) diastereomer: 0.80 (s, CH₃), 1.06
(s, CH₃), 2.28-2.84 (m, CH), 5.27 (s, C₅H₃); third (15%)
diastereomer: 0.71 (s, CH₃), 1.05 (s, CH₃), 2.28-2.84 (m,
CH), 4.69 (s, C₅H₃); fourth (10%) diastereomer: 5.20 (s,
C₅H₃).
Chemoselectivity Experiment

5e (0.07 g, 0.06 mmol) in acetone (5 ml) was treated at -10 °C with an equimolar amount of DMD in the same solvent. After 2 h the solution was taken to dryness at -10 °C. NMR spectroscopic analysis of the residue showed besides starting material 5e (25%) and final product 7e (15%) the presence of intermediates:

A: 35%, C₆H₅₂F₂O₃·P₃RuS. ¹H NMR (acetone-d₆): 1.69 (s, CH₃), 1.84 (s, CH₂), 3.20 (s, CH₂), 4.00 (dd, ²J(H-H) 13.6 Hz, ³J(H-H) 9.2 Hz, CH₂), 4.32 (dd, ²J(H-H) 13.6 Hz, ³J(H-H) 7.2 Hz, CH₂), 5.30 (s, C₅H₅), 5.42 - 5.48 (m, CH).

B: 25%, C₆H₅₂F₂O₃·P₃RuS. ¹H NMR (acetone-d₆): 1.22 (s, CH₃), 1.28 (s, CH₂), 2.65 (s, CH₂), 2.89 (dd, ²J(H-H) 13.6 Hz, ³J(H-H) 8.4 Hz, CH₂), 3.02 (dd, ³J(H-H) 8.4 Hz, ³J(H-H) 2.8 Hz, CH), 5.08 (s, C₅H₅).

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